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CLAY MINERALS SOCIETY

XVII ICC
ISTANBUL 2022
25 -29 JULY

New Interfaces Bridging Continents and Cultures with Clays



SCIENTIFIC RESEARCH

ABSTRACTS

AIPEA – XVII INTERNATIONAL CLAY CONFERENCE
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AIPEA – XVII INTERNATIONAL CLAY CONFERENCE
ICC 2022
25–29 JULY 2022
HILTON MASLAK ISTANBUL, TURKEY
Organized by
THE CLAY SCIENCE SOCIETY (TURKEY)
THE CLAY MINERAL SOCIETY (USA)
AIPEA
Scientific Research Abstracts
Editors: Selahattin Kadir, Paul A. Schroeder, Asuman Günal Türkmenoğlu, Fahri Esenli, Emin Çiftçi

PREFACE

The AIPEA-17th International Clay Conference has been co-organized by The Clay Science Society (Turkey) and The Clay Minerals Society (USA) during July 25-29, 2022, in Istanbul, Turkey. Because of the COVID-19 pandemic, the Conference was conducted in a hybrid format. The Conference venue was the İstanbul Hilton Maslak, next to the İstanbul Technical University Ayazağa Campus in Maslak. The theme of the Conference is expressed, as **"New Interfaces: Bridging Continents and Cultures with Clays"** was selected as a suggestion for the motivation of the Conference.

The scientific program of the 17th ICC 2022 has brought together scientists and researchers coming from many countries who belong to different disciplines related to clays and clay minerals. In addition to the oral and poster presentations, one keynote and eight plenary lectures have been delivered.

This book of abstracts contains the contributions presented during the Conference on a diversity of topics that include: Clays and the molecules of life, Nanoporous fibrous clays, Clays and health, Pedogenic clays, Clays in the solar system, Clays and contaminant control, Clays and cultural heritage, History of clay science, Soil mineral quantification, Paleoenvironments, diagenesis, provenance of sedimentary deposits, Sepiolite, palygorskite and bentonite, Clays in petroleum, oil, and gas, Rare-Earth elements and clays, High temperature bentonite barriers, Clay geochronology, Clays - burial diagenesis – low temperature metamorphism, Computational modeling of clays and fluid interfaces, Advanced microscopy in clays, Layered double hydroxides, Clays, organics, hybrid materials, Clays geotherms, fluid migrations in sedimentary basins, Clay geotechnical applications, Clays for ceramics, Hydrothermal Clays, Teaching Clay Mineralogy (Keynote), and a General Session.

The Organizing Committee appreciates the participant's effort to present and exchange ideas on their research and consider the future developments in the field of clay science. We are most thankful to all participants who have made an invaluable contribution to the success of the Conference. Many thanks also go to the Scientific Committee members for proposing topics, organizing the thematic sessions, reviewing abstracts and returning critical comments to the authors.

On behalf of the Organizing Committee

Selahattin Kadir
Paul A. Schroeder
Asuman Günal Türkmenoğlu

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Plenary Lectures

Using atomic structure-property relationships to understand environmental Earth

Michael F. Hochella, Jr.

Virginia Tech

Over my Earth science career, our group and my colleagues has found it possible to connect atomic structure-property relationships of minerals into a better understanding of environmental Earth at local, regional, and even global scales. I will give several examples of how these discoveries came about and exactly how they are relevant to environmental Earth. These examples include: 1) very early experiments with calcite and sorbed cations, like aqueous cadmium, proving that sorbed species can readily move into the host calcite phase through near-surface solid state diffusion; 2) our work on pyrite surface electronic structure and reactive sites, atomically resolved, and relating that to acid mine drainage; 3) experiments concerning hematite reactivity as a function of its size in the nanoscale regime, and its effects on manganese redox chemistry and groundwater chemistry in general; 4) determining the nature of the formation and atomic structure of green rust and its reactivity for metal transport; 5) discovery of massive titanium suboxide generation, its remarkable defect atomic structure, and its human lung toxicity; and 6) expanding these themes to global impact scenarios, including a new generation of artificial ocean fertilization designed to draw down atmospheric carbon dioxide to reduce global warming.

George W. Brindley Clay Science Lecture, 2022

New directions in clay science: A medicinal application of antibacterial clays?

Lynda B. Williams

Arizona State University, School of Earth & Space Exploration, Tempe, AZ 85287-1404 USA

lynda.williams@asu.edu

It is an honor to present the George W. Brindley Clay Science Lecture, after two years lapse due to the Covid Pandemic. I will tell you the story of how my antibacterial clay research has evolved over two decades and discuss our current understanding of how clays may be applied to fight antibiotic-resistant infections. Developing our understanding of how clays interact with microbes in nature allows us to design new strategies for employing clays to benefit society. I hope that future generations of clay researchers will be inspired to explore new clay applications in medicine, because we are just at the beginning of understanding, for example, 'What makes reduced iron clays effective in killing human pathogens?' The goal of this research was to gain insights from natural clay geochemical processes, to develop better drug designs. This approach has been called Geomimicry, meaning the study of natural geo-processes that one can mimic to improve human and environmental health.

At the turn of the 21st century, curiosity among members of the Clay Minerals Society (CMS) was ignited by a report that reduced-iron clays from France were successfully used for treating Buruli ulcer; a mycobacterial skin infection suffered by indigenous people in Africa. In collaboration with CMS colleagues (Dennis Eberl and Ross Giese) and microbiologists, we investigated the chemical and mineralogical properties of French Green Clays to discover what made them antibacterial. This led to recognition of more reduced iron clays effective at killing antibiotic-resistant bacteria. The research inspired a major shift toward understanding clay-microbe electrochemical interactions in nature, that could potentially be useful in medicinal applications.

The mineralogical mechanisms, determined over a decade of research, indicate that human bacterial pathogens, cannot quickly adapt to the changing pH and oxidation state imposed by reduced iron clays. The oxidation of reduced iron clays, when hydrated, drives production of reactive oxygen species (e.g., hydroxyl radicals) that damage bacterial membranes and intracellular proteins. *In vitro* testing shows that even antibiotic-resistant bacterial pathogens, forming biofilms that cause infection, are reduced, or eliminated in just 24 hours. However, there is a challenge in the wound environment, where the effectiveness of the clays is limited due to overall reduction of the mineral reactants. This episode of the investigation is the most exciting because of the myriad of biogeochemical processes to be studied and manipulated to perfect the application of clays in wound care. Future research will focus on the electrochemical exchange between minerals and wound components; fluids, skin cells, bacterial exudates and membranes, which are genetically adapted for defense against oxidative stresses.

Transformation of 1:1 type clay minerals into smectite under hydrothermal condition

Hongping He[1,*], **Shichao Ji**[1], **Shangying Li**[1], **Qi Tao**[1], **Jianxi Zhu**[1]

[1]Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

*hehp@gig.ac.cn

Understanding clay mineral transformation is of importance to unraveling geological processes and to utilizing clay mineral resources. So far, two pathways have been identified, *i.e.*, the transformation between 2:1 type clay minerals (Stixrude and Peacor, 2002) and from 2:1 type to 1:1 type (Altschuler et al., 1963). However, the conversion of 1:1 to 2:1 type has rarely been reported.

In this study, we demonstrate that 1:1 type clay minerals can transform into 2:1 smectite under hydrothermal condition (He et al., 2017; Ji et al., 2018). XRD patterns of the hydrothermal products display characteristic basal spacing of smectite group minerals at 1.2 - 1.3 nm, consistent with HRTEM observations. The consumption of surface OH in precursor minerals during the transformation led to a dramatic decrease of mass loss of dehydroxylation in TG curves. Note that the transformation from kaolinite and halloysite to smectite was much easier than that from serpentine to smectite. The difficulty for the transformation of serpentine may be due to the lack of enough available Al in the reaction system, in which the substitution of Al^{3+} for Si^{4+} in the neo-formed tetrahedral sheet is critical to control the size matching between the neo-formed tetrahedral sheet and octahedral sheet in starting minerals. For kaolinite, halloysite and lizardite, exfoliation occurred during their conversions, leading to a prominent decrease in the number of phyllosilicate layers contained in the hydrothermal products. However, the transformation could only take place at the edges of an antigorite layer rather than the whole one, due to the strong Si-O covalent bonds between adjacent layers in antigorite. The inheritance of such Si-O covalent bonds also resulted in non-swelling property of the neo-formed smectite from antigorite. Two main pathways were proposed for the transformation of 1:1 type clay minerals into smectite: 1) conversion of one 1:1 type layer to one smectite layer via attachment of Si-O tetrahedra onto the octahedral sheet surface of the starting minerals and 2) two adjacent 1:1 type layers merging into one smectite layer. The present study suggests that solid state transformation is the main mechanism for conversion of 1:1 type clay minerals to smectite.

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The wonders (and implications) of disorder in clay minerals

David Bish

Indiana University, Molecular Structure Center, Department of Chemistry, Bloomington IN 47405-7102, USA

bish@indiana.edu

When I began studying clay minerals with Professor G. W. Brindley in 1974, I dreamed of locating a single crystal of montmorillonite. With this crystal I would determine the structure accurately and solve all of the unknowns about this fascinating material. Of course my dreamwas unrealistic; if I had somehow miraculously found a suitable (ordered, >10's of μm in size)single crystal, this "unicorn" would not have been representative of montmorillonite. In lieu of such an impossible crystal, macroscopic examples of phyllosilicates (e.g., micas, chlorites,dickite) have been used for almost a century to infer the structures of their finer-grained and disordered counterparts, and these provide a framework for understanding many aspects of the silicate clay minerals.

It is well known that the phyllosilicate clay minerals are distinct from their macroscopic varieties by virtue of their very small crystallite size, their layer structures that usually exhibitstacking disorder, and, for many, the isomorphous substitutions that occur in their structures. The implications of these attributes to diffraction studies are profound and complicate analysisof the phyllosilicate clay minerals. X-ray crystallographers learn early in their careers about three-dimensional symmetry and order, and about Miller indices, which are integer values. We also learn the well-known formula for the structure factor, $F_{hkl} = S\ f_j\ e^{2\pi i(hx+ky+lz)}$, where *hkl* are the Miller indices for a particular reflection and x, y, and z are the fractional atomic coordinates for a given atom (the summation is over all atoms *j* in a unit cell).

W. F. Bradley famously said that the interference function is the window through which we view the Fourier transform (Brindley and Brown, 1980, p. 260); the structure factor "exists" everywhere, but we "see" it for macroscopic ordered crystals only where *h*, *k*, and *l* are integers. Theoretical peaks for perfect materials are thus delta functions, and any width is dueto the instrumental optics. However, the assumption that *h*, *k*, and *l* are integers does not apply for disordered and/or fine-grained materials. Thus, application of methods using this assumption involves an approximation and is usually unwarranted. For example, one cannot simply determine the *b* unit-cell parameter of a smectite from the centroid of the 06*l* (not 060) peak. Similarly, the popular Rietveld method is based on the assumption of integer *h*, *k*, and *l* values, so great care is required when applying it to disordered or even very fine-grained or highly strained materials. Allowing profiles to broaden is not an acceptable method to model disorder (or very small crystallites), as the Rietveld method calculates the structure factor onlyat reciprocal lattice nodes. Given this complication, other approaches that do not rely on 3-D order (e.g., the Debye scattering equation, DSE) are better suited to studying scattering from disordered materials. Ultimately, the factors that make clay minerals difficult to characterize accurately are those that make them fascinating and useful, and the DSE can illuminate manyfascinating features.

Brindley, G. W., & Brown, G. (1980) *Crystal Structures of Clay Minerals and their X-rayIdentification*. London: Mineralogical Society.

Nanoscale chemical processes of phyllosilicates influence macroscale geologic CO_2 storage capacities and seals

Young-Shin Jun

Department of Energy, Environmental & Chemical Engineering, Washington University in St. Louis, MO, 63130, USA

ysjun@wustl.edu

It is a great honor for me to receive the 2022 Marion L. and Chrystie M. Jackson Mid-Career Scientist Award of the Clay Minerals Society. This talk will introduce an account of my research group's efforts to better understand the roles of clay minerals in important energy-related subsurface engineered systems.

The safety and efficiency of long-term geologic CO_2 sequestration and other CO_2-enabled subsurface energy storage methods depend on the seal integrity of the overlying caprocks. In particular, to examine the fate and transport of injected CO_2 during geologic CO_2 sequestration and to develop a better predictive framework, we need a deeper understanding of the chemical reactions at brine−clay mineral interfaces and the impacts of chemical alterations of clay minerals. Phyllosilicates are an important mineral group for understanding the dynamic chemistry of clay minerals, a major component of caprocks at GCS sites. They have an intrinsic nanoscale dimension in each layer, which possesses distinctive nanoscale properties that can affect kilometer-scale subsurface operation. In this talk, I will introduce two interesting findings about nanoscale chemical reactions of phyllosilicates in subsurface environments.

First, using biotite (an Fe-bearing phyllosilicate), we investigated the effects of various subsurface-abundant inorganic (potassium, sodium, sulfate, and phosphate) and organic ligands (acetate, oxalate, and phosphonate) on the dissolution and precipitation of clay minerals and assessed their impacts on mineral surface wettability. We conducted these experiments under conditions relevant to geologic CO_2 sequestration and supercritical CO_2-enhanced energy recovery/storage processes (e.g., 95 °C and 102 atm of CO_2). We found that the different ligands influenced biotite dissolution distinctively through surface complexation and/or aqueous complexation. In addition, although sulfate, acetate, and oxalate did not promote secondary mineral formation, phosphate and phosphonates significantly promoted secondary precipitation of Fe- and Al-bearing minerals. This coupled dissolution and precipitation of phyllosilicate minerals can affect the pore geometry, surface chemical affinity, and permeability. Specifically, the surface wettability of minerals was affected by the types and concentrations of ligands in the subsurface systems, which could specifically affect the transport of injected CO_2 in subsurface porous media.

Second, we examined the roles of abundant Fe-bearing phyllosilicates in the degradation of injected additive chemicals that can be introduced during CO_2-enabled subsurface engineered projects. To test the phyllosilicate-facilitated degradation of additive chemicals, we reacted 0.5 mM DTPMP (diethylenetriaminepenta(methylene) phosphonate, a model phosphonate-based scale inhibitor) with phyllosilicates under subsurface relevant conditions (50–95 °C and 102 atm CO_2). An Fe-poor muscovite, an Fe(II)-rich biotite, and an Fe(III)-rich nontronite were tested as Fe-bearing phyllosilicates that are often found in shales. These three phyllosilicates showed different extents of DTPMP degradation: No distinguishable effect by muscovite, slight promotion by nontronite, and remarkable promotion by biotite. We found that Fe associated with phyllosilicates is key to the redox degradation of DTPMP. Reactive oxygen species were generated through the reduction of molecular oxygen by Fe(II) adsorbed on the mineral surface or in the mineral structure, and hydroxyl radicals further degraded DTPMP to form phosphate, formate, and DTPMP residuals.

These findings highlight how nanoscale chemical reactions at brine−clay mineral interfaces can impact more efficient and safer geologic CO_2 sequestration and supercritical CO_2- enabld energy recovery/storage processes.

Clay-bio nanohybrids with 1 : 1 heterostructures: discoveries and impacts

Jin-Ho Choy

Intelligent Nanohybrid Materials Laboratory (INML), Institute of Tissue Regeneration Engineering (ITREN), Dankook University, Cheonan 31116, Korea
Department of Pre-medical Course, College of Medicine, Dankook University, Cheonan 31116, Korea
Tokyo Tech World Research Hub Initiative (WRHI), Institute of InnovativeResearch, Tokyo Institute of Technology, Yokohama 226-8503, Japan

jhchoy@dankook.ac.kr

New findings in fundamental science has never been realized without scientific curiosity and passion for learning. Of course, one might has found something lucky, but manydiscoveries and inventions are made up of abundant basic knowledge with long, constant efforts as well appeared in our long history of science and technology. The same goes for the Clay-Bio Nanohybrids (CBNs) that I am about to introduce you today, how the CBN was designed and eventually discovered. In 1999, the anionic clay-DNA nanohybrid, as the first example of CBN, was reported in JACS (J. Am. Chem. Soc.) after a long time of frustration, because it was not easy to treat ultra-low concentration of biological samples quantitatively. And that we have been presented various CBNs such as Clay-vitamers, Clay-Drugs, etc to academia. Now, I would like to share my research experiences with clay intercalation compounds (CICs), since I used to look into details of nanostructured materials such as 1:1 (neutral) and 1:2 (cationic) clay minerals like kaolinites and montmorillonits, etc., including anionic clays like hydrotalcite-like ones. Before the Nano- Initiative announcement by President Clinton in the year of 2000, I found that there were no chance for researchers to consider CICs as the 2D nanoscale-structured materials. In this sense, I was lucky enough because I have been trained to familiar with CICs during my PhD course (Prof. Armin Weiss laboratory) at the Ludwig-Maximilians-Universitaet (LMU) Muenchen from 1976 to 1979. During this period of time, I have been familiar not only with clay minerals, but also with 2-dimensional materials such as graphitic carbon, metal chalcogenides, transition-metal oxide, hydroxides and oxyhalogenides etc.

When I came across with anionic clays on the way of searching for novel gene delivery systems around 1995, I became interested in biocompatible hydrotalcite-like clays, layered double hydroxides with large anionic exchange capacity, which were different from conventional cationic clays with cationic exchange capacity (CEC). At that time, these experiences of clay intercalation chemistry helped me a lot to understand novel CBN systems. In particular, the clay-bioactive molecular hybrid systems have attracted great attention not only to academia from the perspective of new emerging NT-BT convergence science, but also to new theranostic industry for nanomedical applications.

I think it is worthy to note that more than 10,000 papers related to nanohybrids have been reported after the new concept of nanohybrid was proposed by us in 1998, and they are still rapidly increasing. It suggests that many researchers are working on those materials and appreciating even after 25 years of the discovery. It is my hope the CBNs will become a major material in our society in near future.

TS02 Nanoporous Fibrous Clays

ORAL PRESENTATIONS

Chemical modification of clay minerals as a versatile tool to improve their properties

Marina Massaro[1,*], Maria Laura Alfieri[2], Giuseppe Cavallaro[3,4], Giuseppe Lazzara[3,4], Rita Sánchez-Espejo[5], César Viseras Iborra[5,6], Serena Riela[1]

[1]Universit degli Studi di Palermo, Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), 90128 Palermo, Italy

[2]Universit di Napoli Federico II, Dipartimento di Scienze Chimiche, I-80126, Napoli, Italy

[3]Universit degli Studi di Palermo, Dipartimento di Fisica e Chimica (DiFC), 90128, Palermo, Italy

[4]Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, INSTM, I-50121 Firenze, Italy

[5]Andalusian Institute of Earth Sciences, CSIC-UGR, 18100 Armilla, Granada, Spain

[6]University of Granada, Department of Pharmacy and Pharmaceutical Technology, Faculty of Pharmacy, 18071, Granada, Spain

*marina.massaro@unipa.it

Clay minerals, are emerging materials which because of their interesting physico-chemical features and morphologies, have attracted considerable attention in the last few years. From a chemical point of view, their different chemical compositions allow to modify the clay surface opening the doorway to several strategies to tune the clay's properties (Massaro et al. 2017). Specifically, it generates nanoarchitectures which have found application in several fields, ranging from biology to industry (Colletti et al. 2020).

Different kind of modification can be envisaged based on the supramolecular interactions of molecules or species with the clay surface or the grafting of specific functionalities (Alfieri et al. 2022, Massaro et al. 2018).

Herein we report the last results in the chemical manipulation of halloysite and hectorite surfaces to develop "smart" and multifunctional nanomaterials which have been used as drug carrier and delivery systems, for environmental remediation and as filler for polymeric matrices.

The advantage to modify the clay surfaces over the use of the pristine ones will be also highlighted.

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Sepiolite-rosemary oil combination as an environmentally oriented insecticide

Giora Rytwo[1,2*], Tamir Kramer[1], Lotem Azoulay[3], Liora Shaltiel-Harpaz[1,3]

[1]Environ. Sci. and Water Sci. Depts., Tel Hai College, Israel
[2]Environmental Physical Chemistry Lab., MIGAL-Galilee Research Institute, Israel
[3]Integrated Pest Management Lab., Northern R@D, MIGAL-Galilee Research Institute, Israel

*giorarytwo@gmail.com

Pest management is an essential tool for cost-effective agriculture. However, due to pest's ability to develop resistance to pesticides, and reinforcement of environmental and health regulations, there is the need to develop novel pesticides, based on reducing the use of hazardous compounds that damage the soil,the water and the biosphere. Certain natural essential oils are known for their ability to repulse and even be lethal- to specific pests, and may therefore serve as a less hazardous alternative to traditional pesticides. However, key- problems to be solved are the high vapor pressure and rapid volatility of such oils, and in some cases- their phytotoxicity at levels that have insecticidal effect.

Clays, organoclays and nanocomposites were suggested as matrices for adsorbing organic compounds leading to their controlled-or slow-release. Thus, such matrices might increase the pesticide efficiency of essential oils by slowly releasing them, and probably reduce phytotoxicity, offering an alternative to conventional pesticides.

This study combines in vitro studies evaluating therate of evaporation of rosemary (Rosmarinusofficinalis) essential oils (ROEO) from clays and organoclays formulations, with in vivo experiments testing efficient doses of clay-essential oil insecticides on onion thrips, while avoiding phytotoxicity damage to chives crop plants.

FTIR kinetic measurements of the evaporation led to the conclusion that sepiolite increases the half-life evaporation period when compared to the free essential oils or oils pre-adsorbed to montmorillonite, palygorskite or halloysite. More detailed gravimetric kinetic analysis showed that the pseudo-order of the evaporation of rosemary oil at room temperature increases from ~2 in raw oil to ~3.2 in sepiolite-ROEO. Apparently, such increase is mistakenly considered as increasing the speed of the process, but this happens only at high concentrations (Rytwo and Zelkind, 2021). The increase in the pseudo-order leads to the fact that thetime that takes to reduce the concentration from 20% the initial value to 10% of it, increases from less than 2 days to more than 30 days.

Indeed, efficiency tests showed significant ROEO lethality to thrips in chives increased considerably in the rosemary oil –sepiolite formulations when compared to raw ROEO. Furthermore, in control treatments damage due to phytotoxicity was observed, whereas in the sepiolite-based formulation plants were healthy and clean. Influence was still substantial even four weeks after application, as the preliminary kinetic evaluations indicated. GCMS analysis of the vapors in equilibrium with the formulation or the raw oil, show clear differences in the pattern for the different components of the essential oil.

This study provides an environmentally oriented approach that might yield to effective alternative and less hazardous pesticides. It also emphasizes the very specific and interesting interactions between organic molecules and fibrous clay minerals.

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Nanostructured materials based on fibrous clays as fillers of improved proton-conducting membranes for fuel-cell applications

Noura Thmaini[1,2], Khaled Charradi[2], Zakarya Ahmed[2], Radhouane Chtourou[2], Pilar Aranda[1*]

[1]Instituto de Ciencia de Materiales de Madrid (ICMM), CSIC, 28049, Madrid, Spain

[2]Nanomaterials and Systems for Renewable Energy Laboratory, Research and Technology Center of Energy, Hammam Lif, Tunisia

pilar.aranda@csic.es

Proton-conducting membranes (PEMs) are considered key-components in polymer electrolyte membrane fuel cells (PEMFC). Among other polymers, Nafion is the most commonly used electrolyte in PEMFC but its low stability and decrease of conductivity at temperature > 80°C influence the fuel cell performance. Thus, the incorporation of nanoparticles (NP), such as TiO_2, SiO_2 or clay minerals, including fibrous clays (Beauger et al., 2013), results in improved reinforcement and a reduction of cross-over effect. The use of clays can contribute also to increase the water uptake of the membrane, which is an important parameter to take into consideration for the required proton conductivity in PEMFC applications. A novel and interesting approach we have explored is the use of modified clays incorporating diverse type of NP as they may introduce also a solution for water management in the Nafion membranes, especially at temperatures above 100°C. An example of this is the use of sepiolite-layered double hydroxide nanostructured materials as filler of Nafion membranes (Charradi et al., 2019). The approach is promising as fibrous clays, sepiolite and palygorskite, are able to assemble numerous types of nanoparticles using variated protocols of synthesis (Aranda & Ruiz-Hitzky, 2018). In this context, this communication will introduce various examples of nanostructured materials based on fibrous clays, sepiolite and palygorskite, incorporating TiO_2 and SiO_2 NP, analyzing the characteristics of the composite Nafion membranes prepared with the resulting systems in view to their potential application in improved PEMFC able to work above 80ºC.

Acknowledgement: PID2019-105479RB-I00 (AEI, Spain) & COOPA20373 (CSIC, Spain) projects.

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Reinforcement and protective coating of natural fibers by biopolymer/halloysite nanotubes mixtures

Giuseppe Cavallaro*, Maria Rita Caruso, Stefana Milioto, Giuseppe Lazzara

Università degli Studi di Palermo, Dipartimento di Fisica e Chimica "E. Segrè", Viale delle Scienze, pad. 17, 90128 Palermo, Italy

*giuseppe.cavallaro@unipa.it

Hybrid materials composed by halloysite nanotubes (HNTs) and several biological macromolecules were investigated for the reinforcement and protective coating of natural fibers, including hair, wool and silk. Among the biopolymers, alginate, keratin, and wax were selected. The treatment of the fibers was carried out by using the dip coating procedure through aqueous mixtures of halloysite and biomacromolecules. The composition of the mixtures as well as the immersion time were systematically varied.

As shown in our previous work (Cavallaro et al., 2020), keratin/HNTs composites are effective for the protective treatment of human hair. Here, we explored the addition of alginate in the keratin/HNTs mixtures as a novel strategy to improve the reinforcement and protection efficiencies of hair fibers. Within this, the crosslinking of alginate by calcium chloride was tested to obtain a gel system that can be perspective for cosmetic applications. Preliminary investigations of the alginate/keratin/HNTs dispersions were conducted through 1-potential, turbidity and dynamic light scattering experiments, while the sol-gel transition was studied by rheological measurements. The reinforcing action of the composites was tested by dynamic mechanical analysis (DMA) conducted on the treated hair. Furthermore, the tensile properties of the hair fibers were determined after their exposure to UV irradiation allowing us to estimate the protection efficiency of the coating by alginate/keratin/HNTs.

Keratin/HNTs composites were employed for the protective coating of wool fibers used for the fabrication of tapestries. We analyzed the colorimetric parameters, the thermal stability and the tensile properties of the treated fibers before and after UV irradiation to evaluate the suitability of keratin/HNTs mixtures for the protective treatment of ancient tapestries. Finally, we tested wax/HNTs hybrids for the coating of silk sutures used for surgical applications. The influence of the wax/HNTs coating on the thermal and mechanical properties of the silk fibers was investigated. In addition, we loaded an antibacterial compound within the wax/HNTs composite with the aim to extend the medical applications of the silk fibers.

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Preparation of wax microparticles stabilized by halloysite nanotubes: a versatile material for restoration of cultural heritage

Giuseppe Cavallaro, Lorenzo Lisuzzo, Maria Rita Caruso, Giuseppe Lazzara*

Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze, pad. 17, 90128 Palermo, Italy

*giuseppe.lazzara@unipa.it

The design of novel composite based on wax/halloysite nanotubes hybrid microspheres will be reported. Besides surfactants, which decrease the interfacial tension between two immiscible liquids, also interfacially active particles can successfully stabilize an emulsion system by attaching at the liquid-liquid interface.

We prepared wax/halloysite Pickering emulsions in various media. The stability and the structure of the obtained pickering and their stability which were characterized. SEM images allowed to have more detailed insights on the nanotubes disposition at the wax/water interface, acting as an outer stabilizing shell. Therefore, the cellulosic biopolymer was added and it was found that it enhances the colloidal stability of the particles, preventing their coalescence and sedimentation. The preparation of the composite films was carried out by solvent casting method, which enabled the development of very homogeneous materials with controlled wettability and heat reservoir features.

Finally, we have investigated the suitability for conservation protocols in Cultural Heritage restoration and in particular for waterlogged archaeological wood consolidation as well as stone surface protection [1,2].

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Acceleration of the one-pot dehydrogenation of D-glucose to 2-keto-D-gluconate in aqueous amino acid *via* hydrated stacked clay nanosheets

Katsunori Nakase, **Tomohiko Okada***

Fac. Eng., Shinshu Univ. 4-17-1 Wakasato, Nagano 380-8553, Japan

*tomohiko@shinshu-u.ac.jp

D-glucose (Glc) is naturally oxidized to 2-keto-D-gluconic acid (2-KGA) by microbes in soils/sediments and on rock surfaces. The organic acid, 2-KGA, is widely utilized in the cosmetic, pharmaceutical, and food industries as an intermediate for the safe production of antioxidants, including erythorbic acid (isoascorbic acid) and sodium erythorbate. The assembly of discrete active species to form periodical nanostructures (e.g., nanoparticles (0D), one-dimensional (1D) nanotubes, two-dimensional (2D) nanosheets, and three-dimensional (3D) nanoporous solids) is essential in realizing low-cost artificial enzymes that mimic natural enzymatic functions in extraordinary bio(chemo)selective reactions [1]. The alternate, stacked, layerstructures are expected to participate in the molecular recognition catalytic reactions [2,3].

In this study, we developed artificial glucose/gluconic acid dehydrogenase from naturally abundant resources: aspartate (Asp) and montmorillonite (a subgroup of smectite natural clay minerals). b-D-glucose (Glc) was dehydrogenated to 2-keto-D-gluconate (2-KGA) at 25°C and 30°C in an aqueous acidic solution (pH: 3, 4, and 5). The reaction involved sequential steps that yielded D-gluconic acid (GA) as an intermediate. The second step of the dehydrogenation (GA to 2-KGA) occurred at a higher rate than the first (Glc to GA), which is comparable to the natural process. A negatively charged carboxylate in Asp was required for the dehydrogenation, which donates an electron pair ($COO:^{-}$) to the hydroxyl group bonded to the C(1)-position of Glc. The acidic sites in clay served as coenzymatic sites (electron acceptor), promoting the Glc dehydrogenation as the Glc reduced by Asp approaches the clay coenzymatic sites. The active coenzymatic structures were developed in 48 h (induction period) through the rearrangement of the adsorbed Asp and Glc molecules on montmorillonite in water (intermediate structure). The spontaneous assembling of the intermediate structures facilitated the one-pot dehydrogenation of Glc to 2-KGA *via* periodic "hydrated stacked layers" comprising clay nanosheets, Asp, and Glc. The facile synthetic route proposed here is inexpensive and would be beneficial in various applications requiring Glc dehydrogenation.

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Photochromism of spiropyran/merocyanine in halloysite

Nattapat (Nut) Leelaphattharaphan, Makoto Ogawa*

School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, 555 Moo 1 Payupnai, Wangchan, Rayong 21210, Thailand

*makoto.ogawa@vistec.ac.th

Reversible color change by external stimuli is a phenomenon useful for smart materials including smart windows, recording, sensing. Color change upon irradiation is named as photochromism, which is applicable for optical recording, optical switch, smart windows, displays and so on. In order to find practical application of the photochromism, solid-state photochromis is required. Accordingly, photochromic molecules have been confined in nanospaces such as zeolites, mesoporous silicas, and clay minerals [1]. The confinements (or the host-guest interactions) are useful to tune the photochromic reactions from the aspects of color tuning, efficiency, and repeatability. In this study, the hybridizationof a spiropyran (Figure 1) with halloysite and sepiolite was examined.

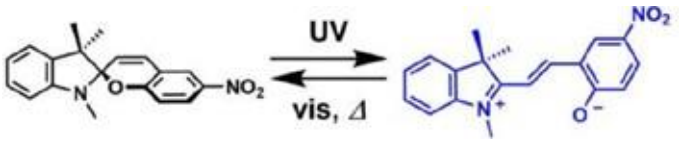


Figure 1. The photoisomerization between closed-ring spiropyran (left, colorless) and open-ringmerocynine (right, colored).

The hybridization was done by a mechanochemical reaction (mixing the two components manually) and the products were characterized by the appearance and UV Vis absorption spectra. Photochromism was seen upon irradiation and the thermal treatment.

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Tubular clay materials: design and orientation distribution function study

Mohcin Akri[1,2]*, Fabien Hubert[1], Eric Ferrage[1], Céline Mariette[2,3], Erwan Paineau[2], Stéphan Rouzière[2], Pascale Launois[2]

[1]IC2MP-Hydrasa, UMR 7285 CNRS, Université de Poitiers, 86022 Poitiers, France
[2]Université Paris Saclay, CNRS, Laboratoire de Physique des Solides, 91405 Orsay, France
[3]Institut de Physique de Rennes, 35000 Rennes, France

*mohcin.akri@univ-poitiers.fr

Tubular clay particles have anisometric shape and their particle arrangement leads to clay porous media ranging from isotropic (random distribution of particle orientations) to perfectly anisotropic (all the particles are aligned in the same direction). The orientation of tubular clay particles defines different geometries of the porosity that in turn significantly modify the transfer and storage properties of fluids (liquid and/or gas) in the porous medium. Establishment of a reference orientation distribution function (ODF) will provide a sound basis for describing the inner-organisation of porous media made of tubular clays, however this reference ODF solely exists for clay particles having platelet shape (Dabat et al., 2019).

This study aims at first obtaining a large panel of porous media made of tubular clays having variable inner-organisations from isotropic to strongly anisotropic. Porous media made of synthetic imogolite (Amara et al., 2013) and natural halloysite ("Dragon Mine", USA) size-fractioned (<0.2µm, 0.2-0.5µm, 0.5-2µm and >2µm) were designed using different methods such as compaction, centrifugation and film deposition. Analysis of their ODFs obtained on two-dimensional X-ray scattering patterns indicates that the orientation distribution of tubular particles could be controlled by tuning the concentration of the dispersion, the sizes of the particles and the method of preparation. These results may offer new opportunities to develop and design innovative porous clay material with controllable anisotropy and porosity.

Comparison with the reference ODF previously defined for platelet shape indicates significant differences. These differences will be discussed in order to pave the way for establishing an analytical reference ODF adapted to tubular clays.

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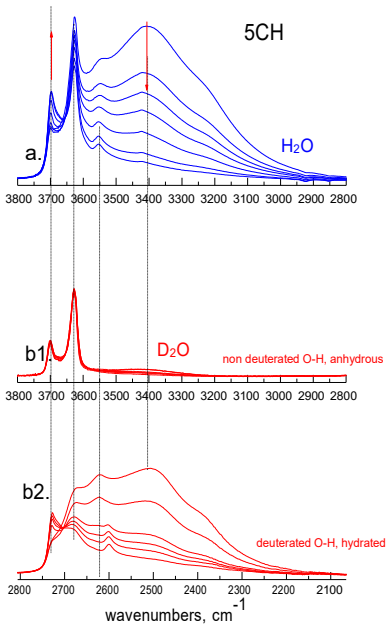
Vibrational study of the halloysite-(10Å) to -(7Å) transition

Eirini Siranidi[1,*], Georgios D. Chryssikos[1], Stephen Hillier[2,3]

[1]Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 11635 Athens, Greece
[2]The James Hutton Institute, Craigiebuckler, Aberdeen, AB15 8QH, UK
[3]Department of Soil and Environment, SLU, SE-75007 Uppsala, Sweden

*esiranidi@eie.gr

Halloysite is a polytype of kaolinite with hollow nanotubular structure and many potential industrial or environmental applications. Natural halloysite is formed with a ~10Å basal spacing owing to a monolayer of interlayer H_2O. Upon exposure to ambient humidity, most of the interlayer H_2O is irreversibly lost and the basal spacing collapses to ~7Å. Some residual H_2O in halloysite-(7Å) is observed at 3550 and 1650 cm^{-1} in the infrared spectra ("hole water").



ATR spectra of halloysite upon drying,(α) - H_2O form, (b1, b2) -D_2O form.

Due to experimental difficulties, most vibrational studies of the various types of halloysite are performed on stable halloysite-(7Å) samples. To our knowledge, this is the first detailed vibrational comparison of two cylindrical and two polygonal halloysites in their original 10Å form, saturated with either H_2O or D_2O, and as a function of *in situ* conversion to the 7Å form, by drying in the 70-2% RH (RD) range.

Attenuated Total Reflectance (ATR) spectra were acquired in the mid infrared (4000–550 cm^{-1}) using a homemade environmental cell coupled with a controlled humidity N_2 gas generator. Supporting XRD and electron microscopy data are presented.

Deuteration was expected to shift the modes of interlayer H_2O and inner surface OH groups, leaving the inner OH vibrations unaffected. Instead, the data showed that there is a significant part of the halloysite structure that is anhydrous and inaccessible to H/D exchange. Only the remaining accessible part responds in the expected manner during the 10Å to 7Å transition. The so-called "hole H_2O" is detected (albeit with broader bands) even in the hydrated state.

Effect of alkaline pretreatment on the functionalization of Halloysite Nanotubes: an experimental and computational study

Lorenzo Lisuzzo*, **Chiara Ferlito, Francesco Ferrante, Giuseppe Cavallaro, Giuseppe Lazzara, Dario Duca**

Università degli Studi di Palermo, Dipartimento di Fisica e Chimica – Emilio Segrè, Viale delle Scienze, pad. 17, 90128 Palermo, Italy

*lorenzo.lisuzzo@unipa.it

It is well known that Halloysite Nanotubes (HNTs) can be used in a wide range of technological applications and, among them, catalysis holds a certain importance. In order to be used as catalytic supports, HNTs should be firstly modified to provide anchoring sites for the adsorption of metal (nano) particles which are needed for the specific reactions.

In this work we investigated the effect of halloysite pretreatment in a strong alkaline medium as initial step for the modification of the nanoclay. After interacting with sodium hydroxide, the functionalization efficiency was investigated by using two alkoxysilanes with different chain: (3-aminopropyl) triethoxysilane (APTES) and [3-(2-Aminoethylamino) propyl] trimethoxysilane (AEAPTMS), respectively.

Thermogravimetric, Fourier-transform infrared spectroscopy, X-ray diffraction and X-ray fluorescence analysis were conducted to assess the effect of the alkaline pretreatment on the final surface silanization. Moreover, a computational study, using a cluster approach within density functional theory, was also carried out to provide further atomistic details. Formation of silanol groups and vacancies on the external surface as well as functionalization with APTES and AEAPTMS were investigated on both the internal and external surfaces of pretreated HNTs.

New hybrid clay-based geopolymers with beeswax and halloysite stabilized microparticles

Martina Maria Calvino*, Giuseppe Cavallaro, Giuseppe Lazzara, Lorenzo Lisuzzo, Stefana Milioto

Dipartimento di Fisica e Chimica "Emilio Segrè", Università degli Studi di Palermo, Viale delle Scienze, pad. 17, 90128, Palermo, Italy

*martinamaria.calvino@unipa.it

In recent years, due to the growing demand of eco-friendly and low-cost materials from natural resources or industrial by-products, research is now focused on geopolymeric materials that offer new perspectives in environmental remediation technologies and can be synthesized from natural clays. Geopolymers are inorganic polymeric materials with an amorphous network of aluminosilicates. They are formed as a result of a geopolymerization process with an alkaline activating solution, leading to the formation of three-dimensional structures with Si-O-Al bonds. Nowadays, in order to modify and improve specific properties, nanomaterials are widely employed to develop modern multifunctional products. For instance, nanoclays are commonly used in cement concrete as performance enhancers because of their peculiar characteristics in terms of physical chemistry, morphology and charge. Among them, halloysite (HNT), an emerging natural aluminosilicate with a singular hollow tubular structure, eco-compatibility, non-toxicity and low cost, can be used as aluminosilicate precursors in geopolymeric synthesis.

The main focus of this work is the preparation and characterization of new hybrid halloysite-based geopolymers with beeswax and microwax particles obtained from dried Pickering emulsion. It is known that halloysite- based geopolymers usually have a hydrophilic surface but the incorporation of bees wax in to the geopolymeric matrix causes a relevant change of water contact angles reaching hydrophobic values. The effect of wax on the structure of these materials and their thermal stability was investigated with TGA, FTIR and XRD. Additionally, DSC analysis provided the enthalpy (ΔH_m) of the melting process, giving information on the variation of crystallinity of wax in the geopolymeric network.

Beeswax was subsequently used as sacrificial material and it was removed from the matrix modifying the porosity of pristine materials. Water vapor permeability tests were carried out and showed an increase in permeability in these samples.

Sonic and electric responsiveness of imogolite nanotubes

Kazuhiro Shikinaka

National Institute of Advanced Industrial Science and Technology, 983-8551 Miyagi, Japan

kaz.shikinaka@aist.go.jp

Imogolite (IG) is a nanotube-shaped alumino-silicate type rigid cylindrical clay with the formula of $(HO)_3Al_2O_3SiOH$ [1]. The external and internal diameters are approximately 2 and 1 nm, respectively. In contrast, their length ranges from several ten-nm to several μm. The outer and inner surfaces of IG are covered with aluminol (Al-OH) and silanol (Si-OH) groups that give the dispersibility of IG in polar solvent. When dissolved in neutral to acidic and relatively low-ionic strength aqueous media, synthesized IG with adequately purification gives opaque colloidal dispersion containing individual nanotubes or thin bundles [2].

Crosslinking of IG nanotube in its water dispersion via hydrogen bonding between Al-OH on IG and dicarboxylic acid (DA) gives a gelated IG colloidal assembly in which IG nanotubes form network structure [3,4]. The mixture of IG and DA consisting of nanotube's network (later denoted as IG-DA mixture) exhibits keen thixotropy, a reversible solid/liquid phase transition behavior in response to mechanical shock. Here, the sonic and electric responsiveness of IG nanotube in the IG-DA mixture are presented.

In this study, original experimental setup can detect the change of ultrasonic velocity caused by the mixing of IG and DA in pure water [5]. Using this setup, the ultrasonic velocity is found to remain unchanged during the macroscopic solid/liquid transition and viscoelastic change of IG-DA mixture, which is consistent with previous literatures. Thus, the ultrasonic velocity measurement proves to be effective for the detection of well-dispersed clay minerals in diluted state, regardless of the phase and viscoelastic change of substances.

The IG-DA mixture can be swelled not only in water but also in ionic liquid (IL). This mixture (later denoted as IG-DA-IL) exhibits thixotropic behavior, high ionic conductivity [6], and electro-responsive birefringence modulation [7]. In this study, to reveal the relationship between physical/electrochemical properties and material composition on IG-DA-IL, phase behavior and ion-conductive properties of IG-DA-IL consisting of various DAs were systematically evaluated [8]. Additionally, a potentiality of current-voltage responsiveness of IG-DA-IL was also verified for the first time. The obtained knowledge will realize future applications of IG-DA-IL for components of electric responsive active materials such as sensors and actuators.

Acknowledgement: This work is financially supported by the JSPS KAKENHI (26870179, 16H04199 and 18K05252).

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Two-dimensional water in halloysite nanotubes: structure and dynamics from neutron experiments

AasimShaffi[1,*], NiaGray-Wannell[2], Tom Headen[3], Sanghamitra Mukhopadhyay[3], Andrew Seel[1], Stephen Hillier[2,4], Neal Skipper[1]

[1]UniversityCollegeLondon(UCL), Department of Physics and Astronomy, London, UK
[2]The James Hutton Institute, Aberdeen, UK
[3]ISIS Neutron and Muon Source, Didcot, UK
[4]Swedish University of Agricultural Sciences (SLU), Department of Soil and Environment, Uppsala, Sweden

*aasim.shaffi.17@ucl.ac.uk

Halloysite is a clay mineral that can form as a nanotube. The structure consists of a spiral of clay layers and water layers (Figure 1). Water is thought to be causal in the rolling of the 1:1 clay layers into a nano-tube. Understanding nanotube formation could inform synthetic routes, leading to optimisation of tubular morphology. The nanotubular property is the biggest driver of halloysite research (Churchman *et al.*, 2016). The molecular structure of the water layer is a long standing challenge (Costanzo *et al.*,1982), andits dynamics, could explain why it readily leaves the structure, under standard conditions. Halloysite is a model to study a two-dimensional water layer, due to its mono layer form and purity. Other model systems have attracted significant attention (Algara-Siller *et al.*, 2015; Ma *et al.*, 2020) because they are analogues, to help understand 2D water in other systems. For example, nanoengineered water channels for membranes (Go-pinadhan *et al.*, 2019).

Neutrons are an ideal probe to study the water layer in halloysite (10Å). They can penetrate the bulk structure, where they are scattered by H/D atoms. Analysis of diffraction data can reveal the short- range water structure. Monte Carlo simulations can be fitted to this data, resulting in an average structure of the water layer. The water dynamics can be revealed by quasi-elastic neutron scattering (QENS). Neutrons-gain or lose energy as they scatter from H atoms, when the water molecules move, along angstrom (Å) distances and picosecond (ps) timescales. Movements that can be probed include: diffusive and localised motion; jumping of water molecules, by fitting to models; and changes in the dynamics, as a function of temperature. Preliminary results will be presented.

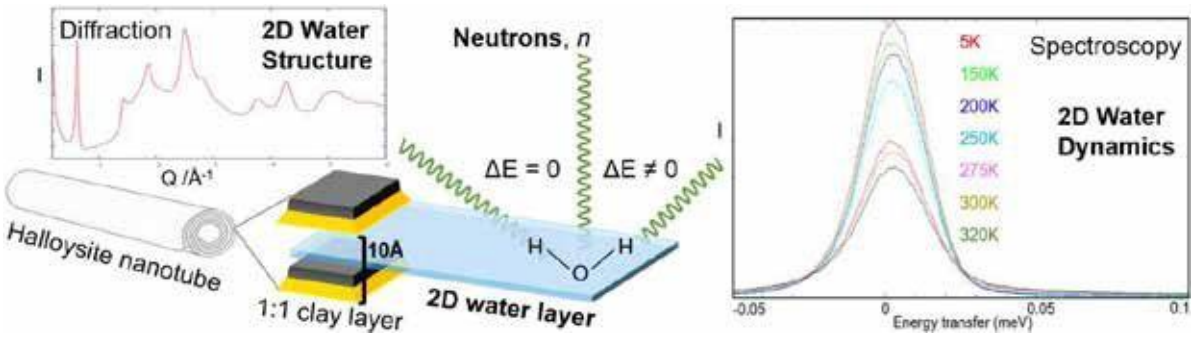


Figure1. Diagram of halloysite nanotube. Neutron diffraction pattern (left) and QENS spectra (right).

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Spectroscopic behavior of an anionic dye in aqueous colloidal dispersions of smectites and sepiolite

Teruyuki Nakato*, Yoshiki Kawanami, Keisuke Taninaka, Emiko Mouri

Department of Applied Chemistry, Kyushu Institute of Technology, Kitakyushu, Fukuoka 804-8550,Japan

*nakato@che.kyutech.ac.jp

There are many aqueous colloidal systems of clay minerals, where negatively charged clay particles are dispersed in water as represented by the colloids of smectites. These clay colloids have often been employed as heterogeneous media for photofunctional molecules. The photofunctional guest molecules adsorbed by the clay minerals are immobilized on the particle surfaces or the interlayer spaces to show various unusual photofunctions. The guest species have been limited to cationic or polar species because of their immobilization mechanism onto the clay particles.

In the present study, however, we examined effects of aqueous clay colloids on the spectroscopic properties of an anionic xanthene dye Acid Red 91 (AR91, also known as Eosin B). When AR91 is dissolved in aqueous colloids of synthetic hectorite (Laponite), its spectroscopic behavior reflects the coexistence of the clay particles. Both of the absorption and fluorescence maxima are red-shifted and the fluorescence intensity increases with increasing the clay concentration (Figure 1). Removal of the clay particles by supercentrifugation recovers the absorption and fluorescence spectra of aqueous solution. The results demonstrate reversible impacts of the colloidal clay particles of smectite on the spectroscopic properties of anionic AR91. Although electrostatically repulsive interactions must exist between the anionic dye molecules and smectite particles, our results strongly suggest the existence of interactions between the anionic clay particles and the anionic dye molecules in the clay colloids.

Spectroscopic behavior of AR91 in aqueous colloids of saponite and sepiolite will also be examined.

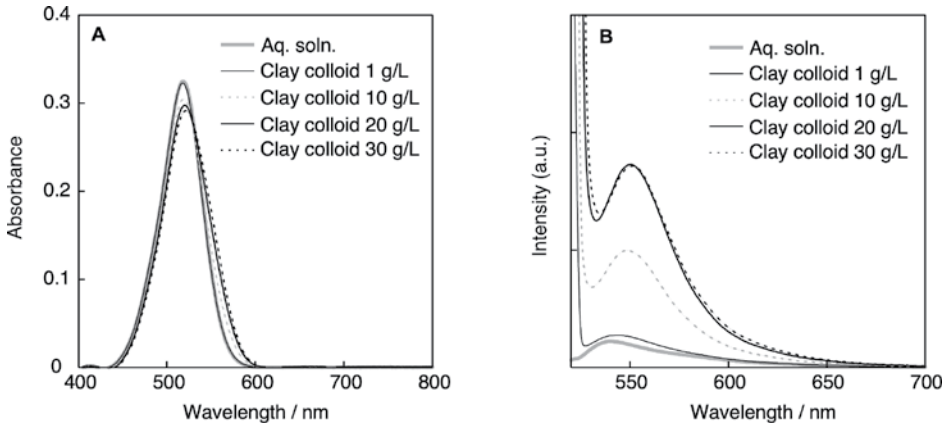


Figure 1. (A) Visible absorption and (B) fluorescence spectra of AR91 (7 ′ 10^{-6} mol/L) in an aqueous solution and clay colloids with different clay concentrations.

Modification strategy of structure and properties of allophane

Shun Wang[1, 2*], Peng Yuan[2], Peixin Du[3], Howard Wang[1], Dong Liu[2]

[1]Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, China
[2]Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[3]Macau University of Science and Technology, Macau, China

*wangshun@sslab.org.cn

Allophane ($1\sim2SiO_2\cdot Al_2O_3\cdot 5\sim6H_2O$) presents an imogolite-like local structure (ImoLS) but shows hollow spherical morphology with a diameter of 3.5~5.0 nm (Figure 1), which can be considered as nano-polymorphs as imogolite. The structure and properties of minerals are hyperosculation with each other, and both of them dominate the applications and performance of minerals. Therefore, to realize the efficient utilization of the natural mineral resource, it is crucial to fully understand the structure and properties of allophane and master their qualitative/quantitative modification.

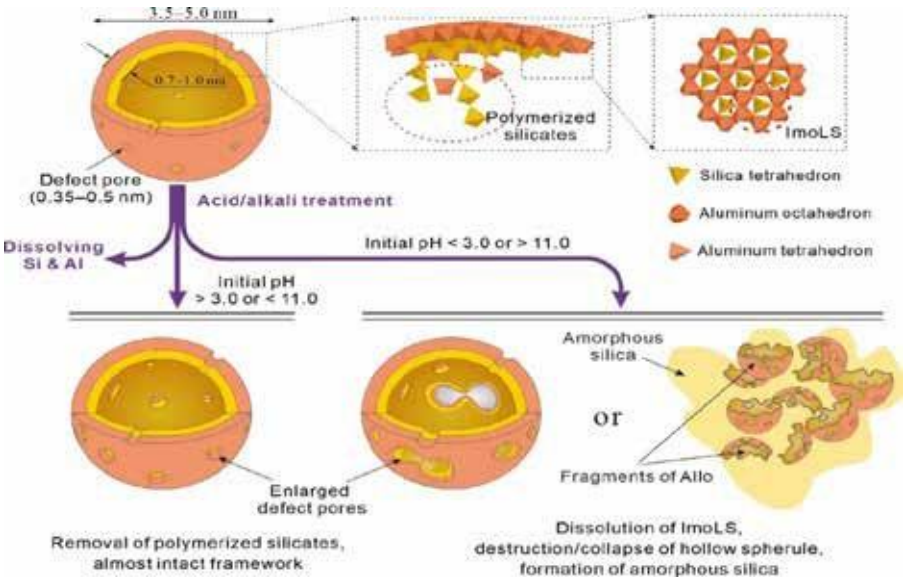


Figure 1. Structural changes and related mechanisms of allophane under different-pH media.

Recently, we have gained some new insights in the following aspects: 1) revealing the changes of microstructure and properties of surface groups of allophane with acid/alkali/thermal treatments and related mechanisms (Figure 1); 2) directional surface modification of hollow spherules by in situ and/or non-in-situ methods and related mechanisms, and achieving stable dispersion of single nanoparticles. Our findings are of use for promoting the applications of allophane in the fields of nano-composite materials, nano-reaction containers, catalyst/drug carriers, and adsorption.

Influence of indigo-hydroxyl interactions on the properties of sepiolite-based Maya blue pigment

Li Li[1,2,*], Guanzheng Zhuang[3], Mengyuan Li[1,2], Peng Yuan[1]

[1]CAS Key Laboratory of Mineralogy and Metallogeny, Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China

[2]University of Chinese Academy of Sciences, Beijing, 100049, China [3]Institute of Resources Utilization and Rear Earth Development, Guangdong Academy of Sciences, Guangzhou, 510650, China

*lily@gig.ac.cn

Maya blue is a greenish-blue and stable pigment which was widely used in the ancient Mayan area. Now it is known as a hybrid pigment of indigo and palygorskite or sepiolite. However, the color causing and stabilization mechanism of Maya blue are still unclear.

In this study, the interactions between different hydroxyl groups of sepiolite and indigo and their effects on the color and stability of Maya blue pigments were investigated. Sepiolite materials were heated at 160, 360, 610, and 880°C to remove zeolitic water, the first coordinated water, the second coordinated water, and structural hydroxyls. A series of Maya blue simulants were prepared by heating the mixture of indigo and sepiolite materials at 180°C. Reflectance spectroscopy and CIE 1976 color space were employed to characterize color properties and color differences of hybrid pigments. Chemical resistance to concentrated HNO_3 and dimethyl sulfoxide (DMSO), and photostability under visible light were evaluated. Micro-porous analysis and Fourier transform infrared spectroscopy were applied to study the indigo-sepiolite interaction.

Coordinated water was essential for the greenish-blue color and outstanding stability of Maya blue, while zeolitic water and structural hydroxyls did not affect pigments' properties. Indigo molecules were con- firmed to be inserted into sepiolite channels and formed hydrogen bonds with coordinated water at oneside. Structural hydroxyls were insignificant for the formation of Maya blue.

Adsorption of iodine anions by halloysite and halloysite/Ag_2O nanocomposites

Wenbin Yu[1], Quan Wan[1, 2,*], Daoyong Tan[3], Zonghua Qin[1], Shuguang Yang[1], Xin Nie[1]

[1]State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou 550081, China
[2]CAS Center for Excellence in Comparative Planetology, Hefei 230026, China
[3]Key Laboratory of Solid Waste Treatment and Resource Recycle, Ministry of Education, Southwest University of Science and Technology, Sichuan, Mianyang 621010, China

*wanquan@vip.gyig.ac.cn

With the development of nuclear energy, large amounts of radionuclides are produced and inevitably released into the natural environment, posing a serious risk to public health and environmental protection (Wang et al., 2019). Among them, radioactive iodine is of the greatest environmental concern because of its low adsorption tendency/high mobility (Kaplan et al., 2014), which is primarily due to its anionic nature in aqueous environments. Iodine exists as iodide (I^-) and iodate (IO_3^-) depending on redox and pH conditions (Fuge and Johnson, 2015), both of which are repulsed from the negative surface charges on most sediments and minerals. Therefore, the efficient adsorption and solidification of radioactive iodine is an important task. In this work, the adsorption of iodine anions (IO_3^- and I^-) by halloysite and halloysite/Ag_2O nanocomposites was carried out. The results show that the nanotubular halloysite exhibited strong adsorption to IO_3^-, with a distribution coefficient (K_d) of 131.6 ± 14.6 mL/g, which is more than 30 times higher than that of flaky kaolinite. The specific surface area normalized K_d value on halloysite is >13.5-fold higher than that on kaolinite. It was proposed that the strong adsorption is because of the curved octahedral sheet causing a geometry match between three oxygen atoms in the iodate and three OH above the vacant sites of the octahedral sheet (Yu et al., 2020). In contrast, halloysite showed very weak adsorption to I^-. Therefore, halloysite/Ag O nanocomposites were prepared to improve the adsorption performance of I^- by halloysite, due to the strong affinity between iodide and silver. The I^- adsorption capacity of nanocomposite with approximately 2.21% Ag O in the lumen of halloysite and with approximately 6.36% Ag_2O on the external surface of halloysite is 39.99 mg/g and 57.5 mg/g, respectively, both of which are significantly higher than that of halloysite. Importantly, the nanocomposite with Ag_2O in the lumen of halloysite is expected to constitute a low radiological hazard after capturing the radioactive I^-, because of the shielding provided by the halloysite wall (Yu et al., 2021). These results indicated that halloysite and halloysite/Ag_2O nanocomposites could be efficient adsorbents for iodate and iodide, respectively. Our findings also provided new insight into the relationship between the structure and property of halloysite and the fundamental knowledge derived from this study was important for the development of new efficient adsorbents based on halloysite in the future.

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The prediction and modification of the surface area and pore volume of natural halloysite nanotubes

Fujin Li[1], Yicheng Hua[1], Liangjie Fu[1,2*], Tianyu Liu[2], Jie Zhang[2], Huaming Yang[1,2]

[1]Engineering Research Center of Nano-Geomaterials of Ministry of Education, China University of Geosciences, Wuhan 430074, China

[2]School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

*franch@cug.edu.cn, franch@csu.edu.cn

Halloysite is a natural clay mineral with nanotube structure, which has been widely used in the fields of catalysis, energy, adsorption, drug loading and releasing. However, the loading ability of halloysites from different deposits still varies in a large range, especially when they are treated by physicochemical methods (Fu et al., 2017; Liu et al., 2021). The relation between the microstructure properties and the intrinsic parameters such as length, inner/outer diameter of halloysite is still obscure. The atomic structures of natural halloysite and their surface area and pore volume were predicted recently (Liu et al., 2021). The equations were proposed to give the theoretical values of the specific surface area and pore volumes of halloysite nanotubes. From theoretical point of view, the surface area and pore volume of halloysite can be greatly enhanced by expanding the lumen diameter of halloysite nanotube. Besides, it seems that the experimental pore volume data of halloysite reported in literatures were generally lowered than the theoretical results, which suggest that the lumen space of HNTs might still be blocked by some residual impurities. It is expected that, in addition to traditional physicochemical purifications, some advanced processing methods to enlarge the lumen diameter and remove the impurities would significantly enhance the lumen loading ability of halloysite as nanocontainer, nanocatalysts and energy storage materials.

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Halloysite nanotubes for long-term biological concrete self-healing

Mohammad Fahimizadeh[1,*], Pooria Pasbakhsh[1], Joash Tan Ban Lee[2], Lee Sui Mae[2,3], R. K. Singh Raman[4]

[1]School of Engineering, Monash University Malaysia, Bandar Sunway, Malaysia
[2]School of Science, Monash University Malaysia, Bandar Sunway, Malaysia
[3]Tropical Medicine and Biology Multidisciplinary Platform, Monash University Malaysia, Malaysia
[4]Department of Chemical Engineering, Department of Mechanical and Aerospace Engineering, Monash University Malaysia, Bandar Sunway, Malaysia

*Mohammad.fahimizadeh@monash.edu

Halloysite nanotubes (HNTs) have been integrated into various composite systems to improve mechanical properties and structural integrity and to implement sustained release behavior by utilizing the lumen of the HNTs as a storage space for desired compounds (Haw et al. 2020). As cement-compatible pozzolans, HNTs have been incorporated into composites intended for construction applications. To extend the service life of cement-based structures, different self- healing systems have been designed to heal cracks and structural faults to prevent environmental corrosion of the cement matrix and steel reinforcements (Fahimizadeh et al. 2022). Biological concrete self-healing is a promising and sustainable strategy to extend the service life of cement-based structures. Such systems rely on specific biomineralizing bacteria which precipitate calcium carbonate to heal structural faults (Fahimizadeh et al. 2020). The long-term self-healing ability of biological concrete self-healing systems remains unexplored. Hence, the current work implemented a sustained release mechanism for the biological healing agents by encapsulating vacuum-loaded HNTs into an engineered hydrogel alongside biological healing agents. The multipurpose nanoclay-hydrogel nanocomposite microcapsules have been characterized using in vitro assessments, thermogravimetric analysis, FTIR analysis, FESEM-EDX and TEM imaging. The cement specimens containing the self-healing system will be assessed for crack healing by optical observation of crack width and crack water tightness at different time point post cracking. Furthermore, the regain of mechanical properties following the self-healing phase will be assessed.

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Partial rehydration of tubular halloysite (7 Å immersed in La(NO_{33} solution for 3 years

Junming Zhou[1,2,*], Mengyuan Li[1], Peng Yuan[1], Yun Li[3], Hongmei Liu[1], Wenxiao Fan[1], Dong Liu[1], Huan Zhang[1]

[1]Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[2]Southern Marine Science and Engineering Guangdong Laboratory (Guangzhou), Guangzhou 511458, China
[3]Southern University of Science and Technology, Shenzhen 518055, China

zhoujunming0109@163.com

Clay minerals are the main carriers of rare earth elements (REE) in weathered crust elution-deposited rare earth (WED-RE) ores. The clay mineral-water interface reaction is among the most important interactions controlling the aggregation and transportation of REE(III) ions. Yet long-term experiments of interactions between REE(III) ions and clay minerals are scarce. Here, two typical clay minerals that commonly occur in WED-RE ores, namely tubular halloysite (7 Å) and platy kaolinite, were immersed in a La(III) solution for 3 consecutive years. Subsequently, these immersed minerals were systematically investigated using X-ray diffraction (XRD), transmission electron microscope (TEM), infrared spectroscopy (IR), and X-ray photoelectron spectroscopy (XPS).

A weak shoulder peak appeared at ~1.00 nm in the XRD pattern of immersed halloysite, which demonstrated the partial rehydration of tubular halloysite (7 Å) occurred after its 3-year-long immersion. TEM observation showed rehydrated halloysite had lattice fringes with $d_{(001)}$-values of ~1.00 and 0.83 nm, whose distribution features indicated that this partial rehydration happened initially at the outermost layers of the halloysite (7 Å). By contrast, both the morphology and structure of kaolinite remained intact after its 3-year-long immersion in the La(III) solution. For both immersed halloysite and kaolinite, La(III) existed as inner-sphere complexes, outer-sphere complexes, and hydroxide particles adsorbed on the surface of minerals. However, La(III) ions partially penetrated the interlayer of halloysite but did not enter that of kaolinite. Accordingly, the intercalation of La(III) in halloysite may facilitate the rehydration of halloysite (7 Å). These experimental results provide novel insight into the conditions for rehydrating tubular halloysite (7 Å), and indicate a new possible state of REE(III) in WED-RE ores, both of which help us to better understand the geochemical behavior of REE and clay minerals in WED-RE ores.

Functionalized halloysite nanotubes-supported bimetallic Pt-Au alloy nanoparticles for highly efficient and selective oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid

Xuemin Zhong[1]*, Peng Yuan[1], Yanfu Wei[2], Dong Liu[1], Dusan Losic[3], Mengyuan Li[1]

[1]CAS Key Laboratory of Mineralogy and Metallogeny/Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

[2]School of Environment, South China Normal University, Guangzhou 510006, China

[3]School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

*zhongxuemin@gig.ac.cn

The oxidation of biomass-derived 5-hydroxymethylfurfural (HMF) to 2, 5-furandicarboxylic acid (FDCA) is a highly important reaction because FDCA is a versatile building-block chemical for the synthesis of bio-based polymers. Noble metals catalysts are employed for the oxidation of HMF to FDCA due to their excellent catalytic activity, but the product selectivity and catalyst stability are still unsatisfactory. Although bimetallic catalysts show higher catalytic performance than monometallic catalysts, the agglomeration of bimetallic nanoparticles or the instability of support, etc. will reduce the catalytic activity. Halloysite is a typical one-dimension clay mineral, and its hollow tubular structure, tunable surface properties and high stability make it promising support for loading metal nanoparticles.

In this work, a functionalized halloysite nanotubes (N-HNT)-supported Pt-Au bimetallic catalyst was prepared through the organosilane-modification of HNT, followed by the in situ formation and dispersion of Pt-Au alloy nanoparticles on the surface of N-HNT. The composition and structure of the catalyst were characterized and its catalytic performance for the oxidation of HMF to FDCA was investigated.

The results indicate N-HNT realized the uniform dispersion of bimetallic nanoparticles on the internal and external surfaces of the tubes. The $1.5Pt_1Au_4$/N-HNT catalyst with the Pt/Au molar ratio of 1/4 and metal loading of 1.5 wt% exhibited outstanding catalytic activity for the selective oxidation of HMF to FDCA, with 100% HMF conversion and 99% FDCA selectivity. N-HNT and Pt-Au alloy nanoparticles play critical roles in the catalytic reaction. N-HNT-enhanced dispersion effect enables bimetallic nanoparticles to generate a high density of metal active sites, improving the catalytic activity. The alloying effects between Au and Pt facilitated the activation of reactants and intermediates, favoring the formation of FDCA. Furthermore, the N-HNT-supported bimetallic catalyst showed high stability and reusability. Therefore, Pt-Au/N-HNT composite is a green, stable and efficient catalyst for the oxidation of HMF to FDCA, and this study may help develop high-performance clay minerals-based nanomaterials for the conversion of biomass.

Effects of precalcination and phosphoric acid concentration on the microstructureand mechanical properties of acid-activated halloysite-based geopolymer

Baifa Zhang[1,2*], Haozhe Guo[1,2], Peng Yuan[1, 2], Liangiang Deng[1,2]

[1]CAS Key Laboratory of Mineralogy and Metallogeny, Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Institutions of Earth Science, Chinese Academy of Sciences (CAS), Guangzhou 510640, China

[2]University of Chinese Academy of Sciences, Beijing 100049, China

*zhangbaifa@gdut.edu.cn

Geopolymer is an inorganic polymeric material with poly-aluminosilicate chains, exhibiting excellent properties (Duxson et al., 2007). Geopolymer can be synthesized by mixing aluminosilicatesand activating solution. Recently, acid-activation geopolymer has attracted increasing attention because of their superior properties. Halloysite ($Al_2(OH)_4Si_2O_5•2H_2O$) is a hydrated polymorph of kaolinite, which has an additional water monolayer between the 1:1 aluminosilicate layers that differs with kaolinite (Yuan, 2016). Halloysite normally possesses a nanosized tubular structure and thus has higher specific surface area than plate-like kaolinite (Yuan et al., 2015). Besides, halloysite is less ordered, less chemically stable and thus more reactive than kaolinite (Yuan et al., 2015).

To get insights into the reaction mechanism of acid-activated halloysite, a combination of techniques was used to study the effects of precalcination temperature of halloysite and phosphoric acid concentration on the microstructures and mechanical properties of geopolymers. The results showed that acid-activation of halloysite calcined at 450 by < 10 mol/L solution produced metavariscite crystals. When the acid concentration was increased to 14 mol/L, however, the acid-activation product became more compact due to the formation of geopolymer with Al-O-P network. Dehydroxylation took place at 750 leading to a more active form of halloysite. The geopolymers produced by acid-activation were mainly composed of Si-O- P-O-Al networks. Higher acid concentration led to the incorporation of more Si and P in the geopolymer matrix, and thus greater compressive strength. Halloysites calcined at 1000 barely reacted with phosphoric acid, however, due to the formation of nanosized γ-Al_2O_3 and the decreased Si-OH content. The low reactivity inhibited geopolymerization from proceeding. These results indicated that the microstructure and mechanical performance of halloysite-based geopolymers are highly dependent on the precalcination temperature of halloysite and the phosphoric acid concentration.

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Morphological features of halloysite nanotubes (HNT's as revealed by various microscopies

Nia Gray-Wannell[1,4], Pablo Cubillas[2], Zabeada Aslam[3], Peter J Holliman[4], Hugh Christopher Greenwell[2], Rik Brydson[3], Evelyne Delbos[1], Laura-Jane Strachan[1], Martin Fuller[5], Stephen Hillier[1,6,*]

[1]The James Hutton Institute, Craigiebuckler, Aberdeen, AB15 8QH, UK
[2]Department of Earth Sciences, Durham University, Durham, DH1 3LE, UK
[3]School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK
[4]CEMEG, Swansea University, Bay Campus, Swansea, SA1 8EN, UK
[5]Astbury Biostructure Laboratory, University of Leeds, Leeds, LS2 9JT, UK
[6]Department of Soil and Environment, SLU, P.O. Box 7014, SE-75007 Uppsala, Sweden

*stephen.hillier@hutton.ac.uk

A set of nine halloysite samples from the USA, China, Turkey and Scotland have been examined by Scanning Electron (SEM), Atomic Force (AFM) and (cross sectional) Transmission Electron (TEM) microscopies to evaluate details of their external and internal morphological features. The samples cover a range of morphologies within the cylindrical to prismatic-polygonal framework proposed by Hillier et al., (2016) and further elaborated on by Drits et al., (2018). The combined microscopies reveal that the 'carpet role' model of HNTs assumed in the conceptualization and design of most technological applications of HNTs is far too simplistic. Both cylindrical and prismatic forms have abundant edge steps traversing their surfaces at acute and obtuse angles to the tube axis. These steps often form a 'saw tooth' arrangement along the tubes suggestive of twining and by analogy with plates of kaolinite correspond to prism faces. Together with the edges at the tube termini they are oriented with respect to the underlying symmetry of the halloysite crystal structure. In all cases, the mean value for the diameter of the central lumen of the tubes is around 12 nm. However, numerous slit-like nano pores, with diameters ranging up to 18 nm also occur between packets of layers, particularly in prismatic forms at the junction between a central cylindrical core and the outer packets of planar layers. Such pores must expose both aluminol and silanol surfaces, but unlike the lumen, which is assumed only to expose an aluminol surface, they do not extend along the entire length of the nanotube. The edge steps seen most clearly in AFM images correspond in height to the packets of layers seen in TEM cross sections. TEM cross sections also suggest that tube growth occurred by accretion of a spiraled thickening wedge of layers as well as revealing that the outer planar sectors of prismatic samples may be joined by either abrupt angular junctions or by short sections of curved layers. Natural samples of HNTs invariably contain both cylindrical and prismatic forms and a more realistic model of the internal and external morphologies of HNTs is proposed. This model should assist understanding of the behavior of HNT's when designing technological applications.

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$(Mg,Co)_3Si_2O_5(OH)_4$ phyllosilicate nanoscrolls: Towards single-walled chrysotile analog

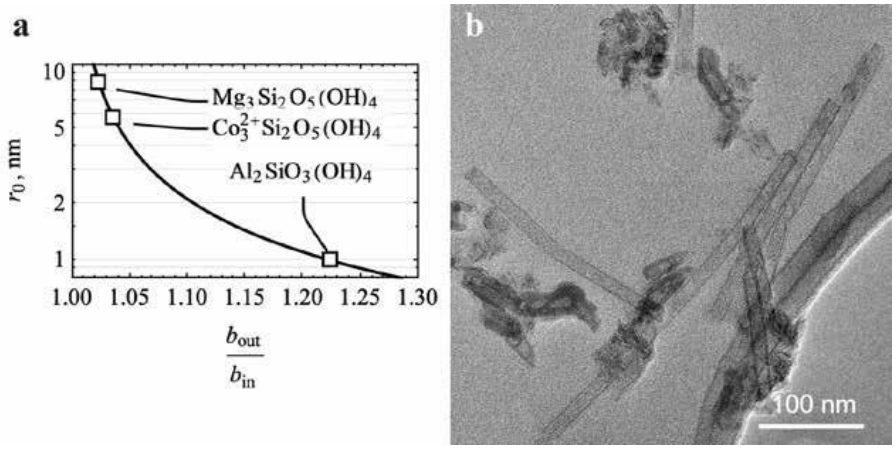
Ekaterina Khrapova, Andrei Krasilin*

Ioffe Institute, 194021 St Petersburg, Russia

*ikrasilin@mail.ioffe.ru

Some hydrosilicates possess an ability of spontaneous curling due to size difference between metal oxide (b_{out}) and silica (b_{in}) sheets. The magnitude of size difference (Krasilin, 2020) is one of the key features which determine preferable morphology – single-walled, multi-walled nanotubes and nanoscrolls, spherical particles etc. In turn, control over the size difference could be achieved by changing chemical composition.

Here we report on successful hydrothermal synthesis and morphology of $(Mg,Co)_3Si_2O_5(OH)_4$ phyllosilicates, which are structural analogues of chrysotile. Change of Mg^{2+} to Co^{2+} decreases the radius of stress-free layer r_0 from 8.8 down to 5.7 nm (Fig. 1.a), that allowed to obtain thin-walled (Fig. 1.b) nanotubes and nanoscrolls. The synthesis is sensitive to Co^{2+} oxidation, so oxygen removal from both gaseous media and solution must be made.



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Krasilin, A.A., Khrapova, E.K., Maslennikova, T.P. (2020). Cation doping approach for nanotubular hydrosilicates curvature control and related applications. *Crystals,* 10(8), 654.

Insight into the defective sites of TiO_2/sepiolite composite on formaldehyde removal and H_2 evolution

Xiaolong Hu[1,2], Junying Song[1], Shuilin Zheng[1], Zhiming Sun[1], Chunquan Li[1,*]

[1]China University of Mining and Technology (Beijing), School of Chemical and Environmental Engineering, Beijing 100083, China

[2]Shandong University of Science and Technology, College of Chemical and Biological Engineering, Qingdao, Shandong 266590, China

chunquanli@cumtb.edu.cn

TiO_2/sepiolite composites (T-S-R) with different contents of Ti^{3+} and oxygen vacancy were successfully prepared through 0D/1D structural assembly and thermal treatment under various atmospheres (R=Air, O_2, N_2, Ar and H). The content of Ti^{3+} and oxygen vacancy was confirmed through electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy (XPS), which exhibited significant effect on the photocatalytic formaldehyde (HCHO) removal and H_2 evolution. The T-S-Ar composite exhibited much higher formaldehyde degradation efficiency (91.8% within 90 min) and H_2 production performance (1974.8 $\mu mol \cdot h^{-1} \cdot g^{-1}$) than other samples under simulated solar light. According to the material characterizations and DFT calculations, the improved photocatalytic activity could be ascribed to the synergistic effect between natural sepiolite and TiO_2. Besides, the generation of mid-gap levels induced by the appropriate content of Ti^{3+} and oxygen vacancy led to the larger specific surface area, smaller nano-sized TiO_2 and higher photogenerated carriers' separation efficiency. Furthermore, it was found that higher content of oxygen vacancies would act as the recombination centers for electron-hole pairs, thereby greatly reducing the photocatalytic performance. Notably, our study provides a promising candidate for effectively addressing the air pollution (e.g. HCHO removal) and energy issues (e.g. H_2 production) based on the defect engineering and mineral support technology.

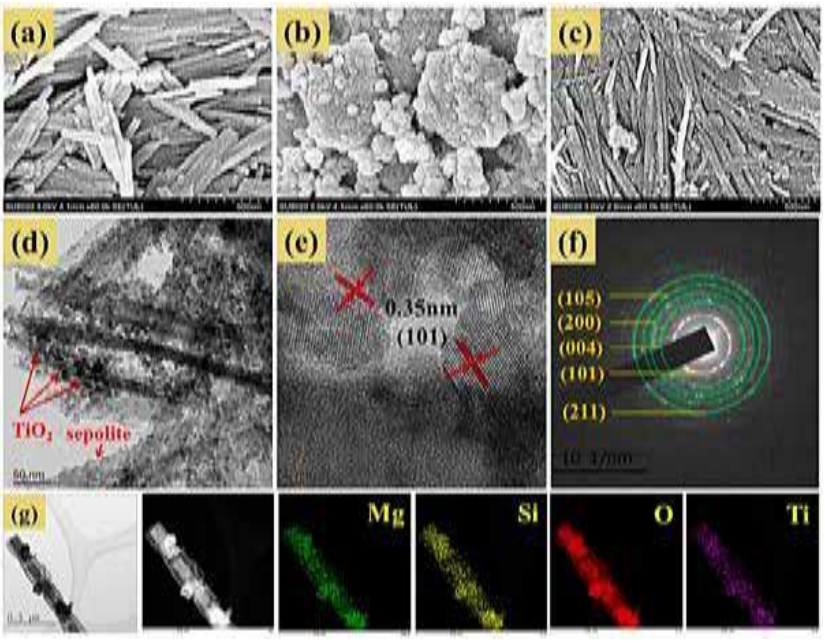


Figure 1. SEM images of sepiolite (a), TiO_2-Ar (b) and T-S-Ar (c); TEM, HRTEM images (d and e), SAED pattern (f) and element mapping for Mg, Si, O and Ti of T-S-Ar (g).

Sepiolite- rosemary oil combination as an environmentally oriented insecticide

Giora Rytwo[1,2,*], Tamir Kramer[1], Lotem Azoulay[3], Liora Shaltiel-Harpaz[1,3]

[1]Environ. Sci. and Water Sci. Depts., Tel Hai College, Israel
[2]Environmental Physical Chemistry Lab., MIGAL- Galilee Research Institute
[3]Integrated Pest Management Lab., Northern R@D, MIGAL- Galilee Research Institute

*giorarytwo@gmail.com

Pest management is an essential tool for cost-effective agriculture. However, due to pest's ability to develop resistance to pesticides, and reinforcement of environmental and health regulations, there is the need to develop novel pesticides, based on reducing the use of hazardous compounds that damage the soil, the water and the biosphere. Certain natural essential oils are known for their ability to repulse and even be lethal to specific pests, and may therefore serve as a less hazardous alternative to traditional pesticides. However key problems to be solved are the high vapor pressure and rapid volatility of such oils, and in some cases- their phytotoxicity at levels that have insecticidal effect.

Clays, organoclays and nanocomposites were suggested as matrices for adsorbing organic compounds leading to their controlled- or slow-release. Thus, such matrices might increase the pesticide efficiency of essential oils by slowly releasing them, and probably reduce phytotoxicity, offering an alternative to conventional pesticides.

This study combines in vitro studies evaluating the rate of evaporation of rosemary (Rosmarinus officinalis) essential oils (ROEO) from clays and organoclays formulations, with in vivo experiments testing efficient doses of clay-essential oil insecticides on onion thrips, while avoiding phytotoxicity damage to chives crop plants.

FTIR kinetic measurements of the evaporation led to the conclusion that sepiolite increases the half-life evaporation period when compared to the free essential oils or oils pre-adsorbed to montmorillonite, palygorskite or halloysite. More detailed gravimetric kinetic analysis showed that the pseudo-order of the evaporation of rosemary oil at room temperature increases from ~2 in raw oil to ~3.2 in sepiolite-ROEO. Apparently, such increase is mistakenly considered as increasing the speed of the process, but this happens only at high concentrations (Rytwo and Zelkind, 2021). The increase in the pseudo-order leads to the fact that the time that takes to reduce the concentration from 20% the initial value to 10% of it, increases from less than 2 days to more than 30 days.

Indeed, efficiency tests showed significant ROEO lethality to thrips in chives increased considerably in the rosemary oil –sepiolite formulations when compared to raw ROEO. Furthermore, in control treatments damage due to phytotoxicity was observed, whereas in the sepiolite-based formulation plants were healthy and clean. Influence was still substantial even four weeks after application, as the preliminary kinetic evaluations indicated. GCMS analysis of the vapors in equilibrium with the formulation or the raw oil, show clear differences in the pattern for the different components of the essential oil.

This study provides an environmentally oriented approach that might yield to effective alternative and less hazardous pesticides. It also emphasizes the very specific and interesting interactions between organic molecules and fibrous clay minerals.

Rytwo, G., Zelkind, A.L., 2021. Evaluation of Kinetic Pseudo-Order in the Photocatalytic Degradation of Ofloxacin. Catal. 2022, 12, 24.

Synthesis and characterization of Ti containing aluminogermanate imogolite nanotubes for photocatalytic hydrogen production from water

Yassine Naciri[1,*], Vien-Duong Quach[2], Marija Knezevic[2], Mohamed Nawfal Ghazzal[2], Erwan Paineau[1]

[1]Universit Paris-Saclay, CNRS, Laboratoire de Physique des Solides, 91405 Orsay, France
[2]Universit Paris-Saclay, CNRS, Institut de Chimie Physique, 91405, Orsay, France

*yassine.naciri@universite-paris-saclay.fr

Imogolite is a naturally occurring clay mineral that is commonly found in soils as a weathering product of volcanic glass or pyroclastic materials. These $(OH)_3Al_2O_3X(R)$ (with X = Si or Ge; R = OH, CH_3...) nanotubes are made of isolated tetrahedral $[(R)XO_3]$ units on the inner surface connected. The singularity of imogolite compared to other clay minerals is its unique structure, identified by Wada et al. in 1970 as a hollow tube 2 nm in diameter (Wada et al.,1970). Due to its morphology, this material has been considered as a shape-selective catalyst (Li et al.,2020). However, because of its chemical stability, incorporating of another element is necessary to generate a chemical function.

Herein, the substitution of Al by Ti in the structure of aluminogermanate imogolite nanotubes was investigated at various mole ratios of Ti/(Al+Ti). The synthesized products were characterized by coupling X-ray scattering experiments, Transmission electron microscopy (TEM) observations, FT-IR and diffuse reflectance spectroscopies. These results confirm that the double-wall shape is preserved up to substitution ratio of 0.3. The photocatalytic hydrogen evolution (PHE) of the as-prepared materials was studied in water/methanol mixtures. The results showed that the Ti containing imogolites have a higher PHE than the pristine nanotubes. A discussion about the involved mechanisms is provided.

Acknowledgement: This work is supported by “Investissements d’Avenir” LabEx PALM (ANR-10-LABX-0039-PALM, project SP3).

Li, J., Jiménez-Calvo, P., Paineau, E., & Ghazzal, M. N, Metal (2020). Chalcogenides based heterojunctions and novel nanostructures for photocatalytic hydrogen evolution. Catalysts, 10, 89.
Wada, K.; Yoshinaga, N.; Yotsumoto, K. High resolution electron micrographs of imogolite (1970). Clay Miner, 8, 487–489.

TS02 Nanoporous Fibrous Clays

POSTER PRESENTATIONS

Essential oil release delivery fabricated from modified palygorskite particles stabilizing Pickering emulsions

Aiping Hui*, Yongfeng Zhu, Fangfang Yang, Yuru Kang, Aiqin Wang

Key Laboratory of Clay Mineral Applied Research of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences

*aphui@licp.cas.cn

Chinese medicinal plant particles display potential application in the field of Pickering emulsions. It is of great significance to develop and design novel green emulsion stabilized particles, such as plant particles as a modifier to prepare clay-based composite particles (Yu et al., 2021). Based on the previous study that indicated combining original plant particles with non-ionic surfactants could prepare oil-in-water Pickering emulsions with better stability. However, to obtain a green approach for preparing oil-in-water Pickering emulsions, one strategy was used to investigate the applications of Chinese medicinal plant particle, which used active components of *Sapindus mukorossi* to modify the surface of palygorskite as composite particles to stabilize Pickering emulsions. Meanwhile, the surface hydrophilic and hydrophobic properties of palygorskite could be changed by loading organic active substances on the surface of palygorskite during traditional semi-dry grinding, and also the *Sapindus mukorossi* modified palygorskite composite particles displayed an enhanced stability and pH-response release of cinnamaldehyde oil-in-water Pickering emulsions (Yu *et al*., 2022).

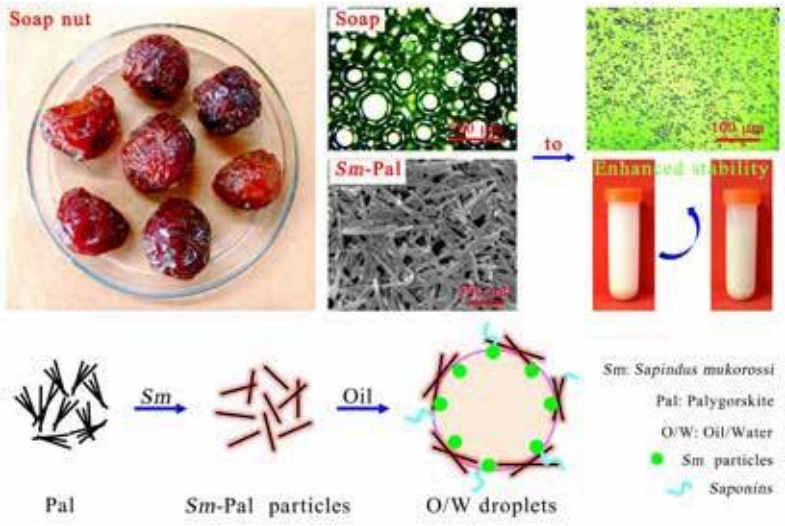


Figure 1. Schematic diagram of *Sapindus mukorossi* modified palygorskite composite particles for preparation of cinnamaldehyde oil-in-water Pickering emulsions.

Yu H., Zhu Y. F., Hui A. P., Yang F. F., Wang A. Q. (2021). Removal of antibiotics from aqueous solution by using porous adsorbent templated from eco-friendly Pickering aqueous foams. *Journal of Environmental Sciences*, 102, 352–362.
Yu H., Zhu Y. F., Hui A. P., Wang A. Q. (2022). Novel eco-friendly spherical porous adsorbent fabricated from Pickering middle internal phase emulsions for removal of Pb(II) and Cd (II). *Journal of Environmental Sciences*, 112, 320–330.

Novel porous materials fabricated from Pickering foam stabilized by natural plant and attapulgite for removal of cationic dyes in water

Fangzhi Duan, Yongfeng Zhu*, Aiqin Wang

Key Laboratory of Clay Mineral Applied Research of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences

*zhuyf@licp.cas.cn

Water-based foam has the advantages of green, environmental protection, simplicity and cleanliness on the construction of porous materials (Yu et al., 2021). However, the fragile stability caused by gravity-induced drainage and evaporation of moisture is the fatal flaw for application. Although synthetic amphoteric particles or surfactant-modified particles can greatly improve the stability of water-based foams, tedious operations, increased costs, and environmental pollution have caused a series of new problems (Zhu et al., 2020). In order to improve the stability of water-based foams and avoid the above-mentioned drawbacks, the replacement of synthetic particles by natural particles has become a new research focus and trend. In this work, a green liquid foam with high stability was prepared by synergistic stabilization of natural plant astragalus membranaceus (AMS) and attapulgite (APT), and then a novel porous material with sufficient hierarchical pore structure was templated from the foam *via* a simple free radical polymerization of acrylamide (AM). The characterization results revealed that the AMS adsorbed onto the water-air interface and formed a protective shell to prevent the bubble breakup, and APT gathered in the plateau boundary and formed a three-dimensional network structure, which greatly slowed down the drainage rate.

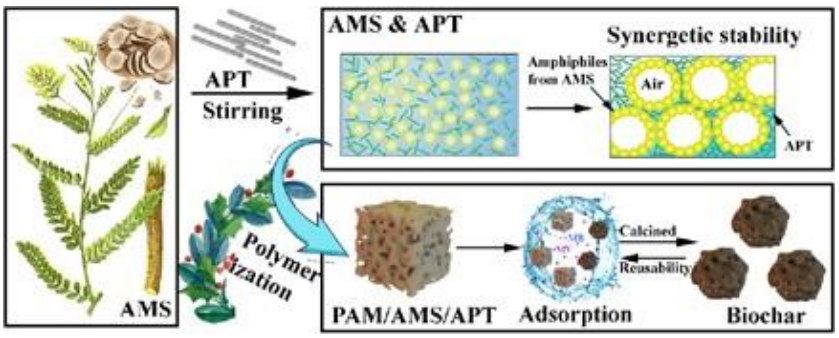


Figure 1. Scheme of the construction of porous adsorbents by Pickering foam stabilized by astragalus membranaceus and attapulgite for removal of cationic dyes.

Yu, H., Zhu, Y. F., Hui, A. P., Yang, F. F., Wang, A. Q. (2021). Removal of antibiotics from aqueous solution by using porous adsorbent templated from eco-friendly Pickering aqueous foams. *Journal of Environmental Sciences*, 102, 352–362. Zhu, Y. F., Wang, W. B., Yu, H., Wang, A. Q. (2020). Preparation of porous adsorbent via Pickering emulsion template for water treatment: A Review, *Journal of Environmental Sciences*, 88, 217-236.

Injectable halloysite nanotube reinforced nanocomposite hydrogels for tissue engineering applications

Li Wen Wong[1,2,*], Pooria Pasbakhsh[3], Wai Teng Cheng[1], Calvin Bok Sun Goh[1], Joash Ban Lee Tan[1,2]

[1]School of Science, Monash University Malaysia, Jalan Lagoon Selatan, Bandar Sunway, 47500, Selangor, Malaysia
[2]Tropical Medicine & Biology Platform, Monash University Malaysia, Jalan Lagoon Selatan, Bandar Sunway, 47500, Selangor, Malaysia
[3]School of Engineering, Monash University Malaysia, Jalan Lagoon Selatan, Bandar Sunway, 47500, Selangor, Malaysia

*li.wong@monash.edu

Injectable hydrogels that can fill irregular defects through a minimally invasive approach have emerged to replace invasive surgeries that are commonly applied in tissue scaffold implantation. Nonetheless, the use of injectable hydrogels is often restricted by the drawback of having poor mechanical properties. Therefore, this project has developed a novel injectable halloysite nanotube (Hal) reinforced nanocomposite hydrogel to serve the dual purpose of providing structural support for tissue regeneration while offering possibilities for drug delivery at a local site. As the acid-treated Hals obtained from South Australia retained a hollow lumen with improved porosity for the applications of fillers and carriers (Wong et al., 2021), the Hals were incorporated into a novel hydrogel for the fabrication of nanocomposite hydrogel. Characterizations including field emission scanning electron microscopy (FESEM), Fourier transform infrared (FT-IR) spectroscopy, gelation, injectability, and mechanical testings were performed on all the hydrogels. Analyses showed that the obtained hydrogels could be injected as a liquid, with an in situ sol-gel transition occurring after 11 minutes at 37°C. As FESEM revealed the dispersion of Hals into the hydrogel matrices, compressive strength and modulus of the nanocomposite hydrogel were increased up to 60% and 40% compared to the hydrogel without Hals, respectively. This study, therefore, demonstrates that the mechanical properties of the injectable hydrogel can be improved with the presence of Hals. With the reported in situ-forming nanocomposite hydrogels, hydrogel scaffold implantation can be achieved in a minimally invasive approach through injection, protecting surrounding cells from the hostile environment and minimizing the risk of secondary infection with the combined local delivery of antimicrobial agents in the near future.

Wong, L. W., Pasbakhsh, P., Arabi, A. M., Keeling, J., Tan, J. B. L. (2021). Halloysite nanotubes from various geological deposits: New insights to acid etching and their impacts on products' characteristics. *Journal of Environmental Chemical Engineering,* 9(5), 106235.

TS03 + TS14 Paleoenvironments, Diagenesis, Provenance of Sedimentary Deposits

ORAL PRESENTATIONS

Geochemistry, mineralogy, and genesis of kaolin deposits of Kachchh, Western India and its diverse industrial application

Jaymeet Solanki*, **Gaurav Chauhan, M. G. Thakkar**

Department of Earth and Environmental Science, Krantiguru Shyamji Krushna Varma Kachchh University, Bhuj. 370020-India

*jaymeetsolanki@gmail.com

Kaolin deposits of Kachchh, Western India were investigated with mineralogical, physicochemical, and geochemical characteristics in order to elucidate the genesis with the potential of industrial applications. The sampling of kaolin deposits was carried out from all three physiographic divisions of Kachchh, viz., the Kachchh Mainland, Wagad Highland, and the Island Belt region. The geochemical characterization of the kaolin was determined using X-ray fluorescence spectrometry (XRF). Further, mineralogical properties were assessed to identify and quantify the mineral phases using X-ray diffraction (XRD). The Scanning Electron Microscopy (SEM) was used to determine the micro-morphology of kaolins. Diagnostic physicochemical tests like color, brightness, whiteness, pH, particle size distribution (PSD) was performed for several possible industrial applications. The results of geochemical indices, including a chemical index of alteration (CIA), chemical index of weathering (CIW), and the index of compositional variability (ICV) were computed to determine the weathering conditions of the kaolin and their different source rock types for the evolution of genesis. The major oxide of the kaolin from Kachchh was dominated by SiO_2, Al_2O_3, Fe_2O_3, and TiO_2. While kaolinite is the major phyllosilicate present in the deposit, accessory minerals are quartz, goethite, muscovite, anatase, and ilmenite. Major, trace and rare earth elements geochemistry of the clay fractions from the study suggest the provenance and environmental condition of Cretaceous-Tertiary kaolin deposits of Kachchh. On the basis of the results obtained from mineralogical, geochemical, and diagnostic analysis, the deposits would require a beneficiation process to remove the existing impurities in order to optimize grade and recovery. Further, the suitable application could be ceramics, cosmetics, rubber, plastic, paints, and paper industries. Thus, the study has the potential to contribute in improving the economic development of kaolin industries in the region.

Oxygen and hydrogen analysis in clay minerals from Lower Cretaceous palaeosols by NanoSIMS: palaeoclimatic deductions

Elisa Laita[1,*], Maria Angels Subirana[2], Dirk Schaumlffel[2], Alfonso Yuste[1], Blanca Bauluz[1]

[1]IUCA-Deparment of Earth Sciences, Faculty of Sciences, University of Zaragoza, 50009 Zaragoza, Spain

[2]CNRS, Universit de Pau et des Pays de l'Adour, E2S UPPA, Institut des Sciences Analitiques et de Physico-Chimie pour l'Environnement et les Matriaux, 64000 Pau, France

*laita@unizar.es

Oxygen and hydrogen isotopic ratios in authigenic clay minerals included in paleosols give key information regarding their genesis (Sheppard and Gilg, 1996). However, the different mineral assemblages in paleosols (clays and oxides) and their nanometer size generates difficulties during isotopic analyses. To avoid this problem, we used Nanoscale Secondary Ion Mass Spectrometry (NanoSIMS) for analysing authigenic kaolinite included in bottom levels and authigenic smectite included in top levels of early Barremian lateritesprofiles located in NE Spain (Laita et al., 2020). The isotopic compositions of pure powder standards of kaolinite and smectite were previously measured to obtain reference values.

A decrease in the $^{18}O/^{16}O$ and D/H ratios from kaolinite to smectite is detected in the lateritic profiles. The $\delta^{18}O_{SMOW}$ (17.6‰ – 10.6‰) and δD_{SMOW} (-83.3‰ – -179.7‰) obtained for kaolinite and smectite, respectively, are consistent with the crystallization of the clays in weathering environment. The calculated temperature for kaolinite formation is 21-22ºC whereas for smectite is 17ºC. These data agree with the climatic change from bottom to top of the laterites deduced by Laita et al. (2020) using mineralogical tools.

As a conclusion, the high resolution of NanoSIMS allows obtaining isotopic analysis from clays separately, and therefore this technique is a useful tool in the study of nanometer-size clay minerals.

Laita, E., Bauluz, B., Aurell, M., Bádenas, B., Canudo, J.I., Yuste, A. (2020). A change from warm/humid to cold/dry climate conditions recorded in lower Barremian clay-dominated continental successions from the SE Iberian Chain (NE Spain). *Sedimentary Geology*, 403, 105673.

Sheppard, S.M.F., & Gilg, H.A. (1996). Stable isotope geochemistry of clay minerals. *Clay Minerals*, 31, 1–24.

Impacts of chemical pre-treatments on the hydrogen isotope composition of clay minerals

Nadine J. Kanik[1,*], Artur Kuligiewicz[1], Arkadiusz Derkowski[1], Jeffrey T. Cullen[2]

[1]Institute of Geological Sciences, Polish Academy of Sciences, Krakow, PL-31002, Poland
[2]Jackson School of Geosciences, University of Texas at Austin, Austin TX 78712, USA

*ndkanik@cyf-kr.edu.pl

The chemical removal of carbonates, organic matter, iron oxides, and oxyhydroxides from a clay or clay-rich material is a common practice that ensures impurities do not impact data quality. However, there is uncertainty regarding to what extent, the structural hydroxyl hydrogen (H) isotope ratio of a clay mineral may be altered during exposure to chemicals. This has impacts for studies investigating the H-isotopes associated with clay-rich geomaterials.

This study investigated the extent to which each pre-treatment, commonly used to extract a clay mineral fraction from associated impurities or phases, affected the structural hydroxyl H-isotope ratios of nontronite, montmorillonite, saponite, and kaolinite samples obtained from the Clay Minerals Society Source Clay Repository. Isotopically labelled water and reagents, with a δ^2H= ~300‰ higher than the clay starting material (SM) of ~δ^2H= –100‰, enabled enhanced isotopic tracing of H-isotope alteration for each pre-treatment. High Temperature Elemental Conversion coupled with an Isotope Ratio Mass Spectrometer was used for H-isotope analysis. Pre-treatment for carbonate removal using an acetate buffer only affected saponite, shifting H-isotope ratios significantly above that of the SM, while 10% hydrochloric acid (HCl) caused montmorillonite to shift dramatically higher. Organic matter removal by 30% peroxide (H_2O_2) did not appreciably alter nontronite, but did shift saponite and montmorillonite to higher H-isotope ratios, while 6% sodium hypochlorite (NaClO) significantly raised the H-isotope ratio of saponite. Fe-(oxy)hydroxide removal by Na-dithionite buffered by a Na-citrate-bicarbonate solution, displayed the largest impact on nontronite by increasing H-isotope ratios considerably compared to the SM. Homoionic cation saturation with a KCl solution followed by washing via dialysis in deuterium-spiked water did not appear to impact the H-isotope ratios for any of the clays studied. Kaolinite was the only clay mineral that was unaffected by any treatment and saponite was the only clay that showed some degree of H-isotope alteration for all treatments, except cation saturation and washing.

The results indicate, that when pre-treating to extract montmorillonite from a bulk sample, where the structural hydroxyl H-isotope ratios will be studied, treatment with HCl and H_2O_2 should be avoided for carbonate and organic removal, respectively. For saponite, organic matter removal with NaClO should be avoided, and all other treatments kept to a minimum or buffered. Despite its utility, Fe-(oxy)hydroxides removal can alter the H-isotope ratios of nontronite, as can treatment with NaClO.

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Crystalochemical control on the hydrogen isotope exchange in smectites

Anna Szreter , Arkadiusz Derkowski*

Institute of Geological Sciences, Polish Academy of Sciences, Senacka 1, 31-002 Kraków, Poland

*ndderkow@cyf-kr.edu.pl

The hydrogen isotope ratio in clay minerals records their formation temperature and fluid H isotope composition during the mineral formation. A mineral resistant to post-formation isotope exchange can preserve its original composition, thus geochemical information; one susceptible to fast exchange would produce misleading interpretations.

Because of the presence of interlayer adsorbed water that instantaneously exchanges with environment and the nm-size crystallite dimensions, smectite is hypothesized to be the most prone to H isotope exchange in structural OH groups among all clay minerals. In this study, the H isotope exchange in smectites and their interstratified varieties was revisited using infrared spectroscopy (IR) – an efficient tool enabling in-situ and ex-situ observation of D/H exchange reaction based on OH and OD stretching bands as a proxy for H isotope exchange in nature. For various D/H exchange tests we used a set of smectites with various layer crystalochemical compositions and interlayer cations, and a few interstratified minerals with different illite-to-smectite ratios.

In any tested sample, no H isotope exchange within OH groups was observed at room temperature (~22°C), nor during short-term water saturation with relative humidity 60-80%, nor after a year in liquid D_2O water. Experiments conducted at 90°C under full D_2O vapor (not liquid) saturation for 12-16 months showeda strong control from the octahedral cation composition on H isotope exchange under these conditions. Dioctahedral smectites with Fe^{3+} substitution for Al^{3+} (nontronite) exchanged most extensively (>20% D/H exchange), followed by the samples with both Mg^{2+} and Fe^{3+} substitution (montmorillonite), whereas those with nearly pure octahedral Al^{3+} (beidellite) exhibited negligible D/H exchange. Trioctahedral saponites did not exchange at all after 16 months. In interstratified illite-smectite, the exchange is controlled by the fraction of fixed illitic interlayers.

High temperature experiments were carried in-situ using diffusion reflectance IR spectroscopy (DRIFT) with constant D_2O concentration at 150-600°C. Under these conditions hydrogen isotope exchange is controlled by the extent of interlayer opening allowing interlayer D_2O diffusion, controlled by particular properties of the interlayer cations. Hydrated Mg^{2+} or Cs^{+} with large ionic radii contribute to increased H exchange. The mechanism and extent of H exchange at temperatures, lower than the mineral's dehydroxylation, change when the state of dehydroxylation, specific for each smectite, is reached.

Hafnium-Neodymium isotopes coupled to clay mineralogy as proxies of provenance and weathering during the late Cretaceous

Pauline Corentin[1,*], Emmanuelle Pucéat[1], Pierre Pellenard[1], Michel Guiraud[1], Justine Blondet[1], Nicolas Freslon[1,2], Germain Bayon[3], Thierry Adatte[4]

[1]Biogéosciences, UMR 6282 CNRS, Université Bourgogne Franche-Comté, France
[2]ISTO - Université d'Orléans, CNRS, BRGM, UMR 7327, France
[3]IFREMER, Unité de Recherche Géosciences Marines, France
[4]Institute of Earth Sciences, Géopolis, University of Lausanne, Switzerland

*pauline.corentin@u-bourgogne.fr

The late Cretaceous is marked by a major climatic turnover leading to modern icehouse conditions and major uplifts along the West African and eastern South-America margins. New geochemical proxies (Hf-Nd isotopic coupled system in clays) and clay mineralogy are used here for the first time to decipher relationships between tectonics and climate through silicate chemical weathering along margins of the eastern South-America.

Sites ODP 356 (Southeastern Brazilian margin) and 1259 (Guiana-Surinam margin, Demerara Rise) were targeted based on their relatively complete record of upper Cretaceous sediments. Detrital clay mineral evolution was used to track climatic evolution through palygorskite, kaolinite and smectite contents while the (illite+chlorite)/smectite ratio was used to track mechanical erosion. Such mineralogical proxies are coupled to the isotopic composition of Nd ($\varepsilon_{Nd(t)}$) in the clay fraction to assess local sources and to the new geochemical proxy $\Delta\varepsilon_{Hf(t)}$ defined by (Bayon et al., 2016) in modern river sediment to track the local silicate chemical weathering. This index of weathering intensity measured in the clay fraction (<2µm), is based on the decoupling behavior of Nd and Hf isotopic systems during chemical weathering process of silicate rocks.

At Site 356, clay mineralogy and $\varepsilon_{Nd(t)}$ indicate that the uplift of the Southeastern Brazilian during the Turonian-Coniacian margin has promoted enhanced mechanical erosion and a change of sources under arid climate, while more hydrolyzing conditions and enhanced silicate chemical weathering, favored by the new created relief, are recorded from the $\Delta\varepsilon_{Hf(t)}$ thereafter (Corentin et al., 2022). By contrast at Demerara Rise (Site 1259), $\varepsilon_{Nd(t)}$ do not depicted major change of sources and clay mineralogy associated to $\Delta\varepsilon_{Hf(t)}$ suggest a coupling between physical erosion and chemical weathering, which may be explained by the presence of persistent hydrolyzing conditions typical of equatorial climate and reduced tectonic activity. From the middle Campanian to Maastrichtian, we thus propose that mountain uplift, although moderate, induced a marked increase in chemical weathering intensity.

History of Şile clays: More detail provenance perspective

Hüseyin Demir[1,2,*], Paul A. Schroeder[2]

[1]General Directorate of State Hydraulic Works, Technical Research and Quality Control Department, Concrete Laboratory, Pursaklar, Ankara, Turkey

[2]University of Georgia, Department of Geology, Athens, GA 30602-2501 U.S.A.

*huseyindemir@dsi.gov.tr

Nearby rock types of Oligo-Miocene clay deposits in the Şile region north of Istanbul consist of Paleozoic meta-sedimentary units, Permo-Triassic sedimentary rocks, Late Cretaceous volcanic/volcano-sedimentary rocks and flysch series. These economically important clay-rich occurrences found on top of volcanic rocks were examined and thought to be derived from the volcanic rocks (Yeniyol, 1984; Çoban et al., 2002; Ece et al., 2003; Ece and Nakagawa, 2003). Similar mineral assemblages consisting of quartz, kaolinite, illite, and mixed-layer clays were also observed unconformably on other the rock types in the region. These assemblages have similar properties regardless of their underlying rocks found in the region. These deposits also include clay-rich, sand-rich, and gravel-rich layers as well as cyclic coal seams. The contacts between clay depositions and the underlying basement were not observed. (Demir, 2021). In order to evaluate these deposits from a broader perspective and understand if the sediments for clay deposits include multiple sourced provenances found in the region, representative samples from mines and potential source rocks were gathered and geochemical data were measured. Data sets obtained by ICP-MS were evaluated by using principal component analysis (PCA), which is a multivariate statistical technique. By reducing dimensionality and retaining most of the variation in the data, the algorithm identifies principal components responsible for most of the variations in the original data set and it displays these as axes (i.e., principal components) with variation explained in decreasing order. Samples were plotted using three axes representing most of the variation. PCA reveals that volcanic/ volcano-sedimentary rocks, flysch series, and Paleozoic rocks were likely the primary sources for the deposits, meaning these deposits were multi- sourced clay deposits. Tectonic influenced morphology and paleoclimate were effectively responsible for these clay-rich sedimentary deposits. Modern critical zone alteration has also influence the top portions of the deposits.

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Ece, O.I., Nakagawa, Z.E. and Schroeder, P., 2003. Alteration of volcanic rocks and genesis of kaolin deposits in the Sile Region, northern Istanbul, Turkey. I: Clay mineralogy. *Clays and Clay Minerals,* 51(6), pp.675-688.

Ece, O.I. and Nakagawa, Z.E., 2003. Alteration of volcanic rocks and genesis of kaolin deposits in the Sile Region, northern Istanbul, Turkey. Part II: differential mobility of elements. *Clay Minerals*, 38(4), pp.529-550.

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Modelling trace-element mobility during tephra alteration in a lacustrine setting using glass phase and clay separate LA-ICP-MS geochemistry

Luka Badurina*, Kevin Werts, Branimir Šegvić

Texas Tech University, Department of Geosciences, Lubbock TX 79401, U.S.A.

*luka.badurina@ttu.edu

Marine and lacustrine bentonites are excellent proxies of physiochemical conditions controlling trace element enrichment or depletion during volcanic glass eogenesis. Rapid deuteric alteration and argillitization commonly affect volcanic glass which dominates volcanic ash deposits. A careful comparison of fresh tephra with its altered equivalents may thus provide an excellent avenue to examine trace-element variability taking into account tephras' diverse alteration assemblages. Sampling fresh and altered tephra from separate localities followed by a whole- rock geochemical analysis of collected material was heretofore a common approach in such investigations. This however involves relatively large amounts of material while failing to avoid artifacts of detrital contamination.

This contribution aims to reconstruct trace-element mobility trends by analyzing spatially linked fresh volcanic glass shards and clay minerals from a single sampling site. Analyzed samples were sourced from partially altered Miocene tephra deposits of Dinaride Lake System (Croatia and Bosnia-Herzegovina). Representative material – thin-section glass shards and clay fraction concentrates – was analyzed by laser ablation inductively coupled plasma mass spectrometry. Resulting data revealed small volumes of clay fraction (i.e. ~50 mg) that successfully produced meaningful trace-element geochemistry, which was subsequently compared with the composition of glass shards to reconstruct trace-element mobility patterns (Fig. 1).

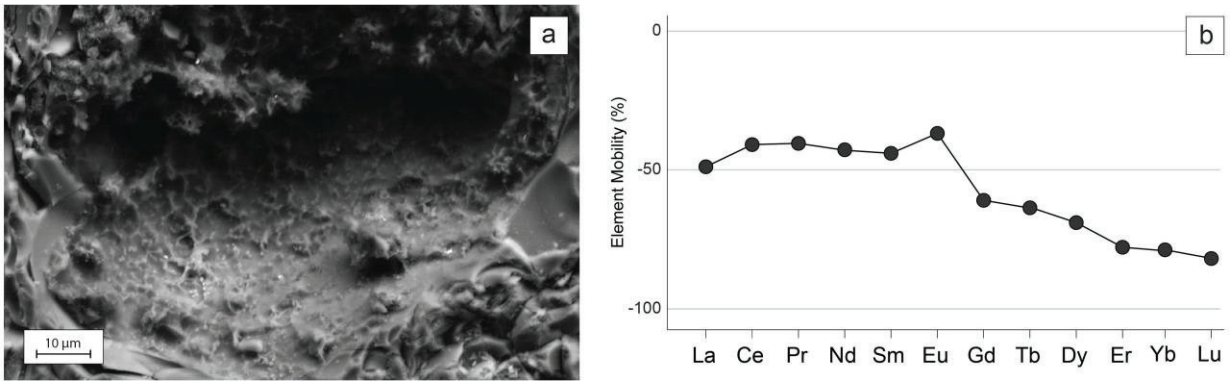


Figure 1. SEM image of (a) smectite coating present in glass shard vesicle and (b) rare-earth element mobility plot of the corresponding sample. Element mobility refers to Al-normalized ratio of clay to glass REE concentrations.

Provenance control on mineralogy and geochemistry of marine sediments of South Aegean Sea

G. Leontopoulou[1], G.E. Christidis[1]*, G. Rousakis[2], N.S. Müller[3], G. Papatheodorou[4], M. Geraga[4]

[1]School of Mineral Resources Engineering, Technical University of Crete, 73100 Chania, Greece
[2] Institute of Oceanography, HCMR, 190 13 Anavyssos, Attiki, Greece
[3] Fitch Laboratory, British Archaeological School at Athens, Souedias Street 52, 10676 Athens, Greece
[4] University of Patras, Department of Geology, 26500 Rio, Patras, Greece

*christid@mred.tuc.gr

Sediments from two deep-sea bottom cores in SE Aegean (ST5 core) and the Myrtoon Basin, SW Aegean (KIM4 core), Greece, were examined by quantitative mineralogical analysis with the Rietveld approach and geochemical analysis in order to infer provenance and paleoenvironmental control on sediment deposition. The results of the Rietveld approach on the clay minerals were compared with conventional semi-quantitative approaches. Both cores consist of muds and contain sapropel S1. The sediments consist of carbonates (calcite and Mg-calcite, dolomite and aragonite), quartz, feldspars, clay minerals (illite, kaolinite, chlorite smectite and palygorskite), amphibole and serpentine. Chlorite is the most abundant clay mineral in SE Aegean while illite is most abundant in the SW Aegean. Comparison of the clay mineral abundances determined by the Rietveld approach with those determined with conventional semi-quantitative analysis showed that the latter overestimates significantly smectite and underestimates illite, kaolinite and chlorite. A well-expressed negative relationship between illite and smectite was obtained from the conventional semi-quantitative analyses, whereas the Rietveld approach yielded a weak positive correlation.

The highest carbonate content is observed in the SW Aegean Sea (Myrtoon Basin) whereas quartz and clay content follow the opposite trend. The sediments are composed of a mixture of biogenic carbonate minerals (main sources of Ca and Sr) and aluminosilicates. Well expressed positive trends were observed between aragonite and Sr, suggesting that this carbonate is the main Sr-host. The increase of organic carbon in the sapropel sediments is accompanied by similar increases in Ba, Ni, Cu, V and U contents. The sediments of SE Aegean are enriched in MgO, Ni and Cr, which decrease with decreasing depth, following the distribution of serpentine and chlorite. The mineralogical and geochemical relationships indicate a strong control from an ultrabasic source influence, most probably the Marmaris ophiolite in the nearby Lycian nappes. The thermal characteristics suggests that smectite is mainly volcanogenic originating from the nearby landmasses of W. Anatolia and the surrounding volcanic islands and that the contribution from SE Mediterranean is very limited or totally lacking.

Geochemical characterization of raw and glazed ceramics from historical buildings of Marrakech area in Morocco as a provenance tracer

Fagel Nathalie[1], El Ouahabi Meriam[2], Rousseau Valérie[3], Cools Catherine[3], El Halim Mouhsin[4], Mattielli Nadine[5], Daoudi Lachen[4]

[1]Universit de Lige AGEs, Geology Lige-Belgium
[2]ESA Saint Luc Chemistry Lige-Belgium
[3]ESA Saint Luc Conservation and restoration of ceramics Lige-Belgium
[4]Universit Cadi Ayad Geology, FST Marrakech-Morocco
[5]Université Libre de Bruxelles G-Time, Geology Brussels-Belgium

The geochemical composition of raw and glazed ceramics was analyzed to identify the provenance of the clays used for decoration of the historical buildings of Marrakech and to track for any temporal evolution. The ceramics have been collected in three main monuments, i.e. the Koutoubia (14th century), the Badi Palace (16th century) and the Saadian Tombs (16th century). The samples include 3 structural raw ceramics and 11 glazed ceramics or zeliges. The analyzed zeliges belong to 3 groups, i.e. the original material, the first restoration material in the first half of 20th century and, the recent restoration material. The trace element content in Sc, Y, Rare Earth Elements (REE), Th and Pb of the shards were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and its Pb isotopic composition by MC-ICP-MS. The samples were dissolved by acids after a mechanical abrasion of the glaze. Regional clayey materials from three modern ceramic production centers (Marrakech, Fes and Sale) were analyzed to compare their geochemical signature with the historical ceramics. The shale-normalized REE pattern of the raw and glazed ceramics display a flat pattern with an average shale-normalised La/Yb ratio of 1.10±0.14 with the highest ratios for the raw ceramics (1.26±0.11). According to their REE pattern, both the raw ceramics and the zeliges fit with the Quaternary clays deposits of the Marrakech area. The Pb isotopic composition of the historical ceramics remains in the field of the regional clays. In contrast, most of the glazed ceramics display an enrichment in $^{207}Pb/^{206}Pb$ associated to an increase in Pb. This enrichment is most probably due to a diffusion from the glaze into the shard.

Kinetics of post-depositional isotopic exchange in clay-water systems

Jonathan D. Smolen[1,*], Reide M. Jacksin[2], Michael T. Hren[1,3]

[1] University of Connecticut, Department of Chemistry, CT 06269 USA
[2] Temple University, Department of Earth & Environmental Science, PA 19122 USA
[3] University of Connecticut, Department of Geosciences, CT 06269 USA

*jonathan.smolen@uconn.edu

The isotopic signatures of hydrogen and oxygen within sedimentary clay minerals has long been used in paleoenvironmental studies – these elements and their isotopic ratios are largely inherited from environmental waters associated with authigenesis and rock weathering processes. In certain systems, primary geochemical signatures have the potential to shift via post-formational exchange with new water sources. Several factors influence the rate and potential extent of exchange such as temperature, residence time, clay mineralogy and clay chemistry. Thus, use of these minerals as isotopic proxies of hydrology, temperature, and input source rely indirectly on the kinetics of isotopic exchange with water – specifically, sedimentary provenance can only be reconstructed from isotopic ratios of clay minerals if the kinetic activation energies of exchange are sufficiently high to prevent alteration of the original isotopic signature (or if the residence time in contact with waters out of equilibrium are sufficiently short). Preservation depends on many environmental factors that can influence the kinetics of post-depositional isotopic exchange: variations in water composition, clay mineral species, grain size, crystallinity, water/clay ratios, pH, and temperature, among others. Unfortunately, rigorous kinetic analyses of clay-water isotope exchange are lacking, considering the long history of using these materials as sedimentary proxies. This study utilizes controlled laboratory exchange experiments to examine the kinetics of hydrogen isotope exchange between kaolinite-water and montmorillonite-water systems and to assess salient factors in mineral-water exchange kinetics (i.e., surface-controlled vs. diffusion, alkali exchange, Ostwald ripening, water/solid ratios, solubility free energies, etc.). The results allow us to assess the ability of clay minerals to be used as faithful recorders of primary hydrogen isotopic composition by quantifying kinetic parameters and applying them predictively to natural scenarios, as well as give insight towards the molecular mechanisms of exchange.

Terrestrial paleoclimate changes recorded by Pleistocene red earth deposits at the Gaolingpo paleolithic site, Bose Basin, South China

Xibing Shen [1*], Hanlie Hong [1,2], Thomas J. Algeo [2,3,4], Ke Yin [1], Qian Fang [1]

[1] School of Earth Sciences, China University of Geosciences, Wuhan, Hubei 430074, China
[2] State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, Hubei 430074, China
[3] State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, Hubei 430074, China
[4] Department of Geology, University of Cincinnati, Cincinnati, OH 45221-0013, USA

*xbshen@cug.edu.cn

The Quaternary River sediments at Gaolingpo, Bose Basin, Guangxi Province contain stone hand adzes and microliths of Paleolithic and Neolithic ages, providing information about the effect of climatic and environmental changes on hominin and early modern human activities. We examined the clay mineralogy and geochemistry of the Gaolingpo soil profile using X-ray diffractometry (XRD), diffuse reflectance spectroscopy (DRS), and X-ray fluorescence (XRF) spectroscopy with the goal of reconstructing paleoclimatic and environmental changes in the study area since the late Early Pleistocene. Within this soil profile, kaolinite and vermiculite increase and illite decreases gradually upsection. The red earth sediments exhibit uniform chondrite-normalized REE distribution patterns, which are similar to those of UCC, PAAS, loess and paleosol of the Chinese Loess Plateau (CLP), and Yangtze River deposits, confirming that the Gaolingpo red earth sediments originated from fine materials of well-mixed weathered continental crust within the upper Pearl River drainage basin. The chemical index of alteration (CIA) of the Gaolingpo sediments is 86.4-92.1, indicating that the sediments have undergone intense chemical weathering. Based on changes in clay mineral contents and geochemical compositions through the profile, the paleoclimatic evolution of the Gaolingpo area since the late Early Pleistocene can be divided into four stages: (1) a warm-cool climate with alternating dry and wet conditions at 1.37-1.1 Ma, (2) a relatively warm climate at 1.1-0.28 Ma, (3) a transition to a warmer and more humid climate (0.28-0.188 Ma), and (4) a hot, very humid climate since 0.188 Ma. This climate pattern is compatible with the $\delta^{18}O$ record at ODP Site 1148 in the northern part of South China Sea and with $\delta^{18}O$ records from cave stalagmites in southern China, documenting the predominant influence of Qinghai-Tibetan Plateau uplift on East Asian climate since the late Early Pleistocene. Development of warm, humid, and only weakly fluctuating climate conditions in the Bose Basin were favorable for early hominid settlement.

Clay mineralogy in Permian–Triassic boundary K-bentonites at Dongpan (Guangxi, South China) and their paleoenvironmental significance

Qian Song[1,*], Hanlie Hong[1], Thomas J. Algeo[2], Qian Fang[1], Chenlei Zhao[1], Chen Liu[1], Yanxiao Xu[1]

[1]School of Earth Sciences, China University of Geosciences (Wuhan), Wuhan 430074, Hubei, China
[2]Department of Geology, University of Cincinnati, Cincinnati, OH 45221-0013, USA

*qiansong_cug@163.com

Volcanic ash deposits of the Permian-Triassic (P-T) transition in South China, in addition to being associated with the Permian-Triassic boundary mass extinction, are useful marker beds for regional correlation of sed-imentary strata. This study investigates the source(s) of P-T volcanic ash layers in South China by studying their clay mineralogy and geochemical characteristics in deep-marine facies at Dongpan. Mineralogically, the Dongpan profile consists mainly of clay minerals and quartz, with small amounts of anatase and feldspar. The clay minerals in the volcanic ash layer are mainly composed of R1 illite/smectite mixed-layer minerals (I/S) (56.9-75%), smectite (14-22.2%), kaolinite (5.6-27.3%) and illite (1.1- 5.5%). The high content of kaolinite and illitization of smectite at Dongpan differ from the features of clay-mineral assemblages in contempora-neous deep-water facies. Our results indicate that an acidic and oxidizing environment inhibits illitization of smectite, and that pH rather than redox is the primary influence on the rate of kaolinization of clay minerals. Trace- element distribution patterns and mixed-layer I/S clay mineral morphologies show that the source of the volcanic ash at Dongpan was a continental magmatic arc on the margin of the South China Plate. The Dongpan section exhibits a uniform REE pattern, indicating a single and stable source of volcanic ash during the P-T transition.

Statistical interpretation of the relation between geochemical and mineralogical data obtained from lake and floodplain sediments (Amuq Valley / Turkey)

Devin Aykasım[1*], Fatma Toksoy Köksal[1], Ulaş Avşar[1], Murat Akar[2]

[1]Middle East Technical University, Department of Geological Engineering, Ankara, Turkey
[2]Hatay Mustafa Kemal University, Department of Archaeology, Hatay, Turkey

*daykasim@metu.edu.tr

Amuq Valley region, that includes Amuq Lake and floodplains of Orontes, Afrin, and Karasu River, and its surroundings have always been a focus of interest for scientists as they provide a unique data collection that preserves both geological and archaeological records of environmental and social turbulences experienced during the Holocene epoch. In the Amuq Valley region, mineralogical and elemental geochemical investigations were carried out along 149 samples from undisturbed sediment cores that were taken from the Amuq Lake and from the vicinity of the archaeological sites of Tell Kurdu, Tell Atchana, and Tell Tayinat. Mineralogical content of the sediments along these cores were examined by X-Ray Diffraction (XRD) and SEM-EDS. Inductively Coupled Plasma – Optical Emission Spectrometry / Mass Spectrometry (ICP-OES/MS) analyses were conducted on the samples to detect quantitative concentrations of major, minor and trace elements. A method was developed by MapInfo software to convert intensities of bulk powder and oriented air-dried clay fraction X-ray diffractogram peaks to numerical values. Numerical values obtained from XRD and ICP-OES/MS analyses were correlated by Correlation Matrix and Principal Component Analysis. Hence, mineral-element relationships were statistically identified. The main purpose of this study is to reveal statistical correlations between geochemical and mineralogical data obtained and characterized from the lake and floodplain sediments of Amuq Valley and uncovering the relationship between geochemistry and mineralogy of the lake and floodplain samples by providing some statistical evidences.

Statistical evaluation of the data revealed that quartz, serpentine, feldspar group minerals and clay minerals have higher correlation coefficients in t he floodplain samples wh ile ca lcite an d ar agonite ha ve higher correlation coefficients in the lake samples. A significant effect of environmental difference was determined on aragonite correlations. It was also examined that the clay mineral peaks before 20° 2θ on bulk powder X-ray diffractograms have stronger correlations with quartz, serpentine, and feldspar group minerals in contrast to the other clay mineral peaks. Moreover, element vs. mineral correlations revealed possible presence of impurities like rutile in quartz due to high correlation coefficients of Si, Al, Fe, Mn, Cu, Ti, Hf, Zr, and Nb, while other minerals generally correlate with their chemical constituents except clay minerals which also correlate with trace elements including rare earth elements such as Hf, ,YLa, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Th, Ga, Er, Yb, Lu, Zr, and Nb. These results also showed that application of this statistical analysis technique is an efficient and timesaving approach on large data sets.

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TS03 + TS14 Paleoenvironments, Diagenesis, Provenance of Sedimentary Deposits

POSTER PRESENTATIONS

Significance of a fibrous clay event in the Lutetian-Bartonian deposits (Eocene of the Paris Basin

Julien Talon[1,2,*], Pierre Pellenard[1], Jean-Marc Baele[2], Florence Quesnel[3], Christian Dupuis[2], Justine Blondet[1], Ludovic Bruneau[1], Christine Fléhoc[4], Anne-Lise Santoni[1]

[1]Biogéosciences Laboratory, UMR 6282 CNRS/uB/EPHE, University Bourgogne Franche-Comté, Dijon 21000, France
[2]Department of Geology, Faculty of Engineering, University of Mons, 7000 Mons, Belgium
[3]Bureau de Recherche Géologique et Minire (BRGM), Georesources Division, Orléans, France
[4]Bureau de Recherche Géologique et Minire (BRGM), Laboratories, Orléans, France

*Julien_Talon@etu.u-bourgogne.fr

Fibrous clay minerals have been well recognized and sporadically studied in the Cenozoic deposits of the Paris Basin from decades and associated to Mg-rich chemical episodes (e.g. Cavelier, 1963; Trauth et al., 1968). However, their occurrence in the basin has been little discussed in relation to the sedimentological and palaeoclimatic contexts. Recent investigations based on 3D geometry and accurate sedimentological model allow to refine the palaeogeographical evolution of the basin and to better constrain the stratigraphy using both biostratigraphy and sequence stratigraphy (RGF program lead by BRGM). In this context, old and recent drilling cores are going to be studied with a high-resolution sampling in order to improve our knowledge of the mineralogy and geochemistry of Eocene deposits in relation to the evolution of the Paris Basin including tectonics, palaeogeography and palaeoclimate. Besides, understanding the spatial distribution and evolution of clay minerals through time in the Cenozoic cover of the Paris Basin is critical for environmental and geotechnical aspects of projects like the ongoing “Grand Paris Express” (a rapid train connection around Paris) project.

During the Eocene, some major climate events known as hyperthermals following the Paleocene Eocene Thermal Event (PETM), namely the ETM2, ETM3, EECO, LLTM and MECO events are marked by a net increase of temperature and negative carbon isotope excursions highlighting carbon cycle disruptions. Since enhanced continental weathering coupled to an increase of temperature and humidity is observed during most of these events, clay mineralogy and C-isotope geochemistry are useful methods to track such events. We thus investigate these proxies at high resolution in the Le Tillet core (north of Paris) to provide a detailed evolution of clay mineralogy and a first C_{org} isotope curve spanning the Eocene (Ypresian-Bartonian) to identify possible Eocene hyperthermal events in the Paris Basin.

Six successive intervals are recognized based on clay mineralogy. Among them, an episode dominated by fibrous clay minerals (palygorskite and sepiolite) accompanied by smectite and clinoptilolite is recorded during the Lutetian-Bartonian transition (~41 Ma) corresponding to the ‘Marnes et Caillasses Formation’. This episode, recognized in other cores and outcrops of the Paris Basin, seems to correspond to the record of an arid climate event in Europe and predates the MECO (Middle Eocene Climatic Optimum) that is marked by the return of more detrital clay mineral and kaolinite input in the basin. Associated to a negative carbon isotope excursion, this hot and arid episode may correspond to the LLTM event (Late Lutetian Thermal Maximum) previously recognized in the deep oceans.

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Assessing clay mineral origins in Pennsylvanian-aged paleosols of the Illinois Basin using stable and radioisotopes

Julia A. McIntosh[1,*], Neil J. Tabor[1], W. Crawford Elliott[2], J. Marion Wampler[2]

[1]Department of Earth Sciences, Southern Methodist University, Dallas, TX 75275 USA
[2]Department of Geosciences, Georgia State University, Atlanta, GA 30302 USA

*mcintoshj@smu.edu

Clay minerals in Pennsylvanian-aged paleosols from Illinois Basin cyclothems may have formed during episodes of soil formation or shallow to deep burial diagenesis or may have been inherited as detritus prior to soil formation. To assess origins of clay minerals in these paleosols, Middle and Upper Pennsylvanian strata of three cores from the northern, central, and southern portions of the Illinois Basin were sampled and isolated to <2.0, <0.2, and <0.1 μm clay-sized fractions by disaggregation and centrifugation. X-ray diffraction of oriented aggregates indicates illite and mixed-layer illite-smectite and kaolinite are present. X-ray diffraction of randomly oriented powders indicates illite has 1*M*, 1M_d, and 2M_1 polytypes. Using thermal extraction and isotopic analysis of Ar and determination of K by atomic absorption spectrophotometry, illitic clay minerals record K-Ar age values around 260 Ma in the northern core, 270 Ma in the central core, and 290 Ma in the southern core. Oxygen and hydrogen prepared by silicate fluorination and thermal dehydroxylation techniques, respectively, from the <0.2 μm clay-sized fractions of the shallowly buried, northern core reported by Rosenau and Tabor (2013), exhibit δ^2H values of −51‰ to −38‰ and $\delta^{18}O$ values of 18.9‰ to 22.4‰, relative to SMOW. Corresponding ranges for the samples from the moderately buried, central core are −96‰ to −42‰ and 11.9‰ to 17.8‰, and for the samples from the deeply buried, southern core those ranges are −72‰ to −38‰ and 14.8‰ to 18.0‰.

Although pedogenic clay minerals were previously thought to be preserved in Pennsylvanian-paleosols of the Illinois Basin, this new, comprehensive dataset indicates that some detrital illite remains and suggests post-Pennsylvanian illitization in these paleosols. It is possible that illitization may have occurred during hydrothermal and diagenetic events spurred by the Alleghenian-Ouachita orogeny beginning in the Permian. These results are significant, because they call into question the general utility of phyllosilicates as reliable paleoenvironmental indicators across space and time and suggest older paleosols may in fact provide more information about diagenesis than paleoenvironment.

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TS04 Clays in The Solar System

ORAL PRESENTATIONS

Investigating the biopreservation potential of martian smectites

Isis Criouet*, Jean-Christophe Viennet, Laurent Remusat, Sylvain Bernard

MNHN, Sorbonne Universit, CNRS UMR CNRS, IMPMC, Paris, France

*isis.criouet1@mnhn.fr

The NASA rover Perseverance has landed on Mars (as will soon do the ESA ExoMars rover) to search for organic traces of life within the old, long frozen, smectite-rich rocks exposed at the surface (Farley & Williford 2017; Vago et al. 2017). Odds to find traces of life in these rocks are seen as very high given the so-called biopreservation potential of smectites (Ehlmann et al., 2008; McMahon et al., 2018). Yet, the Martian subsurface has not been a perfectly functioning freezer: orbital and *in-situ* exploration revealed that most ancient clay-rich sediments are intruded by veins at all scales, attesting to the circulation of acidic/oxidizing brines at low to relatively high temperatures (Schwenzer et al. 2016; Kronyak et al. 2019; Bristow et al. 2021). Here, we report results of laboratory experiments designed to investigate the impact of such circulation of fluids on the preservation of organic compounds under Martian conditions following a proof of concept study (Viennet et al., 2019). Phospholipids and *E-coli* cells were experimentally submitted to hydrothermal conditions at 150°C for 10 days under a Martian-like (CO_2-rich) atmosphere in the presence of smectitic materials, either Mg-saponite, Fe-nontronite or Al-beidellite. The EA-irMS, XRD, FTIR and XANES characterization of the experimental solid residues evidenced that, depending on their crystallochemistry, smectites can efficiently trap organic carbon onto their surfaces and within their interlayer spaces while impacting it more or less from chemical degradation, confirming the relevance of searching for organic carbon in ancient clay-rich Martian sediments. Among the smectites investigated here, Mg-saponite is the one exhibiting the highest preservation potential, Fe-nontronite and Al-beidellite displaying lower storage/entrapment capacities.

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Formation of Fe(III) (hydr)oxides from Fe(II) sulfides: Implications for akaganeite detection on Mars

Tanya S. Peretyazhko[1*], Douglas W. Ming[2], Richard V. Morris[2], David G. Agresti[3], Wayne P. Buckley[1]

[1]Jacobs, NASA Johnson Space Center, Houston, TX 77058, USA
[2]NASA Johnson Space Center, Houston, TX 77058, USA
[3]Department of Physics, University of Alabama at Birmingham, Birmingham, AL 35294, USA

*tanya.peretyazhko@nasa.gov

Akaganeite (β-FeO(OH,Cl)) is a Fe(III) (hydr)oxide with a tunnel structure typically occupied bychloride. This mineral was first proposed to be present in Meridiani Planum and Gusev crater on Mars and akaganeite was subsequently detected by X-ray diffraction in Yellowknife Bay and VeraRubin Ridge locations in Gale crater. Akaganeite in Gale crater has been proposed to form from Fe(II) sulfides but formation conditions remain unconstrained.

We investigated akageneite formation by oxidative alteration of natural Fe(II) sulfide pyrrhotite exposed to HCl and oxidation-hydrolysis of Fe(II) HCl-leached from pyrrhotite at initial pH_0 1.5, 2, 3, and 4. X-ray diffraction and Mössbauer analyses revealed formation of poorly-crystallized akageneite in oxidative alteration experiments. Air-exposure of the HCl-reacted dry pyrrhotite let to an increase in akageneite formation and precipitation of Fe(II) hydrated sulfates, goethite, and hydronium jarosite. Iron(II) oxi- dation-hydrolysis was sensitive to Si dissolved from phyllosilicatesin one pyrrhotite sample. Akaganeite and goethite formed at pH_0 1.5 and 2 with akageneite more abundant at dissolved Si/Fe ratio of 0.08 and goethite more abundant at Si/Fe of 0.01. Akaganeiteformed together with hematite, ferrihydrite, and goethite at pH_0 3, and formation was suppressed at pH_0 4. Well-crystallized akageneite precipitated at pH_0 1.5 while akaganeite of poorer crystallinity formed at pH_0 2 and 3.

Akageneite in Gale crater could form from sulfides by both mechanisms: oxidative alteration of sulfide minerals and oxidation-hydrolysis of leached Fe(II). The processes likely occurred duringlate diagenetic events triggered by interactions of acidic Cl-bearing groundwater with Fe(II) sulfides. Akaganeite in Yellowknife Bay, Gale crater could have formed by Fe(II) oxidation- hydrolysis either as a sole Fe(III) (hydr) oxide at pH<2 or along with ferrihydrite and hematite at 2<pH<4 in Si-enriched conditions. Akaganeite formation at Vera Rubin Ridge, Gale crater could have occurred through oxidative alteration of sulfides in Cl-bearing pH 1.2-1.5 solutions. The presence of well-crystalline akageneite in Vera Rubin Ridge indicates that Fe(II) oxidation- hydrolysis contributed to akageneite formation.

Magmatic production of clay minerals on Mars

Sylvain Bernard[1,*], Jean-Christophe Viennet[1], Corentin Le Guillou[2]

[1]MNHN, Sorbonne Universit, CNRS UMR 7590, IMPMC, Paris, France
[2]Universit de Lille, INRA, ENSCL, CNRS UMR 8207, UMET, Lille, France

*Sylvain.Bernard@mnhn.fr

Mars is seen as a basalt covered world that has been extensively altered through hydrothermal or near surface water-rock interactions. As a result, all the Fe/Mg-rich clay minerals detected on Mars so far have been interpreted as secondary, i.e. as products of aqueous alteration of pre-existing silicates by (sub) surface water (Ehlmann & Edwards, 2014). Yet the fine scale petrographic study that we conducted on two unaltered nakhlites archetypal of the martian crust, i.e. Nakhla and NWA5790, revealed the presence of Fe/Mg-rich clay minerals of magmatic origin (Viennet et al., 2020; 2021), as is the case of some clay minerals on Earth (Mas et al., 2008; Meunier et al., 2008; Berger et al., 2018). These Fe/Mg-rich clay minerals display a typical structure of smectites, with layers of a few hundreds of nanometers in length stacked over a few tens of nanometers and d-spacings of 10-12 . They are chemically heterogeneous, with a mean chemical composition falling between nontronite, celadonite, and saponite, and exhibit a high Cl content, likely incorporated in the structure as suggested by the observed anticorrelation between Mg and Cl. These magmatic clay minerals exhibit a vesicular texture that forms a network of microcavities or pockets, which could act as microreactors and allow molecular crowding, thereby facilitating a potential emergence of life. Because the production of such clay minerals does not depend on climate, such niches for emerging life may have been generated on Mars at many periods throughout its history, regardless of the stability or availability of liquid water at the surface. In any case, the existence of magmatic smectites justifies a re-evaluation of the exact origin of the clay minerals detected on Mars so far, with potential consequences for our vision of the early magmatic and climatic histories of Mars.

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Reappraisal of the clay mineralogy of the Orgueil meteorite by using X-Ray diffraction profile modelling

Viennet J-C.[1,*], Hubert F.[2], Beck P.[3], Alp E. E.[4], Lavina B.[4,5], Hu M.Y.[4], Zhao J.[4], Bernard S.[1], Le Guillou C.[6], Gounelle M.[1], Remusat L.[1], Roskosz M.[1]

[1]IMPMC, MNHN, CNRS, SU, Paris, France
[2]IC2MP, Universit de Poitiers, CNRS, Poitiers, France
[3]IPAG, Universit Grenoble Alpes, CNRS, Grenoble, France
[4]APS, ANL, Argonne, IL 60439, USA
[5]Center for Advanced Radiation Sources, Univ. Chicago, Chicago, IL 60637, USA
[6]UMET, Universit de Lille, France

* jean-christophe.viennet@mnhn.fr

Tracking water from the formation of the solar system to the present-day Earth's ocean is a major focus of the sample return missions (Hayabusa 2 and OSIRIS Rex). In this context, CI carbonaceous chondrites are extremely rich in clay minerals and display chemical composition closely to the elemental of the sun's photosphere. They therefore represent an invaluable insight into the protoplanetary disk from which the solar system formed. Such CI meteorite are made of fine Mg-smectites interpreted as the alteration product of coarse Mg-serpentine on their parent body (Tomeoka and Buseck, 1988). To better understand the geochemical process leading to the formation of such meteorites, we determine the crystal structure of the clay minerals (layer types, stacking and proportions in clay phases, and relative proportion of clay phases) by combining quantitative particle size fractionation (<0.02 µm, 0.02-0.05, 0.05-0.2, 0.2-2, 2-50 µm) and X-ray diffraction profile modeling (Viennet et al., 2015). In addition to smectite and serpentine-rich clay phases, a three component interstratified clay minerals (R0 serpentine-smectite-mica) never described by SEM-TEM technique accounts for more than 80% of the sample mass. Furthermore, the crystal structures of the clay minerals do not appear to vary with particle size, which seems most likely indicated their genesis in a single step from homogeneous medium than by alteration as previously proposed. However, many questions remain: What does the crystal structures of these minerals suggest us about the pH/redox/ temperature conditions? Was the water liquid and/or in vapor form during the formation of these clay minerals? In other words, is this clay mineralogy an indicator of fluid circulation on the asteroids or the product of a gas-grain reaction within the disk?

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Clay-sulfate transitions at Mawrth Valles, Mars point to habitable conditions and energetically favorable environments

Janice L. Bishop[1,*], Megan E. Elwood Madden[2]

[1]SETI Institute, Carl Sagan Center, Mountain View, CA, 94043, USA
[2]University of Oklahoma, Norman, OK 73019, USA

*jbishop@seti.org

Phyllosilicates are found in numerous ancient environments on Mars through orbital spectroscopy, providing evidence of aqueous environments. The Mawrth Vallis region contains a thick deposit of Fe/Mg-rich smectite, together with a wealth of additional aqueous alteration products including Al-phyllosilicates, silica, allophane, ferric oxides/hydroxides, and even sulfates in isolated outcrops (Bishop et al., 2020). Evaluating transitions from the dominant clay-rich zones to these smaller sulfate-bearing outcrops is possible with visible near-infrared (VNIR) CRISM imagery at 18 m spatial resolution. This study compares CRISM observations at Mawrth Vallis with terrestrial field sites and lab studies to place constraints on the aqueous geochemical environment at this region of Mars during formation of these deposits about 4 Gya.

The phyllosilicate-bearing strata in this region form expansive horizons, similar to those found at the Painted Desert of Arizona, while the sulfates are observed sandwiched in between the lower Fe/Mg-smectite unit and the upper Al/Si-rich horizon. The types of sulfates present appear to vary regionally, with jarosite occurring preferentially in the north, alunite in the south, and hydrated sulfates near the channel. These small sulfate-bearing outcrops vary in thickness, width, and chemistry in between the two dominant phyllosilicate-rich horizons and may have formed in warm hydrothermal waters, or as evaporites, orby brine percolating through the clay-rich horizons.

A spectrally unique material is observed near the jarosite outcrops that is consistent with a mixed jarosite-gypsum system (Bishop et al., 2020). This is unusual on Earth, but is found in shallow brine pondsin Western Australia (e.g., Benison & Bowen 2006) and in the Painted Desert (Perrin et al., 2018). Lab experiments demonstrate formation of gypsum from smectite in Cl/S brines as Ca is removed from the interlayer sites and also fromjarosite in $CaCl_2$ brines as Cl attacks the jarosite, releasing Ca and sulfate (Elwood Madden et al., 2021). Thus, these islands of sulfates in the clay-rich Mawrth Vallis region may represent chemically-active sites containing complex clay-sulfate assemblages that were energetically favorable environments for life on early Mars.

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Indigenous organic matter associated with unusual low temperature aqueous secondary phases in the Mars meteorite nakhla

Kathie L. Thomas-Keprta[1,*], **Simon J. Clemett**[1], **Everett K. Gibson**[2], **Zia Rahman**[1], **Neha Baskar**[3], **Susan J. Wentworth**[4], **Nathaniel T. Keprta**[5] , **David S. McKay**[2]

[1]Jacobs Technology Inc., NASA Johnson Space Center (JSC), Mail Code (MC) XI3, Houston, TX 77058, USA
[2]NASA JSC, MC XI3, Houston, TX 77058
[3]Texas A&M, College Station, TX 77843
[4]HEPCO, Inc, NASA JSC, MC XI2, Houston, TX 77058
[5]University of Houston-Clear Lake, Houston, TX 77058

[*]kathie.thomas-keprta-1@nasa.gov

In freshly fractured chips of the Mars meteorite Nakhla, we found carbonaceous phases intimately associated with secondary aqueous alteration phases, both mineral and amorphous, interpreted to have formed through the low-temperature, mineral-water dissolution of the host Martian basalt. The nature of carbonaceous matter and spatially associated secondary phases within Nakhla were characterized using a multidisciplinary suite of optical and electron beam instrumentation (Thomas-Keprta *et al*., 2022). *Secondary Phases*: The preserved secondary mineral phases are best described as 'juvenile' hydrated amorphous silica formed when water interacts with mafic rocks. Although amorphous silica on Earth rarely persists through geologic time due to alteration into other phases, *e.g*., microcrystalline opal-CT and eventually quartz, the lack of maturation of primarily amorphous silica with embedded nanophase ferrihydrite in Nakhla infers these phases formed in a limited water environment by low temperature, circumneutral pH fluids stabilized by the presence of coexisting amorphous silica. Additionally, we report the presence of the ferrous hydroxycarbonate mineral chukanovite ($Fe_2(OH)_2CO_3$) within some of the secondary mineral aggregates studied. *Organic Matter*: Indigenous Nakhla carbonaceous matter is present both in condensed phases and in a dispersed state spatially associated with secondary alteration phases. In the former, discrete refractory micron to submicron assemblages were identified that appear macromolecular in nature and, in several cases, associated with F and, in one case, significant N. While organically bound F has yet to be detected remotely on Mars, the identification of organic N within one of the carbonaceous phases is considered a prerequisite for Martian astrobiological potential.

Summary: Neither the intimate association of carbonaceous matter with secondary phases nor the identification of chukanovite have been previously reported in any Martian meteorite. A variety of habitability-related metastable solid-phase, oxidation-reduction, and organic-molecular attributes in Nakhla formed hundreds of millions of years ago near Mars' surface; these alteration products persisted on Mars until very recently and resemble the amorphous materials observed at Gale crater by Mars Science Laboratory Curiosity Rover (Rampe *et al*., 2020). Similar phases may be expected to occur elsewhere on Mars (*e.g*., Jezero crater).

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Allophanes with varied Si/Al molar ratios - structure characteristics and feasibility of differentiation by visible and near-infrared spectroscopy

Peixin Du[1,2]*, Shun Wang[3], Peng Yuan[2], Jiacheng Liu[4], Dong Liu[2], Haozhe Guo[5], Xinyi Xiang[1], Xiaolong Guo[1]

[1]State Key Laboratory of Lunar and Planetary Sciences, Macau University of Science & Technology, Macau, China
[2]CAS Key Laboratory of Mineralogy and Metallogeny / Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, ChineseAcademy of Sciences, Guangzhou 510640, China
[3]Neutron Science Platform, Songshan Lake Materials Laboratory, Dongguan, 523808, China
[4]Department of Earth Sciences, The University of Hong Kong, Hong Kong, China
[5]Institute of Resources Utilization and Rare Earth Development, Guangdong Academy of Sciences, Guangzhou 510650, China

*pxdu@must.edu.mo

Allophane ($1{\sim}2SiO_2{\cdot}Al_2O_3{\cdot}5{\sim}6H_2O$) occurs ubiquitously in soils of volcanic origin on Earth and is also a probable constituent on martian surface (Du et al., 2020). It not only controls the transport, migration, and fate of guest materials in Earth surface environments (Wada, 1989), but also gives constraints on the geochemical settings and water-rock interaction history on Mars (Rampe et al., 2012). However, up to now, it remains to be one of the few minerals/mineraloids whose structure has not been unequivocally defined, as a result of its ultrasmall particle size (external diameter of 3.5−5.5 nm), extremely low structural order and highly variable Si/Al molar ratios (Parfitt, 2009).

To gain insights into the structure and probably also the formation process of allophane, we hydrothermally synthesized allophanes at varied initial Si/Al molar ratios (0.5, 0.57, 0.66, 0.75, and 1.0), followed by characterizing their structure using a combination of advanced techniques. X-ray diffraction (XRD) patterns, Fourier transform infrared (FTIR) spectra, and $^{27}Al/^{29}Si$ magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectra show that bayerite was obtained at initial Si/Al molar ratios of 0.5 and 0.57. FTIR and $^{29}Si/^{27}Al$ MAS NMR spectra also suggest the presence of oligomeric silicates in all the products and the significant amount of Al^{IV} occurring invariably in both natural and synthetic allophanes is in these oligomeric silicates. A possible explanation for the presence of oligomeric silicates is that the formation of imogolite local structure (ImoLS, *i.e.*, the aluminosilicate framework of allophane) and the attachment of oligomeric silicates to it occur simultaneously. Scanning transmission electron microscopy (STEM) and atomic force microscopy (AFM) images showed that these products exhibited different aggregation states, probably resulting from different structural order and formation of byproducts such as bayerite and proto-allophanes. The visible and near-infrared (VNIR) spectra of the products were also recorded for potential comparative studies on Mars. No obvious differences resulting from Si/Al molar ratios were observed in the VNIR spectra of allophanes, indicative of the weakness of this technique in detecting the geochemistry of Al and Si in poorly ordered aluminosilicate components at Mars' surface.

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NH_4-smectites - a potential source of N compounds in analyses by the Sample Analysis on Mars instrument onboard the Curiosity rover?

Slavka Andrejkovičová[1,2,3,*], Amy C. McAdam[2], Jennifer C. Stern[2], Christine A. Knudson[2,3,4], Rafael Navarro-González[5†], Maëva Millan[2,6,7], Elizabeth B. Rampe[8], Douglas W. Ming[8], Fernando Rocha[1], Paul R. Mahaffy[2]

[1]Aveiro University, GeoBioTec, Geosciences Department 3810-193 Portugal
[2]NASA Goddard Space Flight Center, Greenbelt, MD, 20771 USA
[3]Center for Research and Exploration in Space Sciences and Technology, NASA GSFC, MD, 20771 USA
[4]University of Maryland College Park, College Park, MD, 20742 USA
[5]Universidad Nacional Autnoma de Mxico, 04510 Mexico
[6]Laboratoire Atmosphre, Milieux, Observations Spatiales (LATMOS), Guyancourt, 78280 France
[7]Department of biology, Georgetown University, Washington DC, 20057 USA
[8]NASA Johnson Space Center, Houston, TX, 77058 USA
†Deceased January 28, 2021

*slavka@ua.pt

The presence of nitrates in Martian near-surface samples has been confirmed by evolution of NO during heating of samples by the Sample Analysis at Mars (SAM) instrument suite on the Curiosity rover, indicating that nitrogen fixation processes occurred in early Martian history (Stern et al. 2017). However, little is known about other possible nitrogen reservoirs on Mars, including those that may contain reduced forms of N in the sediments. Thus, understanding whether reduced N compounds such as NH_4^+ are present in Martian regolith is important to assess habitability in the Martian environment. Ammonium may be sequestered in surface materials by inclusion of NH_4^+ in certain phyllosilicates. Smectite clay minerals have been detected in most drilled rock samples analyzed by Curiosity (Bristow et al., 2021). Therefore, the presence of reduced N in the form of NH_4^+ on clay mineral exchange sites would have important implications for the development of a nitrogen cycle on Mars, and therefore Mars' past habitability. Oxychlorine phases, such as perchlorates, have also been detected in many samples analyzed by SAM (Sutter et al., 2017) and when heated they evolve oxygen. The main aim of this study is to determine if reduced N in the form of NH_4^+ sequestered in the interlayer space of the smectites, when heated with perchlorate salts, produces N compounds (NO) during heating comparable to those observed during heating in SAM.

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Clay minerals and amorphous materials from source to sink in Martian analog sedimentary environments

Michael T. Thorpe[1,*], Elizabeth B. Rampe[2], Juergen Thieme [3], Eric Dooryhee[3], Steven Lee[4], Roy Christoffersen[5]

[1]Texas State University, JETS, Astromaterials Research and Exploration Science Division, Houston, TX 77058, USA [2]NASA Johnson Space Center, Houston, TX 77058, USA

[3]Brookhaven National Laboratory, Building 817, 33 North 28 Renasissance Road, Upton, NY 11973, USA
[4]Luna and Planetary Institute, Universities Space Research Association, Houston, TX 77058, USA
[5]Jacobs, JETS Astromaterials Research andExploration Science Division, Houston, TX 77058, USA

*michael.t.thorpe@nasa.gov

Clay minerals and secondary X-ray amorphous materials make up a significant fraction of fluvial and lacustrine sedimentary rocks traversed by the Mars Science Laboratory (MSL) *Curiosity* rover (e.g., *Rampe et al*., 2020; *Tu et al*., 2021; *Sheppard et al*., 2021; *Thorpe et al*., accepted). These alteration products are inherently small in grain size and difficult to characterize. On Earth, extended sample preparation methods are required to concentrate the finest fraction, and even still, traditional benchtop techniques lack the reso-lution necessary to fully characterize the composition and structure of these materials. On Mars, we cannot do sample preparation like on Earth and arelimited to bulk rock analyses. In Martian analog sedimentary environments on Earth, we have the unique opportunity to expand our understanding of how clay minerals and X-ray amorphous materials evolve along transport pathways from source terrains to sedimentary ba-sins (i.e., source- to-sink). Here, we explore the fine-grained fraction of fluvial sediments from the basaltic terrains of Iceland with both rover-like capabilities (e.g., X-ray Fluorescence (XRF) and X-ray diffraction (XRD)) and high-resolution analytical techniques (e.g., Transmission Electron Microscopy, Synchrotron XRF and XRD) to serve as a terrestrial

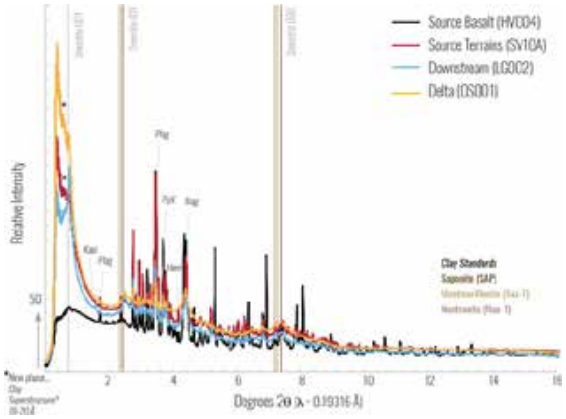


Figure 1. Synchrotron XRD patterns. Abbreviations: Kaol (Kaolinite), Plag (Plagioclase), PyX (Pyroxene), Hem (Hematite), and Mag (Magnetite).

reference frame for the secondaryalteration products observed in Gale crater, Mars. Results demonstrate that the clay sizefraction of sediments from Martian analog environments is composed of an intimate mixture of multiple clay minerals (e.g., smectites, ka-olinite, and a clay-mineral super structure. Fig. 1) and multiple X-ray amorphous phases (e.g., ferrihydrite) with different morphologies. These results suggest that the clay mineral and X-ray amorphous composition of sedimentary rocks in Gale crater, Mars may be Figure 1. Synchrotron XRD patterns. Abbreviations: Kaol (Kaolinite), Plag (Plagioclase), PyX (Pyroxene), Hem (Hematite), and Mag (Magnetite). Equally complex, and that the sedimentary history may only truly be unraveled with Mars Sample Return and high-resolution analysis.

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[4] Thorpe et al., (accepted). JGR-Planets, Special Issue on Glen Torridon Region

TS04 Clays in The Solar System

POSTER PRESENTATIONS

Mineralogical controls on carbon preservation in carbon limited Mars analog vitrisol soils of Iceland

Brad Sutter[1]*, Rebecca Lybrand[2], Doug Ming[3], Cherie Achilles[4], Amy McAdam[5]

[1]Jacobs, NASA Johnson Space Center, Houston, TX 77058 USA
[2]U.C., Davis, Department of Land, Air, Water Resources, Davis, CA 95616 USA
[3]NASA Johnson Space Center, Houston, TX 77058 USA
[4]U. Maryland College Park, NASA Goddard Space Flight Center, Greenbelt, MD 20771 USA
[5]NASA Goddard Space Flight Center, Greenbelt, MD 20771 MD USA

*brad.sutter-2@nasa.go

A goal of the Mars Science Laboratory's Curiosity rover mission to Gale Crater, Mars was to search for organic carbon and thus the possible evidence of ancient microbiology preserved in clay mineral-rich sedimentary deposits. The Sample Analysis at Mars instrument on board Curiosity has detected low concentrations (< 10 ppm C) of S and Cl bearing organics in martian sediments (e.g, Freissinet et al., 2015; Eigenbrode et al., 2018). However, up to ~ 2000 ppm C has been detected as CO_2 and CO consistent with martian surface carbon being dominated by oxidized organics and carbonates. No clear correlation of clay mineral (smectite) abundances with SAM carbon detections has been established suggesting other phases may preserve organic C in martian sediments. The X-ray amorphous component (20 to 73 wt%) dominated by Si, Fe, and Al has received little consideration and could have role in organic C preservation in Gale Crater (e.g., Yen et al., 2017; Rampe et al., 2018). Terrestrial volcanic ash soils consisting of Fe-, Al-oxyhydroxide phases and allophane are known to sequester organic C and thus could serve as an analog to understanding the role amorphous material may have in organic C preservation in martian sedimentary materials.

The goal of this work is to evaluate soil C along a chronosequence (young to older soils) of basaltic glass-bearing Icelandic soils to determine the role that poorly crystalline phases have in accumulating organic C in carbon limited soils. Icelandic basaltic glass bearing soils are martian analogs because of their high basaltic amorphous material contents and carbon concentrations (500-4000 ppm C) that are similar to Gale Crater materials (< 2000 ppm C). The objectives of this work in progress are 1) Determine what mineralogical/geochemical factors control carbon preservation in these carbon limited soils. 2) Utilize carbon isotope analyses ($\Lambda^{13}C$, $\Lambda^{14}C$) to determine carbon sources, carbon age, and presence of any microbial processing. 3) Utilize laboratory SAM analog thermal evolved gas analysis to search for correlations between X-ray amorphous materials and evolved CO_2, CO, major organic fragments that could serve as analog indicators of organo-amorphous phase associations in Gale materials. Results of this terrestrial analog work will be utilized to understand organic C preservation potential of the X-ray amorphous component in the C limited sediments/soils of Gale Crater.

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Experimental study on the transformation of nontronite to kaolinite: implications for the formation of clay minerals on Mars

Xiaorong Qin[1,*], **Wei Tan**[1], **Jiacheng Liu**[2], **Hongping He**[1], **Joseph Michalski**[2]

[1]Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[2]Division of Earth and Planetary Science & Laboratory for Space Research, The University of Hong Kong, China

*qinxiaorong@gig.ac.cn

A unique aspect of Martian geology is the presence of similar compositional stratigraphy observed in many locations throughout the surface, where kaolinite is typically overly nontronite but the formation mechanism is still under debate. The compositional stratigraphy has been attributed to by the climate-induced chemical weathering and kaolinite could be the result of further weathering of the nontronite (Gaudin et al., 2011; Liu et al., 2021). However, the process of nontronite transform into kaolinite remain ambiguous, which is important to understanding the minerals observed at the Martian surface.

In this study, laboratory experiments on the conversion of nontronite to kaolinite were carried out to investigate the conversion process. XRD patterns of the hydrothermal products display characteristic reflections at 7.2 nm and 0.27 nm, which corresponding to the (001) reflections of kaolinite and (104) reflections of hematite. Evidence for a physical mixture of nontronite and kaolinite, rather than interstratified N-K, is evident in the separation of the (060) region into two peaks, one produced by nontronite and one by kaolinite. The (060) reflections of kaolinite fix at 0.149 nm suggest that the dominant cation in the octahedral sheets of kaolinite is Al^{3+}. This reveal that the Fe^{3+} released from the octahedral of nontronite is not incorporated into the neo-formed kaolinite while formed hematite. Hence, the formation of kaolinite during the weathering of nontronite into kaolinite is more comparable to neoformation than to a solid-state transformation. The Fe^{3+} released from nontronite and formed hematite result in the position of absorption band related to Fe^{3+} at around 0.9 μm (P900) shift from 0.95 to 0.86 μm. The position of absorption band at 1.39 μm (P1396) gradually increase, which suggests that the kaolinite crystallinity gradually increase. The leaching of water complexes with interlayer cations (Ca^{2+}) in precursor minerals nontronite during the transformation led to a dramatic decrease of mass loss and temperature of dehydration in TG curves. Our results indicate that dissolution-reprecipitation transformation is the main mechanism for conversion of nontronite to kaolinite. The spectral features show good correlations with the crystal-chemistry of hematite and kaolinite. The interlayer cations (e.g., Ca^{2+}) is leached away from the structure of clay minerals may form some calcium sulfate mineral, (e.g., gypsum), which could explain the formation of gypsum on Martian surface. This study provides the mineral characteristics of nontronite transform into kaolinite and sheds new light on the formation process of the clay minerals and sulfate mineral on Mars.

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TS05 + TS24 Pedogenic Clays

ORAL PRESENTATIONS

Oxygen isotope composition of soil clay minerals and rainwater in the Tatra Mountains, Poland

Artur Kuligiewicz[1,*], Ilya Bindeman[2], Wojciech Szymański[3], Mariola Kowalik-Hyla[1], Kazimierz Różański[4]

[1]Institute of Geological Sciences, Polish Academy of Sciences, Krakow, PL-31002, Poland
[2]Department of Earth Sciences, University of Oregon, Eugene, OR, 97403-1272 USA
[3]Institute of Geography and Spatial Management, Jagiellonian University, 30-387 Krakw Poland
[4]Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, 30-059 Krakow, Poland

*ndkuligi@cyf-kr.edu.pl

Pedogenic clay minerals are commonly considered to be formed in isotopic equilibrium with water at mean average temperature (MAT) and mean annual precipitation (MAP) of an area (Lawrence & Taylor, 1971), which is the key assumption in isotope-based paleoclimatic studies of paleosols. The main aim of the present research was to test this assumption for postglacial soils of the Tatra Mountains, Poland.

Four soil profiles developed from +9.3‰ $\delta^{18}O$ granitic material were sampled. Representative MAT and MAP of sampling sites are 2.6°C and 1100 mm, respectively, leading to expected pedogenic clay minerals' $\delta^{18}O$ values in the +18-22‰ range. The clay fraction (<0.2 μm) was separated and characterized by X-ray diffraction, Fourier transform infrared spectroscopy, andchemical analysis. The oxygen isotope composition of the material was determined on a CO_2 laser fluorination line connected to isotope ratio mass spectrometer using an airlock sample chamber and GC column for O_2 gas purification.

Major mineral components in the clay fractions were dioctahedral mica, mixed layered minerals such as illite-smectite, vermiculite and/or a high-charge smectite, and kaolinite. Values of $\delta^{18}O$ of the clay fractions were between 6.4 and 13.0‰ indicating disequilibrium with the isotopic composition of rainfall and stream water in the area. No clear trends between $\delta^{18}O$ values of the clay fractions and depth of the soil horizon were noted; however, material separated from eluvial horizons seem to have $\delta^{18}O$ values closer to values expected for pedogenic clay minerals from the area.

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Lawrence, J.R., Taylor, H.P. (1971) Deuterium and oxygen-18 correlation: Clay minerals andhydroxides in Quarternary soil compared to meteoric waters, *Geochimica et Cosmochimica Acta,* 35, 993-1003

Formation of iron oxyhydroxides as a result of glauconite weathering in soils of temperate climate

Magdalena Makiel[1], Michał Skiba[1], Marta Kisiel[1,*], Katarzyna Maj-Szeliga[1], Artur Błachowski[2], Wojciech Szymański[3], Dorota Salata[1]

[1]Institute of Geological Sciences, Jagiellonian University, 30-387 Kraków, Poland
[2]Institute of Physics, Pedagogical University, 30-084 Kraków, Poland
[3]Institute of Geography and Spatial Management, Jagiellonian University, 30-387 Kraków, Poland

*m.kisiel@doctoral.uj.edu.pl

The aim of the present study was to investigate glauconite weathering in soils of temperate climate. Special focus was put on iron oxides *s.l.* which formed at the expense of the glauconite. Five soil profiles developed on parent material in which glauconite was the main (if not the only) phyllosilicate and source of Fe were investigated. Color, texture, pH, and carbonate and soil organic carbon content were determined for the bulk soil samples. Clay fractions and green pellets were separated from the studied soils and analyzed using X-ray diffractometry, Fourier-transform infrared spectroscopy, Mössbauer spectroscopy, and inductively coupled plasma - optical emission spectrometry.

Three of the soils were acidic with pH from 4.3 to 5.5 and two of the soils were alkaline with pH from 6.8 to 8.6. Parent glauconite pellets from each profile showed similar chemical composition, but in one case Fe(II) was much more abundant than in the others. In both acidic and alkaline soils glauconite weathering products included Al-smectite-rich glauconite-smectite mixed-layered minerals (G-S), kaolinite, and Fe oxides. G-S likely formed by transformation of glauconite due to the at least partial, incongruent dissolution (i.e. leaching of Mg, K, and Fe from the structures). Kaolinite and iron oxyhydroxides crystallized in the studied soils from substrates leached due to dissolution of parent glauconites Presence of discrete kaolinite indicated likely occurrence of more advanced dissolution of primary glauconites.

Mössbauer spectroscopy indicated that nanocrystalline iron oxides were substantial products of glauconite weathering in all the studied clays. Goethite was the most common and abundant, lepidocrocite and perhaps ferrihydrite occurred in certain soil horizons. Formation of the Fe oxyhydroxides was controlled by hydrological conditions (and related redox activity) and by soil pH. Alkaline conditions favored goethite crystallization, whereas redox activity led to formation of lepidocrocite and likely ferrihydrite. Soil color was mostly controlled by the presence of glauconite. Only the relatively significant lepidocrocite content in few of the studied soil horizons was marked by brown or rusty colors indicating high redox activity.

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Silicate rock weathering and transformation to clayey soil material in cold regions

Sofia N. Lessovaia[1,*], Michael Plötze[2], Gennady Kopitsa[3,4], Tatiana Romanis[5]

[1]St. Petersburg State University, Universitetskaya nab., 7/9, St. Petersburg, 199034, Russia
[2]ETH Zurich, Institute for Geotechnical Engineering, CH-8093, Zurich, Switzerland
[3]B.P. Konstantinov Petersburg Nuclear Physics Institute NRC KI, Orlova roshcha, 1, Gatchina, 188300,Russia
[4]I.V. Grebenshchikov Institute of Silicate Chemistry RAS, nab. Adm. Makarova, 2, St. Petersburg,199155, Russia
[5]Melnikov Permafrost institute SB RAS, ul. Merzlotnaya, 36, Yakutsk, 677010, Russia

*s.lesovaya@spbu.ru

The research aim was to study the trends of rock weathering in the soil environment. The objects are located in the cold regions of Russia – the Ural Mountains and Siberia. They are represented by the shallow stony soils derived from and underlain by solid rocks that are sensitive to weathering, in detail (i) dolerite (traprocks of the Central Siberia Plateau) and (ii) dunite (the Polar Urals). The mesostructure data (structural parameters in the range 2–100 nm) and fractal properties of the rocks were investigated by the small angle neutron scattering (SANS) method. Quantitative mineralogical composition of the rocks' powders and the soil fine size fractions was determined with Rietveld analysis of XRD-data. The thin sections of soils and rocks' fragments sampled from the soil profiles were studied by optical microscopy. Based on SANS data the ultramafic rock can be seen as a mass fractal structure. That helps to explain the fact that dunite transformation to clayey material occurs throughout all sample volume. The olivine and serpentine proportions significantly decreased in the soils comparing with the rock. Whereas smectite(s) that was not identified in the rock itself has occurred in the soil horizons. Smectite is a result of olivine weathering (Eggleton, 1984) and/or serpentine transformation in the rock fragments from the fine earth. Oppositely, dolerite was characterized as an object with fractal-type surfaces. Dolerite weathering led to occurrence of loose rims on the rock fragments and accumulation of inherited smectite(s) in the soils. Thus, two pathways of the solid rock weathering and transformation to clayey material in the soil profiles were shown. Rock weathering occurs (i) mostly on the rock fragment surface and (ii) throughout all rock volume that resulted in considerable differences in the mineralogical composition of the soil and rock.

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Eggleton, R.A. (1984) Formation of iddingsite rims on olivine: a transmission electron microscope study. *Clays and Clay Minerals*, 32, 1–11.

New insight into biotite weathering in the subtropic Tongcheng granite regolith, Hubei province, south China

Shi Cheng[1,*], Hanlie Hong[1,2], Kaipeng Ji[1], Fan Li[3], Xinghong Wang[1]

[1]School of Earth Sciences, China University of Geosciences (Wuhan), Wuhan 430074, Hubei, China
[2]State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, China
[3]Anhui Institute of Geological Experiment, Hefei, 230041, Anhui, China

*chengshi@cug.edu.cn

Alteration of biotite during igneous rock weathering plays an important role in global geochemical cycle and formation of ion-adsorption type rare earth elements ore resources. In order to better understand the mechanism of mineral and geochemical processes during biotite weathering, alteration of biotite was investigated in the granite regolith in subtropical Tongcheng, Hubei province, south China, using X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), differential scanning calorimetry-thermogravimetry (DSC-TG), field emission scanning electron microscopic (FESEM), and high-resolution transmission electron microscopic (HRTEM) methods. Our results show that weathering of biotite synchronously produced randomly interstratified biotite/vermiculite (B/V) and halloysite, and the B/V clay partially decomposed to discrete vermiculite in the topsoil due to further weathering. B/V clays persist throughout the weathering profile with a limited vermiculite layer content of 4-18%. Vermiculitization of biotite and the formation of neoformed clay phases are induced by oxidation of Fe^{2+} in early stage, involving leaching out of K^+ and accumulation of hydrated Mg^{2+} and Fe^{3+} in the interlayer space of biotite precursor and thus displaying a solid-solid state transformation. The vermiculite components in B/V phaseare hydroxyl-interlayered vermiculite, and the neoformed halloysite is not expanded by formamide treatment, indicative of a dehydrated halloysite species. Halloysite exhibits two occurrences, *i.e.*, in tubular morphology growing on the edge surfaces of biotite or in well-oriented lath-like clusters forming on the basal surface of biotite crystals. The former crystallized from solutions, and the later formed from local leaching of Si-O sheets of biotite and subsequent *in situ* recrystallization. The parallel lath-like halloysite clusters occur in distinct extending directions with angles of ~30° and ~60°, respectively, resulting from the size misfit between the tetrahedron and octahedron of the crystal structure of biotite precursor. Thus, the formation of halloysite can be considered as a dissolution–precipitation process.

Hydrologic regulation on clay mineral transformation in a redoximorphic soil in subtropical monsoonal China

Lulu Zhao[1,*], Hanlie Hong[1], Qian Fang[2], Thomas Algeo[3]

[1]China University of Geosciences and Geology Wuhan -China
[2]Peking University, Department of Geology Beijing-China
[3]University of Cincinnati, Department of Geology Cincinnati, OH 45221, USA

*llzhao@cug.edu.cn

Clay mineral evolution in supergene environments is usually a complex process. Hydrologic variation can exert important influences on clay mineral transformations, yet these influences remain insufficiently investigated to date. A Quaternary red soil profile with evident redoximorphic features in subtropical monsoonal China was investigated with a focus on process and kinetics of secondary clay mineral transformations. Evidence provided by soil physical and chemical descriptions, clay mineral analysis, thermogravimetric and spectroscopic characterization, pedogenic Al and Fe extractions, and geochemical compositions suggested that the clay and iron phases and pedogenic weathering conditions were complex and vary as a function of depth in the studied soil profiles. The homogeneous surface horizon (HH; 0-2.0 m), the redoximorphic middle horizon (RH; 2.0-6.0 m), and the bottom layer (BL; 6.0-7.2 m) are dominated by various intermediate clay phases. The vermiculite group minerals are only detected in the HH, which has a progressive dominance of hydroxy-interlayered vermiculite (HIV) in the clay phases towards the surface. The HH is characterized by moderately acidic conditions (mean pH = 5.2), low organic content (TOC $\leq$ g kg^{-1}), and monsoonal climate with annually wet and dry cycles. More importantly, compared with the lower horizons, HH contains significantly more active acid-forming cations, as reflected by significantly more active Al phases (mean Al_o/Al_d = 0.66) and higher aluminum saturation percentage (mean Al/CEC = 2.9%). We suggest that the occurrence of the HIV is strongly related to the nature of the soil acidic pools, which include both H^+ ions (i.e., pH) and active acidic cations (e.g., Al^{3+} and Fe^{3+}). We further propose that the reaction pathway (weathering) from primary minerals, including the inherited minerals like illite, to final weathering products (e.g., kaolinite and Fe/Al-(hydr)oxides) are highly sensitive to the dynamic hydrological processes. The formation and alteration of the intermediate clay minerals are mainly regulated by the surrounding aqueous properties. Among them, the vermiculite group minerals are favored in generally oxic, well-drained soil systems with adequate acidic cations to maintain acidic weathering. If these soils were more water-logged and the aqueous solution was dominated by base cations, the primary minerals would tend to weather to smectite group minerals. Therefore, discrete smectite and interstratified kaolinite-smectite (K-S) were only observed in RH and BL. The kaolinite group minerals are favored over broad hydrologic and weathering scales. We, hereby present a novel framework that links clay mineral transformation processes driven by varying hydrological conditions, providing new insights to understand the kinetics of water-mineral interactions in a natural soil system.

Decoding pedogenesis process at flow contacts of Deccan Volcanic Provinces, by clay mineral characterization

Piyush Sriwastava[1,*], Veer Vikram Singh[1], Toshihiro Kogure[2], George Mathew[1], Sher Singh Meena[3]

[1]Department of Earth Sciences, Indian Institute of Technology Bombay, 400076, India
[2] Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, 113-0033, Japan
[3] Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India

*piyush.ks@iitb.ac.in

Large igneous provinces consist of several volcanic flows that erupted at different times. Each flow top interacts with the climate until the next flow covers them. Hence Flow contact may preserve the signature of incipient pedogenesis. Sometime upper flow may obliterate the signatures of pedogenesis. In Deccan volcanic provinces, flow contacts are often represented by colored clay-rich beds, called bole beds. This study aims complete characterization of clays from bole beds of Deccan Volcanic Provinces (DVP) and proposing possible mechanism of origin.

Bole beds are either red, green or brown in color. Clay fraction of <0.6 µm has been characterized. In XRD, some bole beds show dominantly smectite 001 peak (*d*~14-16Å), while the others are associated with celadonite (*d*~10Å) or kaolinite (*d*~7Å). Hematite and ilmenite are associated with red boles but green and brown boles are lacking in hematite but richer in ilmenite. STEM-EDS shows smectite octahedral sheet composition $Al_{1.12}Fe^{+3}_{0.56}Mg_{0.32}$ with 27% tetrahedral layer charge in red boles consists both smectite and celadonite, and $Al_1Fe^{+3}_{0.6}Mg_{0.4}$ with 48% tetrahedral layer charge in red boles consists only smectite. Brown bole has smectite clay octahedral sheet composition $Al_{0.86}Fe^{+3}_{0.76}Mg_{0.38}$ with 50% tetrahedral layer charge. All smectites can be classified as beidellitic montmorillonite. Green-colored boles shows dominantly smectite and celadonite with hematite (small amount) and ilmenite (Fig. 1). Smectite is dioctahedral with octahedral sheet composition $Al_{0.82}Fe^{+3}_{0.88}Mg_{0.30}$ and 44% tetrahedral layer charge.

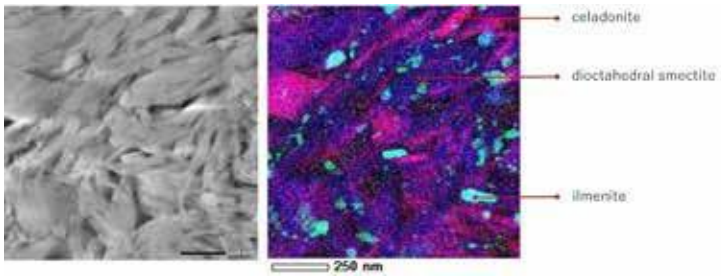


Fig. 1. (Left) STEM-HAADF image of Green-colored bole clay. The clay of <0.6 µm in size was collected and pressed to a pellet. Then a thin film was prepared using FIB for the TEM observation. (Right) Mixtured STEM-EDS maps with K (red), Fe (blue) and Ti (green).

Bulk TGA analysis of all red and green boles clay has given a dihydroxylation peak temperature (T_{DHX}) <550°C, indicating dominantly *trans*-vacant smectite. This type of octahedral sheet growth is preferred in a higher temperature condition. But variation in clay mineral assemblage and their textural relation is being investigated using FIB sections of boles grain. This study will enable to infer possible processes happened at different time.

Investigating the effects of electron shuttle induced redox cycling on Fe-bearing clay mineral reactivity and structure

Harry J. L. Brooksbank, Anke Neumann*

Newcastle University, School of Engineering, Newcastle upon Tyne, NE1 7RU UK

*anke.neumann@ncl.ac.uk

The Fe(III)/Fe(II) redox couple plays an important role in the cycling of nutrients and the fate of contaminants in the Critical Zone. A range of Fe-bearing minerals has been investigated upon initial formation or reduction of their structural ferric iron (Fe(III)) to ferrous iron (Fe(II)) but less work has focused on how multiple cycles of reduction and oxidation might impact the long-term performance of Fe-bearing minerals in the Critical Zone, where redox conditions fluctuate over time. In this context, Fe-bearing clay minerals are of particular interest as their structural Fe is resistant to reductive dissolution due to the surrounding silicate framework. Hence, clay mineral Fe has been suggested to be a renewable source of electron equivalents in subsurface environments, which can be redox-activated by a range of naturally occurring processes and reductants, including microbial activity. However, the use of microorganisms in laboratory experiments requires additional solutes to enable metabolism (e.g. trace elements, nutrients in the growth medium) and results in the formation of poorly characterized organic byproducts such as extracellular polymeric substances (EPS) or electron shuttles, which are either ignored for their function or even added to increase mineral Fe reduction extent. Here, we investigate how microbially produced electron shuttles affect clay mineral Fe reactivity and structure over three consecutive cycles of reduction and re-oxidation.

We used the commonly applied electron shuttle anthraquinone-2,6-disulfonate (AQDS), which was electrochemically reduced to anthrahydroquinone-2,6-disulfonate (AH_2DS). We then subjected the high Fe content clay mineral (NAu-1) to three subsequent cycles of reduction with AH_2DS and oxidation with hydrogen peroxide. We confirmed quantitative electron transfer from AH_2DS to clay mineral Fe by combining UV-vis quantification of AH_2DS oxidized and Mössbauer spectroscopy derived measurements of clay mineral Fe reduced. Clay mineral Fe reduction extents were consistent across the three redox cycles and amounted to 9-10% Fe(II)/Fe(total), despite significant excess of the reductant AH_2DS remaining in solution. These results suggest that clay mineral Fe reduction by the AH_2DS/AQDS redox couple thermodynamically limited. Subsequently, we assessed mineral reactivity by monitoring the reductive degradation of our reactive probe compound 3-chloronitrobenzene (3ClNB). Analysis of 3ClNB degradation kinetics showed no significant changes over the cycles of reduction and re-oxidation, neither in rate constants nor reactive site distribution. Particle size analysis and Mössbauer spectroscopy both corroborate these findings, as they, too, showed no significant changes in overall morphology and structural Fe binding environment. Our combined results suggest that clay mineral Fe in conjunction with microbially produced electron shuttles can indeed function as a renewable source of redox equivalents for contaminant and nutrient cycling in the Critical Zone.

Formation of palygorskite in the soil - calcrete profiles of the contemporary and past Mediterranean region controlled by the Quaternary paleoclimate

Selahattin Kadir[1,*], Claudio Zucca[2], Selim Kapur[3], Muhsin Eren[4], Asuman Günal Türkmenoğlu[5] , Erhan Akça[6], Amir Sandler[7], Salvatore Madrau[2]

[1]Eskisehir Osmangazi University, Department of Geological Engineering, TR-26040 Turkey
[2]University of Sassari, Dipartimento di Agraria Viale Italia 39, 07100 Italy
[3]Çukurova University, Departments of Soil Science and Archeometry, TR-01330 Turkey
[4]Mersin University, Department of Geological Engineering, TR-33343 Turkey
[5]Middle East Technical University, Department of Geological Engineering, TR-06800 Turkey
[6]Adıyaman University, School of Technical Sciences, T R- 02040 Turkey
[7]Geological Survey of Israel, Ministry of National Infrastructure, Jerusalem 95501, Israel

*skadir.icc@gmail.com

Palygorskite in the soil-calcrete profiles is a widespread pedogenic occurrence in contemporary arid and semi-arid climatic zones of the Mediterranean region. The pedogenic palygorskite in this region has different origins including alteration of smectite and transformation to palygorskite under saline and alkaline conditions via either dissolution-precipitation mechanism, precipitation from soil water or groundwater, or detrital deposition from Saharan dust. This study aims to compare the micromorphological characteristics and genesis of palygorskite in soils and calcretes in different Mediterranean regions, namely in Turkey, Israel, Hungary, Italy, and Morocco. The palygorskite-calcrete succession of southern Turkey (Adana and Mersin region) is associated with Quaternary soft to hardpans and laminated crusts occurring in this region in a variety of forms at the upper part and nodules and/or tubes at the lower part as the columnar horizon. In this context, palygorskite fiber and fiber bundle crystals developed authigenicaly on calcite crystals and at the edges of smectite flakes in the calcrete host-rocks. The palygorskite from Nava Zavo'a within a Turonian subaerial event in Israel represents a thin continental stratigraphic unit embedded within a thick shallow marine Cretaceous carbonate sequence where a calcrete was developed in the paleosol profiles exhibiting high pedogenic maturity and neoformed wool-like stacked palygorskite accumulations. The rare and individual palygorskite crystals, that precipitated in the rhombohedric matrix of the legendary Akhtar soil calcrete in Hungary, is the evidence of the changing environment since the end of the last ice age (~ 10000 years ago). The palygorskite-calcrete profiles in Italy (Alghero, north-western Sardinia) is a buried palaeosol of a Late Quaternary succession with climatic pulses highlighted during the Eemian. This calcrete soil is similar to the palygorskite-calcrete succession in southern Turkey but differing by a diffuse columnar horizon containing moderate amounts of neoformed palygorskite and smectitic coatings. The unique Quaternary calcareous crusts of the Al Haouz region in Morocco are widespread on surface sedimentary units and composed of abundant calcite associated with palygorskite, minor quartz, illite/ mica, feldspar, and chlorite. Palygorskite occurs as fibers, fiber bundles, and networks grown on and/or enclosing calcite rhombs in both the Italian and Moroccon calcrete sites. Consequently, the development of the authigenic long fiber and fan-shaped fiber bundle palygorskite in Israel and in Turkey compared to those in Hungary, Italy and Morocco reveal supersaturated evaporitic and progressive aridization environmental conditions in the eastern Mediterranean region compared to those of the western regions.

TS05 + TS24 Pedogenic Clays

POSTER PRESENTATIONS

Clay mineralogy and geochemistry of upper Jurassic bauxites and their immediate cover, Istria, Croatia

Ivor Perković*, Darko Matešić, Goran Durn

Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb 10000, Croatia

*Ivor.Perkovic@rgn.unizg.hr

This study was focused on the paleoclimate and paleoenvironmental reconstruction of the bauxites formed during the early Kimmeridgian to the late Tithonian emersion phase in the succession of the Western Istrian anticline. They are especially interesting because they contain three types of bauxites: red bauxite, grey bauxite, and white bauxite. Their footwall consists of porous limestones of the Muča unit, and they are capped with the cyclic alternation of clays, marls, emersion breccias and schizohaline limestones, which are gradually replaced with the marine limestones of the Kirmenjak unit, as the transgression progressed. The emphasis of this study was on the mineralogy of the bauxite, and the overlying clays, especially. Mineralogical analysis was principally based on the XRD measurements of the bulk samples and <2μm fraction. We also wanted to relate the differences and trends of trace and rare earth elements with the mineralogy of clays and other phases in the bauxite. For this purpose, several samples of bauxite were selected for the XRF and ICP-MS analysis. The red bauxite is principally composed from hematite, boehmite and kaolinite, with variable amounts of dioctahedral chlorite, illite, rutile, anatase and goethite. The grey bauxite has a similar composition, but with pyrite instead of hematite. The white bauxite is devoid of iron minerals. Trace elemental patterns are concordant with the absence or presence of different iron phases. Rare earth elements seem to be fractionated differently in different sections of the bauxite body, with the enrichment in heavy rare earth elements and a positive cerium anomaly in the topmost section, and the enrichment in middle and light rare earth elements in the lower sections of the profile. This is likely a consequence of increased leaching of the topmost section of the bauxite during its formation, which is confirmed with higher concentrations of immobile components in the upper section, such as Al_2O_3, TiO_2 and lower concentrations of leachable SiO_2. Although there were no significant differences in clay mineralogy between different bauxite types, the clay mineralogy of overlying clays differs significantly from that of the bauxites. The clay beds overlying the bauxite are composed from dioctahedral vermiculite, kaolinite, illite and a mixed-layer clay mineral (MLCM) consisting of illite and dioctahedral 14 Å phyllosilicate. They display an apparent gradual increase in illite, with respect to kaolinite, towards the upper sections of the profile. This most likely signifies a progressive climate change towards a more temperate climate, as the weathering mode on land gradually shifted from monosialitization towards bisialitization. A certain portion of illite and MLCM could have originated from the fixation of K^+ from more potassium-rich marine waters. This coincides well with the blue-hole sequence model which has been proposed for the mode of transgression that followed the deposition of bauxite, as this leads to more increased marine influence as the transgression progresses.

Clay mineralogy in soils formed on Miocene marls and Plio-Quarternary sediments in temperate climate

Zvonka Gverić[1]*, Nenad Tomašić[1], Marta Kisiel[2], Katarzyna Maj-Szeliga[2], VedranRubinić[3]

[1]University of Zagreb Faculty of Science, Department of Geology, 10 000 Zagreb, Croatia
[2]Jagiellonian University, Institute of Geological Sciences, 30-387 Kraków, Poland
[3]University of Zagreb Faculty of Agriculture, Department of Soil Science, 10 000 Zagreb, Croatia

*zgveric@geol.pmf.hr

Four soil profiles developed on Miocene marls and two soil profiles developed on Plio-Quarternary (PlQ)molasse-type proluvial and fluvial-lacustrine sediments have been investigated at the foothills of Mt. Med- vednica (Croatia). Soils that formed from both sediments were found to be genetically young, consisting only of the topsoil and the transitional horizon overlying the parent material (A-AC-C profile). The aim was to study clay mineral composition of the soils developed on different parent materials and to establishthe major processes determining clay minerals occurrence within the soils.

Clay minerals were determined by XRD (<2 mm and <2 μm fractions) and FTIR (<2 μm fraction). Fraction <0.2 μm was additionally separated from the PlQ profiles to analyze its clay minerals composition inmore detail and to measure the layer charge of swelling clays using O-D method proposed by Kuligiewiczet al. (2015).

It was determined that the clay mineralogy of marls consists of mixed-layered smectite-rich illite- smectite, illite, kaolinite, vermiculite, and trace of chlorite, while the one of PlQ sediments consists of smectite,vermiculite, kaolinite, and illite. The observed changes in clay mineralogy within soil horizons (compared to the underlying parent material) include a) the appearance of mixed-layered chlorite-vermiculite in soilson marls and b) the appearance of HIMs and the increased content of vermiculite in soils on PlQ sedi- ments. Layer charge measurements show and increasing trend towards topsoil in PlQ profiles (from 0.61 and 0.50 p.f.u. measured for the parent material to 0.66 and 0.59 p.f.u. in topsoil, respectively), confirmingthat the high-charge swelling clay minerals are more abundant in the soil than in the parent material.

The results show that the main process responsible for the clay mineralogy of the analyzed soils is inheritance. However, indication of early stages of clay minerals (trans)formation processes is reflected in the occurrence of mixed-layered chlorite-vermiculite in soils developed on marls, and hydroxyl-interlayered phases, as well as increased content of vermiculite in soils developed on PlQ sediments.

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Characterization of clay minerals in the soil around Fukushima contaminated area, Japan

Shun Ebisawa , Toshihiro Kogure*

Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, 113-0033, Japan

*kogure@eps.s.u-tokyo.ac.jp

A significant amount of radiocesium (RCs) was released into the environment by the Fukushima nuclear accident in March 2011, causing radioactive contamination of soil mainly around the region toward north- west of the nuclear power plant. Owing to the high radiation dose, habitation and agriculture in this region are still inhibited. On the other hand, the concentration of RCs in the groundwater and river water in this region is extremely low, which suggests that RCs is strongly fixed to specific clay minerals in the surface soil. Hence, deep understanding of soil-forming clay minerals developed by the pedogenic process in this area is required for further researches to solve the contamination problem. In this paper, we report detailed characterization of clay minerals comprising surface soils in this region using XRD and SEM/TEM, and discuss their origins.

Geology of this area is granite or granodiorite of Cretaceous period (120Ma ~90Ma), which forms a hilly geography. Generally thick weathered-granitic sand covers the original rock and surface soil of up to 1 m in thickness has been developed with vegetation on the sand. Coarse weathered granitic sand contained partially to fully-vermiculitized biotite ("weathered biotite") abundantly. Our previous works indicated that the weathered biotite is a major RCs-fixing mineral in this region (Mukai et al., 2014, 2016, Kikuchi et al., 2015). However, the weathered biotite was considerably kaolinitized and almost not detected in the XRD pattern of surface soils in several areas. On the other hand, the XRD pattern from the soils showed a rather broad 14 Å peak. Examination of the 060 peak region suggested that this mineral is a dioctahedral 2:1 phyllosilicate. The 14Å peak did not change with EG treatment and not completely shift to 10 Å until 500°C in *in-situ* XRD analysis. TEM/STEM analyses showed that the mineral grains corresponding to this phase consist of almost equal amounts of Si and Al, and frequently contain a small amount of K. In the 00*L* reciprocal row, the basal reflection was at ca. 13 Å but higher-order reflections were not regularly positioned, indicating a mixed-layer structure. From these results, we conclude that the mineral phase is similar to so-called hydroxyl-interlayered vermiculite (HIV), which was suggested as an effective Cs- fixer (Goto et al., 2014).

Besides, XRD and TEM analyses indicated the existence of illite and chlorite as other 2:1 phyllosilicates in the soil. These minerals are probably originated from eolian dusts from China. The northern limit of the contaminated region partly consists of Neogene basalt and saponite was found probably as a weathering product of the basalt.

Fired shards from selected ancient Anatolian ceramics: a brief review of their mineralogical nature and pedological-microstructural evolution

Selim Kapur[1]*, Selahattin Kadir[2], Gilbert Kelling[3], Erhan Akça[4], Mustafa Topaksu[5], Necdet Sakarya[6], Zehra Yeğingil[5], Muhsin Eren[7]

[1]Çukurova University, Departments of Soil Science and Archeometry, TR-01330 Turkey
[2]Eskişehir Osmangazi University, Department of Geological Engineering, TR-26480 Turkey
[3]University of Keele, School of Geography, Geology and Environmental Science, UK
[4]Adıyaman University, School of Technical Sciences, TR- 02040 Turkey
[5]Çukurova University, Department of Physics, TR-01330 Turkey
[6]Çukurova University, Department of Ceramics, TR-01330 Turkey
[7]Mersin University, Department of Geological Engineering, TR-33343 Turkey

*kapurs@cu.edu.tr

This review is concerned with some key features observed within ancient ceramics that provide important evidence concerning the selection of appropriate raw materials and the evolution of the firing technologies employed in their production. It also demonstrates the importance of distinguishing and accounting for the mineralogical attributes and microstructural evolution processes of these ancient ceramics. The mineralogy largely reflects both the nature of the raw materials used and the maximum temperatures achieved during firing to produce specific high temperature minerals (HTMs). The microstructural evolution processes determined by micromorphology, as displayed in specific features, observed in the matrix and slip, are largely controlled by the firing methods used in manufacturing**.** Thus, the application of micromorphological principles, methods and observations derived from the sphere of "pedology", to the study of ancient ceramics most likely seems to provide valuable insights into the independent evolution of ceramic production methods in ancient societies. Many of the observations recorded here concern the ancient raw materials and firing processes used in their manufacture and demonstrate that these ancient potters made use of a variety of temper materials (quartz and chaff, together with fragments of locally available rocks and minerals) that are now present in the matrix. Furthermore, analyses of the micromorphological attributes displayed by these ancient ceramics are helpful in determining and explaining the shrinkage features (stress coatings or poro-striated b-fabrics) and the preferred orientation of the elongated pores that have developed after firing in controlled and slow-fired furnaces. Post-burial processes, such as the illuvation-deposition of the clay minerals, i.e., the clay coatings, probably indicated the Mid-Late Holocene climatic fluctuations as wet-dry cycles. The calcification-decalcification process, which may be due to an intra ceramic leaching-deposition of the local carbonate present in the source material of the pottery, may also be in line with the wet-dry cycles of the mid to late Holocene pedogenesis (soil formation) reflected by the clay coatings and the faunal activity.

Mineralogy and geochemistry of the paleosol sequences in Milas-zlce (SW Turkey

Merve Gülcan*, **Ceren Küçükuysal, Murat Gül**

Muğla Sıtkı Koçman University, Department of Geological Engineering, 48000 Muğla

*mervegulcn.93@gmail.com

This study aims to characterize the mineralogical, geochemical, and micromorphological properties of the paleosols in Milas and Özlüce regions, Muğla, SW Turkey and to evaluate the proxies to refer to the past climatic conditions of the Late-Miocene-Early Pliocene. Two different sites were selected in Muğla to define the paleosol sequences. The Milas section with 7.15 m depth consists of 3 distinct paleosols and white-colored tuff units resembling the Özlüce section with similar paleosol and tuff layer features. The common field criteria for both sections are the sharp contact between the paleosol levels and the overlying tuff units. A subangular blocky structure is another common feature of the paleosols of both sections.

Experimental works define the clay and non-clay minerals and geochemical compositions of the samples taken from both sections. Whole-rock mineralogical investigations reveal the presence of quartz, calcite, dolomite, and feldspar for both paleosol sequences. Hematite is defined as the main reddening agent of the paleosols. Clay minerals are dominantly smectite and illite with kaolinite and chlorite.

Molecular weathering ratios are used to interpret the chemical weathering intensities at the time of soil formation. For the Özlüce section, the salinization values are less than 2 (between 0.01 and 0.86%); calcification values fluctuate in a wider range (0.09-5.51%) in coherence with salinization. Clayeyness does not show remarkable shifts but the calculated values are greater than 0.3% (0.50-0.71%). Mean annual precipitation (MAP) values fall in a range of 300 to 1000mm/year. All these climofunctions refer to a low intensity of evaporation and low to moderate humidity. For the samples of the Milas section, salinization values are calculated between 0.04 and 4.95%. Except for the old paleosol-bearing level at the bottom of the section, the salinization and calcification values are less than 1. The calculated clayeyness values fall in a range of 0.32 - 1.53%. On the other hand, MAP values fluctuate within a wider range between 100-1000 mm/year, pointing low to moderate humidity.

The paleoclimate proxy data strongly mark the warm and humid climates with intensified chemical weathering and development of red-brown colored, hematite-bearing paleosols in Muğla during the Late Miocene-Early Pliocene. The findings of this study show a very good correlation with the Late Miocene- Early Pliocene warming and can be concluded to carry the fingerprints of this global warming event (Gülcan, 2020).

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Preliminary findings on the field occurrences of calcretes in a palaeosol section of the Karacadağ volcanics (Diyarbakır, SE Turkey)

Ceren Küçükuysal[1], Felat Dursun[2], Murat Gül[1], Tuğçe Akbulak[1]*, Oğuzhan Çamcı[1]

[1]Muğla Sıtkı Koçman University, Department of Geological Engineering, 48000 Muğla, Turkey
[2]Dicle University, Department of Mining Engineering, 21280 Diyarbakır, Turkey

*tugceakblk123@gmail.com

One of the known global climatic phenomena of the Quaternary is the Middle Brunhes Event that happened during the mid-Pleistocene (EPICA, 2004). This warming triggered the accumulation of calcium carbonates in terrestrial deposits along the Mediterranean, especially in Anatolia. The Quaternary-aged Karacadağ volcanics show intercalations with paleosol-calcrete sequences. The Karacadağ volcanics have long been studied in different aspects; however, little is known about their intercalations with paleosols. To unlock the paleoclimatic archive of these paleosol-calcrete sequences and to address the Mid-Brunhes Event, the first step is the identification and characterization of the calcrete occurrences of the paleosol sequences. A representative section was selected from the southern part of Diyarbakır province along a roadcut where a calcrete-bearing red-colored paleosol section is overlain by a basaltic flow.

Two dominant morphotypes of the calcretes are identified in this buried soil/paleosol section: nodular and laminated. Both are indurated. Nodular calcretes are rounded, subspherical to spherical concretions having a size range of 5x7 cm to 15x25 cm. Nodular calcretes occur mostly as isolated bodies; however laminar calcretes are connected in a way to align horizontally and vertically. Nodular calcretes dominantly have smooth surfaces with rare droplet forms at the bottoms. All nodules of calcretes exhibit concentric fabric. Munsell colors of the calcretes are mostly between the hue values of 5-7.5 Y (with one having 10YR). Nodular calcretes are classified as semi-mature; while laminar ones refer to mature stages (Wright and Tucker, 1991). From the bottom to the middle of the section, both laminar and nodular calcretes are dominant; however, starting from the middle to the top of the section, laminar calcretes become the major morphotype. Faunal and floral passages filled by manganese dioxide coatings are recognized on laminar calcretes; while nodular calcretes show desiccation cracks dominantly.

Nodular and laminar calcretes of this paleosol sequence found in Karacadağ volcanics are important indicators of arid to semiarid climatic conditions and therefore, would be the proxy providers to assess the relationship between the formation of calcretes and the Mid-Brunhes Event.

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Characterization of granular weathering (grus products in the southern part of the Çine submassif: preliminary results

Ceren Küçükuysal[1*], Murat Gül [1], Merve Gülcan[1], Göksu Uslular[1,2,3]

[1]Muğla Sıtkı Kocman University, Department of Geological Engineering, 48000 Muğla, Turkey
[2]University of Geneva, Department of Earth Sciences, Rue des Maraichers 13, 1205, Geneva, Switzerland
[3]TÜBİTAK Marmara Research Center, Polar Research Institute, 41470 Gebze-Kocaeli, Turkey

*cerenkucukuysal@mu.edu.tr

Subsurface weathering and subsequently surface weathering developed as a product of coarse-grained crystalline rocks in temperate regions are referred to as grus. Among the major factors affecting the characteristics and intensity of grus; topography, parent rock, and climate appear to play key roles. Weak chemical decomposition but intense degradation along the microcracks and expansion of biotites are the major processes during the formation of grus (Kajdas et al. 2017). Weathering product of metagranites (orthogneiss) in Çine Submassif (southwest Turkey) is proposed to be very representative of grus. Within the scope of this study as a part of an ongoing project, the granular weathering products/profiles in the northern part of the Yatağan (Muğla) district of the Çine Submassif are investigated to reveal the mineralogical compositions of both bulk and clay fractions (<2 mm) of the grus samples.

Bedrocks of gneiss, meta-granite, and leucogranite are the main lithologies of the submassif in the proximity of Gökbel Mountain along the Yatağan-Çine highway. Grus with variable thicknesses observed around structures like tor, split, and blocks together with weathering profiles were sampled. Changes in the transparency of primary minerals like quartz and feldspars, oxidation of micas, and spheroidal weathering patterns are the main field characteristics regarding the weathering intensity. The sediments including moderately sorted, medium-coarse grained, sand-size materials are alternated with poorly sorted gravels in the grus profile. Grus was observed as a 0-10 cm cover on host rock, 1.5 m thick profile in the valley. Bulk mineralogical compositions of the grus samples consist of quartz, cristobalite, pyroxene, K-feldspar, plagioclase, and clay minerals. Minerals of clay fraction are dominantly of illite (>80%) in association with kaolinite and chlorite; however very rare smectite.

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TS06 Clays and Contaminant Control

ORAL PRESENTATIONS

Designer Ag@clay nanocomposites for ultrasensitive surface-enhanced Raman scattering detection

Chun Hui Zhou[1,2,*], Chao Peng Fu[1]

[1]Research Group for Advanced Materials & Sustainable Catalysis (AMSC), College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China

[2]Qing Yang Institute for Industrial Minerals, Qingyang, Anhui, 242804, China

* smectman@126.com

Clay, such as laponite (Lap), has been used as a template to induce the growth of metal nanoparticles (NPs). The synthesized metal@clay nanocomposites exhibited great scattering enhancement for surface-enhanced Raman scattering (SERS) assay. However, the morphology of metal NPs was uncontrolled (Eric et al., 2016), which would affect their SERS activity.

Here, a newly-discovered clay-surfactant-Ag^+ materials can be developed and used to prepare uniform spherical Ag@laponite (Ag@Lap) nanocomposites for ultrasensitive SERS analysis. Sodium dodecyl sulfate (SDS), an anionic surfactant with negatively charged headgroup and alkyl tail (Huibers 1999), acts as a charge bridge to connect the positively charged edge of Lap and Ag^+ via electrostatic interaction, forming a bridging nanostructure of Lap-SDS-Ag^+ nanomaterials to promote the uniform dispersion of Lap NPs. When Ag^+ was reduced to Ag^0 by glucose, it grows on the surface of disc-like Lap NPs with template effect to form uniform spherical Ag@Lap nanocomposites. The prepared Ag@Lap nanocomposites showed an ultrasensitive SERS response to methylene blue with a detection limit as low as 10^{-12} mol/L. Such functional nanostructured materials with tunable particle size have good potential in environmental, biological, and medical applications. Also, this work provides broader implications for the study of other types of clays, such as montmorillonite.

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Preparation and characterisation of Iron-based Bentonite-Chitosan composites for Arsenic (III) adsorption

Hassan Majiya[1, 2,*], **Francis Clegg**[1], **Chris Sammon**[1]

[1]Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield, S1 1WB, United Kingdom

[2] Ibrahim Badamasi Babangida University, Lapai-Nigeria

[*]b7040316@my.shu.ac.uk

Contamination of water sources with toxic arsenic (As) is a serious global environmental problem. Therefore, its removal is of fundamental importance in both the developed as well as developing worlds to protect the environment and ensure the wellbeing of their populations. Composites made from geological materials (such as clays) and biodegradable polymers seems to be promising adsorbent for the removal of toxic metals from water. However, the preliminary experimental work has demonstrated that the unmodified Bentonite-Chitosan (Bt-Ch) composites show a poor removal efficiency towards As (III) ions. In that regard, Iron-based Bentonite-Chitosan (Fe-Bt-Ch) composites were prepared and subsequently tested as an adsorbent for the removal of As (III) ions from aqueous solutions. The synthesised composites were characterised by thermogravimetric analysis, X-ray diffraction, and Fourier transform infrared spectroscopy. Batch adsorption procedures and statistical design of experiments were used to study the factors affecting the removal of As (III) ions from aqueous solutions. The composite modified with Fe (III) proved to be a better adsorbent compared to the unmodified counterpart. The adsorption of the As (III) onto Fe-Bt-Ch composites follows the pseudo-second-order kinetics and it is well described by the Elovich kinetic model. Also, the adsorption experimental data correlated well with Langmuir, Freundlich and Dubinin-Radushkevich isotherm models. The Langmuir-maximum adsorption capacities of As (III) ions estimated for Fe-Bt-Ch composites exceeded the adsorption capacities of the individual precursors. According to thermodynamic results, the adsorption process can proceed spontaneously and occur exothermically. Adsorption mechanism, regeneration studies of adsorbents (Fe-Bt-Ch composites), and selectivity towards As (III) adsorption were all investigated.

Mesoporous architecture magnetite nanoparticles loaded halloysite nanotubes biopolymer hydrogel beads for efficient removal of streptomycin

Amal Kanti Deb[1,2,*], Mohammad Mahmudur Rahman[1], Bhabananda Biswas[1], Yunfei Xi[2], Ravi Naidu[1]

[1]GCER, The University of Newcastle, Callaghan, NSW 2308, Australia
[2]ILET, The University of Dhaka, Dhaka 1000, Bangladesh
[3]School of Chemistry and Physics, QUT, Brisbane, QLD 4001, Australia

[*]amal.deb@uon.edu.au

Streptomycin (STR), although classified as "highly toxic" for aquatic biota, is the most common antibiotic that is extensively prescribed to treat various infectious diseases for humans and animals (Petrie et al., 2015). While removing STR from water is essential, clean-up efficiency relies on technologies utilised, with one such technology being materials that adsorb STR. Here, we developed magnetic halloysite (Fe_3O_4@HNT) hydrogel beads (SPHM) for STR removal from water.

SPHM was produced by dissolving Fe_3O_4@HNT into the mixture of sodium aligiante and polyvinyl alcohol at 50 °C for 6 h, then drop-casted into $CaCl_2$ solution. SPHM was characterised by SEM-EDS, BET and XRD analyses. Batch adsorption was studied at 25±1 °C and spectrophotometric technique was used to determine the concentration of STR.

SPHM (1-2 mm size) shows porous structure under SEM (Fig. 1a-d) with average porosities of 6.27 nm, indicating the mesoporous surfaces of the material. EDS analysis shows the well distribution ofelemental composition of SPHM (Fig.1e). XRD data also confirms the crystalline structure of Fe_3O_4@ HNT. Adsorption results support Pseudo-second-order (PSO) and Langmuir models (R^2=0.99 in both cases), implying that the chemisorption occurred over the porous surfaces of SPHM (Fig.1 f, g). SPHM exhibits much higher adsorption capacity (235.70±13.97 mg/g) than Fe_3O_4@HNT (30.84±3.04 mg/g) at optimum pH 5.6 (Fig. 1h).

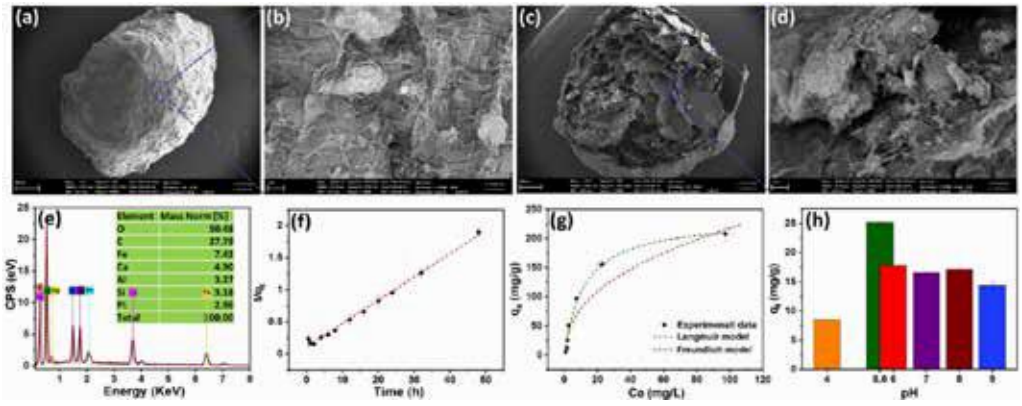


Figure 1. (a-b): SEM images of SPHM, (c-d) Cross-sectional images, (e) EDS elemental composition of SPHM, (f) PSO kineticsmodel, (g) Langmuir and Freundlich models, and (h) STR sorption at various pHs.

SPHM hydrogel is a potential material for streptomycin removal. Moreover, SPHM is biocompatible, low cost, easy to handle and fast magnetically separable, which signify its viability in the bulk treatment of pharmaceuticals wastewater.

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Surfactant intercalated smectite group minerals: the effect of host mineral and surfactant type on the styrene adsorption/desorption

Jakub Matusik*, Anna Koteja-Kunecka, Paulina Maziarz, Anna Kunecka

AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, al. Mickiewicza 30, 30-059 Krakow, Poland

*jmatusik@agh.edu.pl

Styrene is considered as one of the most important industrial chemical belonging to volatile organic compounds (VOCs). It is widely used in the production of e.g.: polystyrene, polyester resins, rubber, and fiberglass. Due to its toxicity it is considered as dangerous even at very low concentration. Therefore,effective removal techniques of styrene alternative to adsorption by activated carbons must be constantlydeveloped.

In our study the styrene adsorption/desorption efficiency by surfactant-modified smectites was evaluated (Matusik et al., 2022). For that, 3 smectite-rich samples were selected: montmorillonite from Wyoming (SWy), montmorillonite from Texas (STx) and beidelite from Idaho (BId). The samples were modified with 6 cationic surfactants (quaternary ammonium salts) differing in head group type and alkyl chain length.

The modified materials showed a remarkable styrene uptake at 40-50%±5% relative humidity (RH). In most cases the uptake was much higher than observed for commonly used activated carbons. The research indicated the importance of specific surface area (S_{BET}) and cation exchange capacity (CEC) of the host minerals. A high S_{BET} was crucial for the STx sample which also had a high CEC (~68.9 meq/100 g). However, effective adsorbents were also based on BId sample which had a lower CEC (~37.8 meq/100 g). In this case a lower charge resulted in lower density of intercalated surfactants. This provided more space for styrene molecules and limited the steric effects. The surfactant to CEC ratio close to 1.0 was optimal for the highest adsorption. This was due to sufficient hydrophobization of mineral surfaces and expansion of the interlayer space. The highest styrene uptake was noticed for smectites intercalated with surfactants having a long alkyl chain. A bulky benzyl head group lowered the adsorption due to steric hindrance. Raman spectroscopy confirmed styrene polymerization after subsequent adsorption/desorption cycles. This led to a significant swelling of the organosmectites attested by XRD and resulted in an increasing styrene uptake in subsequent cycles. However, it also inhibited the styrene desorption and the adsorbent regeneration. The research also indicated the negative impact of high humidity (80%±5%) which significantly lowered the adsorption by organosmectites as well as activated carbon. Thus, the application of adsorbents for styrene removal must be accompanied with strict humidity control.

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Superparamagnetic stevensite for easy removal of tetracycline in open aqueous media

Andrea Snchez-Monedero[1,2], Ana I. Ruiz[2], Pilar Aranda[1,*]

[1]Instituto de Ciencia de Materiales de Madrid (ICMM), CSIC, 28049, Madrid, Spain
[2]Facultad de Ciencias, Universidad Autnoma de Madrid, 28049 Madrid, Spain

*pilar.aranda@csic.es

In recent years there are numerous studies related to the elimination of the so-called emerging pollutants, being probably one of the most relevant group the one dealing with drugs, such as analgesics, anti-inflammatories, antibiotics, etc., which are found in increased concentration in wastewater. Amongst these contaminants are tetracyclines, as it turns out to be the antibiotic most frequently used in livestock but, so far, wastewater treatment plants do not have a process to eliminate them effectively. Amongst the diverse technologies explored to remove tetracycline from water, the use of clay minerals (montmorillonite, kaolinite, rectorite, palygorskite, sepiolite,...) as adsorbents has been deeply explored, being of particular interest the use of a certain stevensites due to the speed and efficiency of the adsorption processes (Cuevas et al., 2019). The main problem the use of this type of material presents is that it has to be incorporated to filtration columns due to the difficulty of collecting it from the water after the adsorption process. In this context, the present work will explore the modification of a commercial product named Minclear N100TM (Tolsa S.A., Spain), which is a raw mineral rich in stevensite (>90%), to produce a superparamagnetic material by incorporating magnetite nanoparticles (NP) that can facilitate its separation from the aqueous medium. Two types of modification, use of a ferrofluid (Ruiz-Hizky et al., 2010) and direct formation of NP in the presence of the clay (Darder et al., 2014), were explored to produce superparamagnetic materials with different NP content. The results show that the most effective material is the one prepared by using a ferrofluid, since it presents the sought-after properties of superparamagnetism, without excessively reducing the tetracycline adsorption capacity. Column retention tests confirm that the retention of tetracycline is slightly higher in the unmodified product, although its effective and rapid removal from the medium is only possible in the case of the material that incorporates the NP, confirming it as an effective system to be used directly in open water.

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Clay mineral-based composites for aqueous organic compounds removal

Agnieszka Solińska*, Tomasz Bajda

Department of Mineralogy, Petrography and Geochemistry, Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, al. Mickiewicza 30, Krakw, 30-059 Poland

*asolinska@agh.edu.pl

Clay minerals have been widely used in many areas of the industry and wastewater treatment techniques. Due to their natural properties have a higher affinity for cationic forms of pollutants, which they can remove with great efficiency. There is, however, an increasing amount of wastewater containing a variety of organic compounds. Because of their complexity and variety of chemical forms, clay minerals are often not efficient enough. A relatively easy approach to improving clay minerals' sorption properties is to create organic-containing clay mineral composites.

In the present study, two clay mineral-based composites were investigated with a mass ratio of 20% bentonite to 80% lignite and 20% halloysite to 80% fly ash containing a relatively high amount of unburned carbon. The obtained composite materials were characterized using X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and X-Ray Fluorescence Spectroscopy (XRF) analysis. Cation exchange capacity (CEC) and anion exchange capacity (AEC) were also determined. Their sorption ability to remove organic compounds (dye and pharmaceutical) have also been studied. The sorption experiments were carried out as a function of varying initial concentrations of dye and pharmaceutical.

The obtained results indicate that the addition of fly ash and lignite significantly improves clay minerals' sorption properties. Based on the investigated analysis, we suggest that morphological parameters of sorbents, including porosity, presence of a significant amount of unburned coal and diverse functional groups lead to immobilization of organic compounds from waters and wastewaters.

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Steps towards sustainable treatment of micropollutants in water using microbially-mediated redox processes in clay minerals

Maggie L White[1,*], Liewen Liu[1], James J N Kitson[2], Anke Neumann[1]

[1]Newcastle University, School of Engineering, Newcastle upon Tyne, NE1 7RU, UK
[2]Newcastle University, School of Natural and Environmental Sciences, NE1 7RU, UK

*m.l.white@newcastle.ac.uk

Water and wastewater treatment are essential for ensuring environmental and human health. However, the incomplete removal of organic micropollutants during conventional wastewater treatment processesposes an emerging threat. Encouragingly, advanced oxidation processes (AOPs), which rely mainly onthe production of reactive oxidizing species such as hydroxyl radicals (OH radicals), have been successful in degrading microp- ollutants. Current AOPs are energetically and chemically expensive witha high-carbon footprint and for a more sustainable future, low-cost and low-input alternatives are required. Recent studies show that OH radicals can also be effectively generated and degrade micropollutants during the oxygenation of natural ferrous iron-bear- ing clay minerals, e.g. nontronite. Currently it is unknown whether and how these redox-active clay minerals could be used to develop a novel, sustainable and low-carbon footprint AOP. This study aims to address this knowledge gap and suggests exploiting the activation of iron-bearing clay minerals by microbial communities (i.e. through iron reduction) to perform sustained and effective oxidative degradation of micropollutants in wastewater.

To prove the concept for our novel sustainable AOP, we have been using laboratory mesocosm experiments to emulate a dynamic water treatment system cycling between reducing and oxidizing conditions. Benchtop col- umn experiments containing the iron-bearing clay mineral nontronite (NAu-2;23 wt% iron) were seeded with a microbial community from a local pond and yielded up to 24% clay mineral iron reduction. For comparison, a second column containing the same clay mineral was set up and the chemical reducing agent sodium dithionite applied, in order to achieve similar iron reduction extents of 25-50%. Oxidized synthetic wastewater containing an organic probe, benzoic acid (BA; representing a micropollutant), was then used to initiate production of OH radicals and to monitor the extent and kinetics of micropollutant degradation within the chemically-reduced column.

Micropollutant degradation occurred in the chemically-reduced column during the first treatment cycle, as HPLC analysis of samples showed that over 3 hours, declining BA concentrations coincided with increases in the BA degradation product, 4-hydroxybenzoic acid (4-HBA). Assuming all 4-HBA was produced via the oxidative degradation of BA, we estimated a cumulative production of >36 µM of OHradicals from the oxida- tion of iron(II) in the nontronite (~8.7 mM iron(II)). Two further treatment cyclesproduced lower concentrations of 4-HBA. Ongoing ICP-MS analyses will provide the basis for mass balance calculations for iron (and other metals) to determine whether clay mineral dissolution and/or colloidal transport out of the chemical column limited subsequent OH radical production. Similar experiments with oxygenated synthetic wastewater and the BA probe are underway to initiate the production of OH radicals with the microbially-reduced columns. We are currently sequencing 16S ribosomal RNA extracted from column porewaters and sediments to characterise the microbial communities mediating iron-reduction in these columns. Molecular microbiological methods will also be used to assess the effect of oxidative BA probe degradation on the microbial community over multiple redox cycles, which will be complemented with investigations of (clay) mineralogical changes using XRD, Mssbauer spectroscopy and infrared spectroscopy (ATR-FTIR).

In summary, this interdisciplinary work will indicate whether it is feasible, in principle, to achieve effective oxidative removal of persistent organic contaminants using this novel clay-based AOP and whether this process can be sustained continuously over several cycles of reduction and treatment by indigenous microbial communities.

Cr(VI) reduction by low molecular weight organic acids enhanced by Mn (hydr)oxides

Chaoyun Ying[1], Bruno Lanson[2*], Caroline L. Peacock[3], Anja B. Frank[4], Bei Yuan[1], Xionghan Feng[1]

[1]Coll. Resources & Environment, Huazhong Agricultural Univ., Wuhan 430070, PR China
[2]Univ. Grenoble Alpes, CNRS, ISTerre, F-38000, Grenoble, France
[3]Univ. Leeds, School of Earth & Environment, Leeds LS2 9JT, UK
[4]Univ. Hamburg, Inst. Geology, D-20146 Hamburg, Germany

*bruno.lanson@univ-grenoble-alpes.fr

Chromium (Cr) is a common metal contaminant of surface and ground waters with redox sensitive mobility and toxicity. A common and efficient remediation strategy involves reducing highly mobile and carcinogenic Cr(VI) to less soluble and less toxic Cr(III) by naturally occurring dissolved reduced metal species, micro-organisms, or organic acids. Redox reactions between Cr(VI) and organic acids are kinetically limited but may be promoted by interactions with mineral (hydr)oxides. Until now manganese (Mn) (hydr)oxides, that are ubiquitous in soils and sediments, are considered as primary oxidants of Cr(III) and assumed to contribute to Cr(VI) production and Cr toxicity in natural environments. Contrastingly, the present study shows that common Mn (hydr)oxides play a positive role in the reduction of Cr(VI) by low molecular weight organic acids. Release of Mn(II,III) from the reductive dissolution of Mn (hydr) oxides, surface-catalyzed redox processes, and formation of reactive intermediate reaction products, such as •COO− free radicals, all contribute to the enhancement of Cr(VI) reduction. The ability of Mn (hydr) oxide surfaces to promote Cr(VI) reduction in the presence of low molecular weight organic acids challenges the current understanding of Cr redox behavior and opens an extensive and fascinating new field of research for Cr environmental geochemistry. Redox cycling of Cr is also associated with isotopic fractionation, making Cr isotopes an increasingly used, innovative proxy for paleoredox conditions. A thorough understanding of Cr redox behavior in the presence of organic acids and Mn hydr(oxides) in surficial environments is key to ensure the applicability of Cr isotopes as a paleoredox proxy.

The influence of pyrophosphate on As(III) oxidation by birnessitein the absence/presence of ferrous ion: (de)passivation effect and reaction mechanisms

Chaoyun Ying[1,*], Xionghan Feng[1], Bruno Lanson[2], Xiaoming Wang[1], Wenfeng Tan[1], Fan Liu[1]

[1]Coll. Resources & Environment, Huazhong Agricultural Univ., Wuhan 430070, PR China
[2]Univ. Grenoble Alpes, CNRS, ISTerre, F-38000, Grenoble, France

*ssuperdizzy@gmail.com

Manganese(IV) oxides, and more especially birnessite, rank among the most efficient metal oxides for As(III) oxidation and subsequent sorption, and is thus a potentially attractive oxidant to be used in large- scale water treatment for arsenic immobilization. The efficiency is limited, however, by the precipitation of low valence Mn (hydr)oxides at the birnessite surface that leads to its passivation. Moreover, aqueous Fe(II), which is present in anaerobic waters, also reacts on the MnO_2 surface, resulting in the formation of hydrous ferric oxides and inhibiting further As(III) oxidation. The present work investigates experimentally the influence of chelating agents on this oxidative process. The precipitation of Mn(III) and Fe(III) on the surface of birnessite is hampered in the presence of pyrophosphate (PP), an efficient Mn(III) chelating agent, thus alleviating surface passivation and highly promoting As(III) oxidation. Presence of PP limits however the efficiency of As(V) removal through sorption on Fe oxide surfaces. Enhancement of As(III) oxidation by Mn oxides strongly depends on the affinity of the chelating agent for Mn(III) and from the induced stability of Mn(III) complexes. Compared to PP, the positive influence of oxalate, for example, on the oxidative process is more limited. The present study thus provides new insights into the possible optimization of arsenic removal from water using Mn oxides, and on the possible environmental control of arsenic contamination by these ubiquitous non-toxic mineral species.

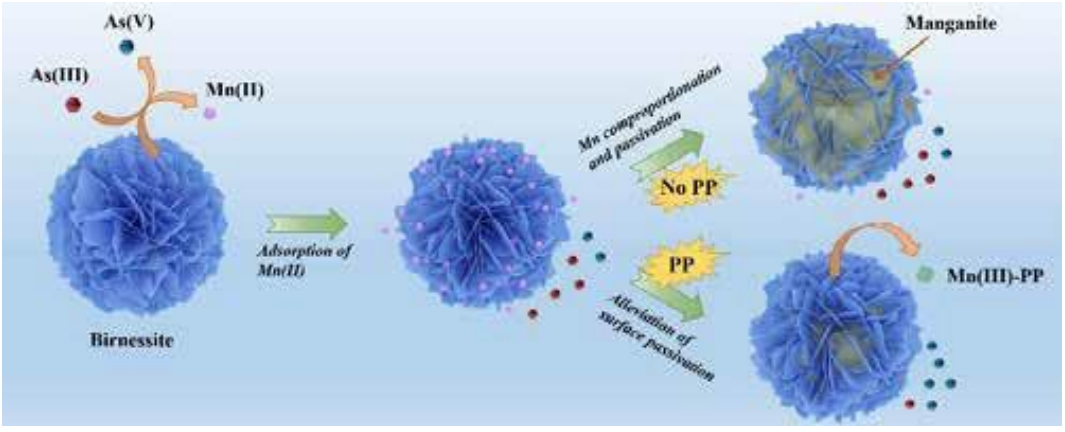


Figure 1. Schematic description of enhancing As(III) oxidation by birnessite in the presence of pyrophosphate.

Influence of minerals on the fate of halogenated contaminants – investigation of hydrophobic organic chemical (HOC)–clay mineralinteractions

Böhm Leonard[1,*], Grančič Peter[2], Tunega Daniel[2], Gerzabek Martin H.[2]

[1]Justus Liebig University Giessen, Institute of Soil Science and Soil Conservation, Giessen, Germany
[2]University of Natural Resources and Life Sciences, Institute of Soil Research, Vienna,Austria

Leonard.Boehm@umwelt.uni-giessen.de

Hydrophobic organic chemicals (HOCs), such as halogenated aromatic hydrocarbons, may be highly persistent in the environment and cause harmful effects on humans and biota. Sorption processes are highly relevant for the assessment of their environmental fate and risk. In this context, especially HOC–organic matter interactions are intensively studied, whereas knowledge of HOC adsorption to minerals is comparatively limited.

In the present work, we determined adsorption of halogenated benzenes (as HOC representatives) to smectite rich bentonites (as mineral phases). Furthermore, we investigated the influence of exchangeable alkali and alkaline earth metal cations on HOC adsorption for one of the specific HOC-mineral systems. Laboratory experiments were performed with a miniaturized batch adsorption method combined with solventless HOC extraction by automatedsolid-phase microextraction (SPME) for straightforward determination of adsorption isotherms. Molecular modeling of HOC–smectite interactions was performed with montmorillonite models with varying mineral structure.

Presented are results for the adsorption of hexachlorobenzene (HCB) and four other halogenated benzenes to multiple bentonites. Results show a large variation in adsorption strength depending on the specific minerals with their adsorption coefficients K_d varying over three orders of magnitude, highlighting the varying influences of HOC hydrophobicity and mineral composition on the extent of adsorption. Adsorption experiments with montmorillonitemodified with alkali and alkaline earth elements revealed a significant effect of exchangeable cations: We observed increasing adsorption for samples modified with varying alkali elementsbut more or less constant adsorption for samples modified with varying alkaline earth elements. These trends matched well with hydration radii of exchangeable cations. Experimental results on adsorption are compared with results from molecular modeling calculations that indicate the relevancy of solvent effects in HOC-mineral interactions.

The in-depth studies on HOC adsorption to minerals are part of the “ClayHOC” project, in which laboratory adsorption experiments and molecular modeling methods are combined to further elucidate mechanisms of HOC–mineral interactions.

Understanding Zn(Ⅱ) sorption on palygorskite at the molecular scale: A coupling XAFS and Zn stable isotope approach

Xinxin Mo[1,2,*], Yoshio Takahashi[2], Matthew G. Siebecker[3], Wenxian Gou, Zhao Wang1, Wei Li[1]

[1]School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China
[2]Department of Earth and Planetary Science, The University of Tokyo, Tokyo 113-0033, Japan
[3]Department of Plant and Soil Science, Texas Tech University, Lubbock, Texas 79409, USA

*xxmo@smail.nju.edu.cn

Sorption reactions at the clay-water interface play important roles in controlling the fate and transport of trace metals in aqueous geochemical environments. While surface complexation theory is well established, the understanding of surface-induced precipitation at mineral/water interfaces, especially the kinetic process of sorption/precipitation, is still limited. Given that the *in-situ* Quick-scanning XAFS technique can achieve monitoring the sorption processes in real time, and Zn stable isotope is widely-used as a tracing tool, we employed a coupling XAFS and Zn isotope approach to elucidate the sorption mechanisms of Zn at palygorskite/solution interfaces.

In this work, the macroscopic and spectroscopic results indicate that at equilibrium, at low pH (e.g., below pH 7.0), Zn(ll) is predominantly sorbed as an outer-sphere surface complex in octahedral coordination at low ionic strength (e.g., below 0.01 M), whereas at higher ionic strength (e.g., above 0.1 M)

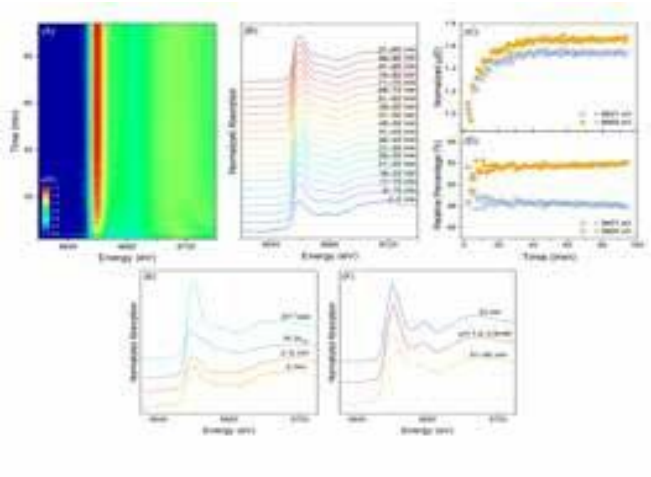


Fig. 1 Real-time Zn-K edge Q-XANES spectroscopy combined with a flow-cell reactor.

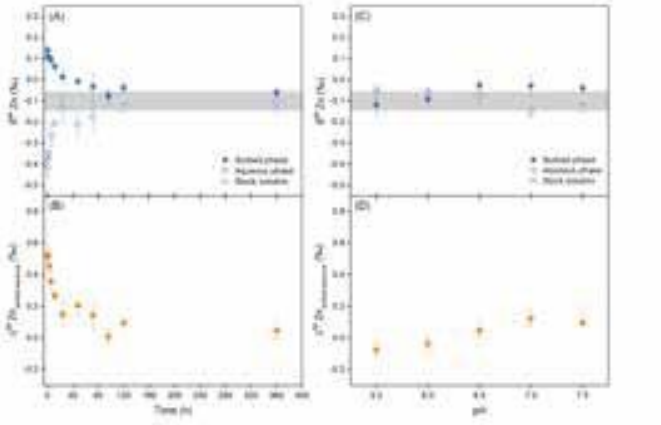


Fig. 2 Isotopic compositions of aqueous Zn and sorbed Zn and Zn isotopic fractionation between the two phases.

the sorption is dominated by the inner-sphere complexation in octahedral coordination along with a possible minority of tetrahedral inner-sphere complexation. At higher pH (e.g., pH 7.5), the formation of Zn phyllosilicate precipitate is observed. In addition, the *in-situ* real-time QXANES results in flow cell corroborate the finding of isotopic evolution in the sorption process at pH 7.5, where the magnitude of fractionation ($\Delta^{66}Zn_{\text{sorbed-aqueous}}$) changes from 0.53 ± 0.05 ‰ to 0.05 ± 0.04 ‰. The combined results indicate that the predominant mechanism evolves from tetrahedral surface inner-sphere complexation in the initial stage to octahedral surface inner-sphere complexation in the later stage, followed by polymerization and/or nucleation and the formation of Zn-phyllosilicate precipitates occurs. The findings presented in this study improve not only the current understanding of surface sorption/precipitation but also try a novel application of metal stable isotope for tracing the sorption kinetic process at mineral-water interfaces.

The role of sulfide-reduced clay minerals and magnetite in the degradation of PCE and TCE

James Entwistle[1], Drew E. Latta[2], Thomas C. Robinson[2], Michelle M. Scherer[2], Anke Neumann[1,*]

[1]Newcastle University, School of Engineering, Newcastle upon Tyne, NE1 7RU UK
[2]University of Iowa, Department of Civil and Environmental Engineering, Iowa City, 52242 IA, USA

*anke.neumann@ncl.ac.uk

Iron-bearing minerals such as clay minerals and magnetite play a significant role for contaminant degradation in subsurface environments. Microbial activity can directly reduce the mineral ferric iron (Fe(III)) to ferrous iron (Fe(II)) or result in the generation of dissolved reductants such as Fe(II) and sulfide (S(-II)), which, in turn, can transfer electrons to structural Fe(III) in the minerals. In our previous work, we studied the reductive transformation of two legacy contaminants, tetrachloroethene (PCE) and trichloroethene (TCE), and demonstrated that magnetite and reduced Fe-containing clay minerals alone did not reduce PCE and TCE under anoxic conditions (Culpepper et al, 2018; Entwistle et al, 2019). Only under experimental conditions that favored active precipitation of reactive minerals such as ferrous hydroxide ($Fe(OH)_2$) did we observe significant amounts of TCE and PCE reduction products. Although it has been shown that sulfide-bearing minerals can reduce PCE and TCE (Butler & Hayes, 1999) it is unclear whether addition of S(-II) can lead to redox-activated clay minerals and magnetite and/or the active precipitation of sulfide-bearing minerals that could degrade PCE and TCE.

Here, we evaluated the reduction of PCE and TCE by S(-II)-reduced clay minerals and magnetite as a function of initial S(-II) concentration. We compared clay minerals with low (SWy-2) and high (NAu-1) structural Fe contents as well as magnetites with a range of Fe(II)/Fe(III) stoichiometries. In control experiments, we evaluated PCE and TCE degradation in solutions containing aqueous Fe(II) and S(-II), in the presence and absence of magnetite. We monitored clay mineral and magnetite reduction extent as well as the formation of new (reactive) mineral phases by ^{57}Fe-Mössbauer spectroscopy and XRD.

Similar to our previous work (Culpepper et al, 2018; Entwistle et al, 2019), S(-II)-reduced clay minerals and magnetite were unable to reduce PCE and TCE under any of our experimental conditions, suggesting that mineral structural Fe(II) was not sufficiently reactive for PCE and TCE degradation. Mössbauer spectroscopy demonstrated that magnetite stoichiometry decreased during the reaction with S(-II) and that an additional mineral phase formed. Although its spectral area increased as a function of S(-II) concentration, this mineral phase was not detectable with XRD and was inconsistent with the formation of mackinawite (FeS), which only formed when aqueous Fe(II) and S(-II) were added. Mackinawite degraded PCE and TCE completely within 50 hours and the presence of magnetite decreased the yield and overall rate of transformation. Our results indicate that magnetite hindered the formation of the reactive mineral phase (FeS). Similarly, the distinct color change of the Fe-rich clay mineral NAu-1 from initially pale- green to black resulted in neither PCE and TCE degradation nor detectable additional mineral phase(s) in X-ray diffractograms and Mössbauer spectra. Our combined evidence suggests that S(-II) reduction of Fe-bearing minerals such as clay minerals and magnetite leads to the formation of non-reactive mineral intermediates.

Butler, E.C. & Hayes, K.F. (1999) Kinetics of the Transformation of Trichloroethylene and Tetrachloroethylene by Iron Sulfide. *Environ Sci Technol.*, 33 2021–2027.
Culpepper, J. D., Scherer, M. M., Robinson, T. C., Neumann, A., Cwiertny, D., Latta D. E. (2018) Reduction of PCE and TCE by magnetite revisited. *Environ Sci: Processes Impacts*, 201340–1349.
Entwistle, J., Latta, D.E., Scherer, M.M., Neumann, A. (2019) Abiotic Degradation of Chlorinated Solvents by Clay Minerals and Fe(II): Evidence for Reactive Mineral Intermediates. *Environ Sci Technol.*, 53, 14308-14318.

Clay minerals for the remediation of per- and polyfluoroalkyl substances in the environment

Binoy Sarkar[1,*], Raj Mukhopadhyay[2]

[1]Future Industries Institute, University of South Australia, Mawson Lakes, SA 5095, Australia
[2]ICAR-Central Soil Salinity Research Institute, Karnal – 132001, Haryana, India

[*]b.sarkar@lancaster.ac.uk; binoy.sarkar.clay@gmail.com

Per- and polyfluoroalkyl substances (PFAS) are extremely persistent, bio-accumulative and cancer-causing contaminants of emerging concern. Owing to high chemical, thermal and biological stability of PFAS compounds, their remediation in the environment is challenging. Clay minerals with or without modification have been shown to remove PFAS compounds from water, or to immobilize the contaminants in soils. High PFAS removal performances were obtained when clay minerals were modified with different organic agents such as surfactants, polymers and amines. Few inorganic-organic combined modification routes were also reported to enhance clay minerals' PFAS removal performance. Clay-based materials adsorb PFAS mainly through hydrophobic interaction and electrostatic attraction. Environmental factors such as solution pH, natural organic matter, background ion types and ionic strength influence the adsorption efficiency of PFAS on clay-based materials. Advanced clay modification approaches such as clay-carbon composites and clay-anchored nano-catalysts and microorganisms hold potential to further improve PFAS remediation via enhanced adsorption-transformation mechanisms. This presentation aims to highlight the advances in clay-based materials for remediating PFAS in contaminated water and soil as one of the inexpensive and sustainable strategies.

Sorption of sulfamethoxazole and diclofenac from aqueous solution on anorgano-bentonite modified with hexadecyltrimethylammonium bromide

Uziel Ortiz-Ramos[1], Roberto Leyva-Ramos[1,*], Esmeralda Mendoza-Mendoza[1,2]

[1]Centro de Investigación y Estudios de Posgrado, Facultad de Ciencias Químicas, Universidad Autonoma de San Luis Potosi, Dr. Manuel Nava 6, 78210, San Luis Potosi, S.L.P., Mexico

[2]Programa de Catedras, Consejo Nacional de Ciencia y Technologia (CONACYT), Mexico

*rlr@uaslp.mx

In this work, the single adsorption of sulfamethoxazole (SMX) and diclofenac (DCF) from aqueous solutions onto bentonite modified with the cationic surfactant hexadecyltrimethylammonium bromide (OBHDTMA) was studied in detail. The organobentonite was characterized by XRD, FT-IR, TGA, N2 physisorption and Zeta potentialtechniques. Furthermore, the effect of pH, ionic strength and temperature on the capacity of OBHDTMA for adsorbing SMX and DCF was analyzed rigorously, and reversibility studies were also carried out. The characterization revealed that surfactant adsorption occurred on the interlayer space and on the external surface of bentonite, and electrostatic attraction and cationexchange controlled the adsorption. The basal space (001) increased from 1.50 to 1.94 nm (Figure 1a), which is consistent with the results reported by Leyva-Ramos et al. (2021). At pH = 7 and T = 25 °C, the maximum adsorption capacity of OBHDTMA towards SMX and DCF was 447 and 787 mmol/kg (Figure 2b); and was 36.2 and 45.5-fold bigger than the adsorption capacity of raw bentonite, respectively. The enhancement in the adsorption capacity of OBHDTMA was related to the following: i) electrostatic attraction among the positively charged surface of OBHDTMA and negative species of SMX and DCF and ii) hydrophobic interaction between SMX and DCF and hydrophobic tails of surfactant. In addition, the SMX and DCF adsorption on OBHDTMA was reversible, which demonstrated that physical mechanisms governed the adsorption of both compounds.

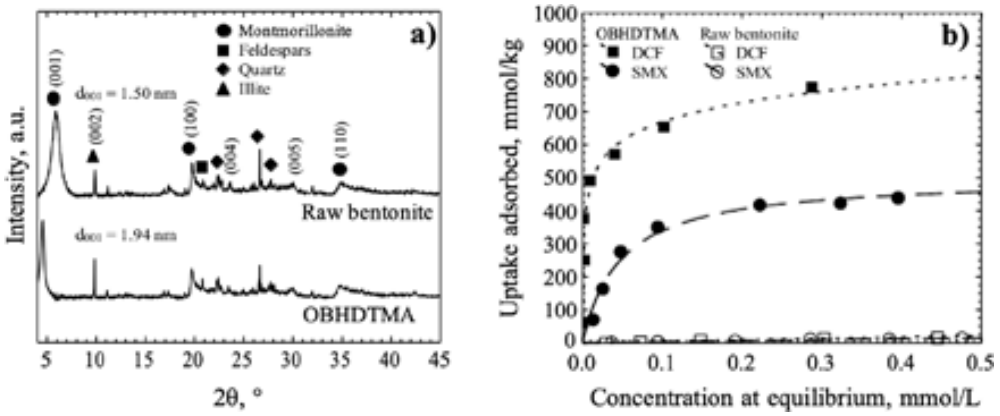


Figure 1. a) X-ray patterns obtained for raw bentonite and OBHDTMA. b) Adsorption isotherms of DCF and SMX on raw bentonite and OBHDTMA at T = 25 °C and pH = 7.

Leyva-Ramos, R., Jacobo-Azuara, A., Martínez-Costa, J.I. (2021). Organoclays. Fundamentalsand Applications for Removing Toxic Pollutants from Water Solution. In. J.C. Moreno-Piraján,
L. Giraldo-Gutierrez, F. Gómez-Granados (Ed.), Porous Materials. Theory and Its Applicationfor Environmental Remediation (pp. 341-363). Switzerland: Springer.

Effects of stacking disordering in sodalite and cancrinite formed in carbonate-rich alkaline solutions on sodium-potassium exchange reaction

Chiawei Lin[1,*], Youjun Deng[1], Julie A. Howe[1], Markus Graefe[1,2]

[1]Soil & Crop Sciences Department, Texas A&M University, College Station, TX, 77845 USA
[2]Bauxite Residue R&D Group, Technology Development & Transfer, Emirates Global Aluminium, PO Box 3627, Dubai, United Arab Emirates

*cwlin@tamu.edu

Sodalite and cancrinite are two common feldspathoids formed in high-alkalinity solutions such as the processed radioactive nuclear wastes and alumina-refinery Bayer liquors. These minerals have large theoretical cation exchange capacities (about 800 cmol/kg) and anion exchange capacities (about 200 cmol/.kg). They should be very reactive in regulating common ions such as K, Na, Ca, and Mg when introduced to the environment. More and more reports indicate that structural stacking disordering occur in both sodalite and cancrinite when they form in alkaline solutions. The disordering can alter their ion exchange properties due to the discontinuity or shifts in the channels and/or cages. The objectives of this study were 1) to characterize the structural disordering of sodalite and cancrinite formed in a high-alkalinity solution in the presence of sodium carbonate and 2) to quantify the Na-K exchange in these feldspathoids and their corresponding structural deformation of the minerals during the exchange.

Fethspathoids were synthesized by mixing kaolinite with NaOH and different concentration of Na_2CO_3 for one day at 100 and 230 °C. The mineral phases, chemical formulas, and cation exchange capacities of synthesized products were examined by XRD, FTIR, SEM, TGA and ICP-OES. Preliminary results showed successful production of pure carbonate sodalite and cancrinite, but stacking disordering occurred. Increasing the concentration of Na_2CO_3 reduced the required reaction time to achieve high kaolinite-sodalite/cancrinite conversion and enhanced the amount of incorporated carbonate in the framework. When potassium was exchanged onto carbonate sodalite, it expanded the unit cell size and induced the T-O vibration shifts, indicating its crystal structure change after cation exchange. The changes were reversible. The low carbonate sodalite exchange more potassium than the high carbonate ones with the first potassium loading, but nearly complete exchange can be achieved for all carbonate sodalite after 3 times loading at room temperature. This suggested that although the structural carbonate hampered the exchange, those cation sites affected by the carbonate were still accessible for the potassium. High-resolution transmission electron microscope and Rietveld refinement offer more insight on the structural disordering in the sodalite and cancrinite formed in the carbonate-rich solutions.

Enhanced copper sorption property of gamma irradiated pristine and chemically modified Philippine natural zeolite

Eleanor Olegario[1,2,*], Mon Bryan Gili[3]

[1]Department of Mining, Metallurgical, and Materials Engineering, University of the Philippines Diliman, Quezon City, 1101 Philippines

[2]LITHOS Manufacturing, OPC, Sta. Maria, Bulacan, Philippines

[3] Philippine Nuclear Research Institute, Department of Science and Technology, Commonwealth Avenue, Diliman, Quezon City 1101, Philippines

*emolegariosanchez@up.edu.ph

Gamma-irradiation of pristine, Na-exchanged, NaOH-, and HCl-modified Philippine natural zeolites (PNZ) have been performed at different irradiation doses. XRD, FTIR, and SEM were used to observe the changes in the structure, crystallinity, and morphology of the zeolite samples. Irradiation results in a general reduction of unit cell volumes of the component zeolites. At low γ-irradiation dose (≤ 400 kGy), raw and NaOH-modified zeolites, experience an improvement in the crystallinity. Higher irradiation dose (700 kGy) leads to structural degradation. In contrast, the crystallinity of HCl-modified zeolites slightly diminishes at a lower dose but improves at a higher dose. On one hand, the exposure to γ-radiation at a dose level of 400 kGy generally degrades the crystal structure of Na-exchanged raw zeolites [1].

Adsorption experiments were done to investigate how γ-radiation affects the Cu^{2+} sorption property of zeolites for possible applications in heavy metal decontamination in the semiconductor and mining industries. Adsorption kinetics and thermodynamic tests were conducted using non-irradiated and γ-irradiated (400 kGy) NaOH-modified PNZ for the removal of Cu^{2+} ions in aqueous solution.

There were no significant changes in the elemental composition of the irradiated zeolite. Irradiation primarily results in the shrinking of the zeolite framework and improvements in the crystallinity. The γ-irradiation increases the sorption uptake according to the kinetic study following a pseudo-second-order model. Thermodynamic tests indicate the adsorption isotherms are described by the Langmuir model. The maximum adsorption capacities of the non-irradiated and γ-irradiated NaOH-modified zeolites are 33.00 and 43.22 mg Cu^{2+} g^{-1}, respectively, suggesting that γ-irradiation might enhance the maximum adsorption capacity by up to 30.8% [2].

Irradiation does not provide an obvious change in the structural, surface and morphological structures of the zeolites. The ɣ-NaOH-modified PNZ obtain a significant increase in Cu^{2+} adsorption upon gamma-irradiation at an absorbed dose of 200, 400 and 700 kGy respectively. For the ɣ-HCl-modified PNZ, a minimal enhancement of adsorption capacity was observed at 200 kGy and reduced sorption uptake of Cu^{2+}/g at 400 and 700 kGy doses respectively. Same sorption effect was observed for the ɣ-unmodified PNZ.

[1] Gili, M.B.Z, Guillermo, N.R.D, Marquez, E.J., Nery, A.L.G, Olegario, E.M., Pares, F.A. (2020). Changes in the structure, crystallinity, morphology and adsorption property of gamma-irradiated Philippine natural zeolites. *Materials Research Express* 6 (12), 125552

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TS06 Clays and Contaminant Control

POSTER PRESENTATIONS

Autothermal reforming of biogas using an extruded honeycomb monolith: A new catalyst based on nickel incorporated illite clay promoted MgO

Mohcin Akri [1,2,4,*], **Ouafae Achak**[2], **Pascal Granger**[3], **Sheng Wang**[4], **Catherine Batiot-Dupeyrat**[1], **Tarik Chafik**[2]

[1]Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), Ecole Nationale Supérieure d'Ingénieurs de Poitiers (ENSIP), Université de Poitiers, UMR CNRS 7285, 1rue Marcel Doré, TSA 41105, 86073, Poitiers, cedex 9, France

[2]Laboratory LGCVR UAE/L01FST, Faculty of Science and Techniques of Tangier, University Abdelmalek Essaadi, Morocco

[3]Unité de Catalyse et de Chimie du solide (UCCS), Université de Lille 1, UMR CNRS 8181, Cité scientifique Bat C3, 59655, Villeneuve d'Ascq, France

[4]Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, PR China

*mohcin.akri@univ-poitiers.fr

The dry reforming of methane was investigated using a novel catalyst based on natural illite clay to which nickel and magnesium has been added into moldable paste easily extrudated into honeycomb monolith. This approach can represent a significant breakthrough offering an alternative to conventional costly wash-coated ceramic substrates usually difficult to optimize, and a gain in efficiency thanks to the minimization of transfer limitations. The best catalytic performance was obtained with illite clay containing 8 wt.%Ni and 3 wt.%Mg, yielding to excellent conversions of CH_4 and CO_2 at 800 °C of respectively 81% and 76%. The catalytic enhancement observed on magnesium-doped systems was attributed to the stabilization of smaller Ni particles associated with the formation of NiO-MgO solid solution which slows down particle sintering. The obtained results suggest different types of nickel-support interactions in addition to improved basic properties inducing synergy effects on the rate of methane and CO_2 conversion and higher resistance to deactivation phenomena.

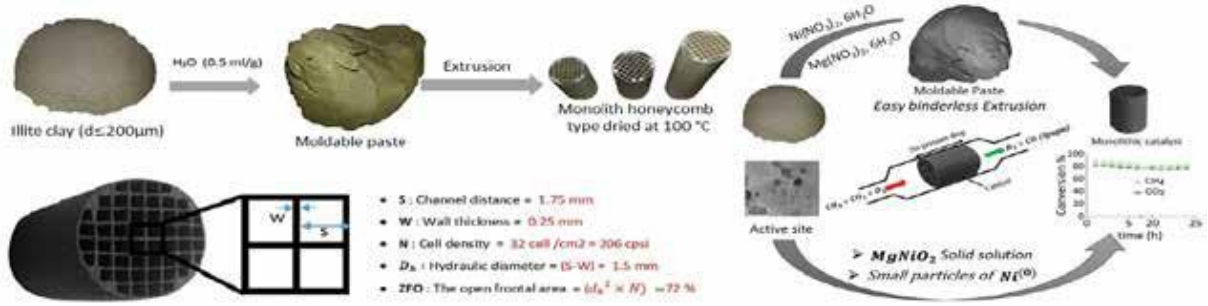


Figure 1. Preparation steps and geometric properties of extruded support and catalysts.

Theoretical study of interactions in the clay-polymer advanced hybrid nanomaterials

Sanam Bashir[1], Eva Scholtzová[1,*], Daniel Tunega[2]

[1]Institute of Inorganic chemistry, Slovak Academy of Sciences, Dbravsk cesta 9, 845 36 Bratislava, Slovakia
[2]Universitt für Bodenkultur, Institut für Bodenforschung, Peter-Jordan-Strasse 82, A-1190 Wien, Austria

*eva.scholtzova@savba.sk

Intense research in the advanced layered hybrid materials uses various clay minerals, mainly from the smectites group, e.g., montmorillonites, providing their layered structure to accommodate various guest species.

The layered structure of smectites consists of the tetrahedral (T and octahedral (O sheets linked together through apical oxygen atoms of tetrahedra, forming a TOT layer. Due to the layer thickness of ~1 nm, they are considered nanomaterials. In the clay structures, the isomorphous substitutions in the T sheets (e.g., Al^{3+}/Si^{4+} and O sheet (e.g., Fe^{2+}, Mg^{2+}/Al^{3+} generate a negative net charge which is compensated by exchangeable hydrated inorganic cations (e.g., Ca^{2+}, Na^{+}, Li^{+} in the interlayer space. The presence of these exchangeable cations is often a key factor for further easy modification with organic surfactants (e.g., quaternary cations or polycations – cationic polymers and polymers.

The design of the clay-polymer hybrid materials was targeted to prepare, e.g., the effective sorbents of organic pollutants, clay-based nanocomposites with antibacterial properties or advanced materials with photoactive properties.

In this work, detailed knowledge on the binding interactions and intercalation energies as a measure of the structural stability of the clay-polymer hybrid structures is studied employing Density Functional Theory (DFT method in the solid state using PBE functional together with D3 scheme for dispersion corrections (Grimme, S. et al., 2010. The hybrid structures of montmorillonite and pentaethylenimine cation, PEI^{+}- Mt, and Mt with penta(2-metoxyoxazolines), PMOX-Mt, respectively, were examined.

Acknowledgement: BS and ES are grateful for the financial support by the Scientific Grant Agency (project No. VEGA 02/0021/19) and Slovak Research and Development Agency (projects No. APVV-18-0075 and APVV-19-0487).

Grimme, S., Antony, J., Ehrlich., S. & Krieg, H. (2010). A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. T*he Journal of Chemical Physics,* 132, 154104-1-154104-19.

TUFFAD: Modified Philippine natural zeolites (PNZ) adsorbents in modular filter tube device for groundwater filtration

Eleanor Olegario[1,2,*], Bryan Alamani[3], Jason Pechardo[1], Hari Hamoy[4], John Paul Renzo Jucar[3], Shawnn Audric Nadurata[5]

[1]Department of Mining, Metallurgical, and Materials Engineering, University of the Philippines Diliman, Quezon City, 1101 Philippines

[2]LITHOS Manufacturing, OPC, Sta. Clara, Sta. Maria, Bulacan, 3022 Philippines

[3]Department of Chemical Engineering, University of the Philippines Diliman, Quezon City, 1101 Philippines

[4]Department of Family and Community Medicine, College of Medicine, University of the Philippines Manila Campus, 670 Padre Fauna Street, Manila City, 1000 Philippines

[5]School of Science and Engineering, Ateneo de Manila University, Katipunan, Quezon City, 1108, Philippines

*emolegariosanchez@up.edu.ph

The Philippine natural zeolite (PNZ) was sourced from Mangatarem, Pangasinan has the silica content of 59.52% and alumina of 12.62%. The PNZ was pre-conditioned using sodium [1], modified using Surface modification [2]. It was also tested for adsorption of heavy metals [3-4] and E. Coli inactivation [5]. Various irradiation techniques like gamma irradiation [6] and plasma irradiation [7] and were also applied to PNZ to enhance its adsorption capacities and bacteria inactivation.

The modification technique used for ***TUFFAD Mineral*** Adsorbent Type 1 is sodium pre-conditioning whereby the K, Mg, Ca, Fe ions of the PNZ were replaced with sodium ions to increase the Cation Exchange Capacity (CEC) of the mineral. For ***TUFFAD Cationic*** Type 2, the PNZ was pre-conditioned with sodium, treated further thermally to make the adsorbent more attractive to heavy metals and ammonia. Additionally, the PNZ was surface modified to produce ***TUFFAD Anionic*** Type 3 to arrest anions present in aqueous solutions such as phosphates and nitrates. A more complex surface modification was done to the PNZ to make it more attracted to non-polar organic toxins thereby naming this ***TUFFAD Organic*** Type 4 adsorbent. Lastly, copper nanowires were structured onto the zeolite surface to inactivate bacteria touching the surface of ***TUFFAD Antibac*** Type 5 adsorbents.

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Recrystallized Philippine natural zeolites (PNZ) adsorbents via hydrothermal synthesis and ion exchange modification techniques for applications in compact air purification

Eleanor Olegario[1,2,*], Bryan Alamani[3], Jose Aldrin Vea[3], Ramuel John Tamargo[3], Jason Pechardo[1], Airah Osonio[4], Christian Mark Pelicano[5],

[1]Department of Mining, Metallurgical, and Materials Engineering, University of the Philippines Diliman, Quezon City, 1101 Philippines
[2]LITHOS Manufacturing, OPC, Sta. Clara, Sta. Maria, Bulacan, 3022 Philippines[3] Department of Chemical Engineering, University of the Philippines Diliman, Quezon City, 1101 Philippines
[4]Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku,Nagoya, Aichi, 464-8603, Japan
[4]Institute of Physical Chemistry, University of Hamburg, Hamburg 20146, Germany

*emolegariosanchez@up.edu.ph

This study aims to impart additional information and possible raw material in the future research and development in air filtration technology. Furthermore, it aims to develop an enhanced aluminosilicate-based air filter using locally sourced raw materials. Morphological, structural, chemical, surface chemistry, and thermal characteristics will be evaluated. The antibacterial (against *E. coli*, *S. Aureus*, *C. Albicans*) and gas (CO) adsorption properties of Cu-exchanged high-silica aluminosilicate will also be examined. This study is limited to the natural aluminosilicate sources in the Philippines both in qualitative and quantitative aspects. The modification of the aluminosilicate will only be focusing on hydrothermal synthesis and copper-exchange. Antimicrobial activity will only focus on the available assays and technique. Multiphysics model will not be part of this study.

Philippine natural zeolite (PNZ) granules from LITHOS Manufacturing in Mangatarem, Pangasinan, Philippines [1-5] is used in this study. The samples were pre-conditioned using basic solution to remove the impurities and enhance the adsorption property of the zeolite. The PNZ will undergo hydrothermal synthesis and ion exchange as its modification techniques.

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TS08 + TS20 Sepiolite, Palygorskite and Bentonite

ORAL PRESENTATIONS

Natural mixtures of palygorskite and smectite clay deposits of Grevena-Kozani, west Macedonia, Greece: A comparison study with similar Spanish and Turkish clay deposits

Konstantinos Vythoulkas[1,*], Michael Stamatakis[1], Manuel Pozo[2], Ariadne Argyraki[1]

[1]National and Kapodistrian University of Athens, Department of Geology and Geoenvironment, 15784 Athens, Greece
[2]Universidad Autónoma de Madrid, Department of Geology and Geochemistry, 28049 Spain

*kvithou@geol.uoa.gr

Large commercial clay deposits composed of natural mixtures of palygorskite and smectite are located between the cities of Grevena and Kozani, west Macedonia, Greece. These deposits are part of the sedimentary succession of Ventzia continental basin that was formed during the Upper Pliocene-Lower Pleistocene on the ultrabasic bedrock of the Vourinos ophiolite complex and the Molassic Tsotyli formation of the Mesohellenic Trough. Four discrete deposits (sub-basins have been reported within the Ventzia basin, those of Knidi, Pilori, Harami, and Velanida. These deposits have similar chemical composition and main mineralogy and were deposited in a fluvial-lacustrine environment with alkaline affinities. The Ventzia smectite and palygorskite have a high Fe and Mg and low Al content that reflect the geochemical background of the major rock type of the substrate. These deposits are compared with similar Spanish and Turkish clay deposits in terms of mineralogy and chemical composition that define the geological characteristics of their depositional environment.

Representative clay samples of the Ventzia basin were characterized by means of XRD, SEM-EDS and ICP-AES. The analytical results led us to conclude that detrital serpentine and smectites were the main precursor materials to form palygorskite in the center of sub-basins where favorable conditions prevailed. The main mineral phases of Ventzia clays are smectite and palygorskite while accessory mineral phases include mainly serpentine, quartz, dolomite, and calcite. SEM investigations reveal that palygorskite fibers are normally very small and tightly interwoven except in Harami palygorskite where larger fibers form skeletal structures. The major source of Si in the Ventzia deposit is most likely derived from the chemical alteration of ultrabasic rocks but local Si could have been available from the detrital feldspars and quartz of the molassic sediments of the substrate.

Similar geological settings between Greek and Turkish clay deposits gave rise to almost identical lithologies and accessory mineral phases. In Greek and Spanish clay deposits palygorskite was formed by syn- or post- transformation/dissolution of precursor minerals, such as smectite and serpentine, whereas palygorskite in Turkish clays was formed by direct precipitation. Direct precipitation of palygorskite has been identified, as a minor event in some of the Greek deposits. Finally, it is suggested that diagenetic mechanisms are more apparent in Turkish and especially Spanish clays since formation age of Greek palygorskite/smectites is the youngest among the deposits studied.

Application of full pattern summation method in quantification of bentonites and smectites

Adrián Lorenzo[1,*], Emilia García-Romero[2,3], Mercedes Suárez[1], StephenHillier[4,5]

[1]Universidad de Salamanca, Departamento de Geologa, Salamanca 37006, Espaa.
[2]Universidad Complutense de Madrid, Departamento de Mineralogay Petrologa, Facultad de Geologa, Madrid 28014, Spain.
[3]Universidad Complutense de Madrid–Consejo Superior de Investigaciones Cientficas, Instituto de Geociencias (IGEO, Madrid 28040, Espaa.
[4]The James Hutton Institute, Craigiebuckler, Aberdeen AB158QH, United Kingdom.
[5]Department of Soil and Environment, Swedish University of Agricultural Sciences (SLU, SE-75007 Uppsala, Sweden

*adrianlorenzo@usal.es

Bentonite is a rock composed in its majority by smectite group minerals and impurities such as quartz, feldspars, and phyllosilicates among others. The properties of bentonites will depend to a large extent on the mineralogy and the proportion in which these minerals are found. A mineralogical quantification of bentonites can be challenging due to the great structural complexity of smectites.

The aim of this work is to apply the full pattern summation (FPS method to quantify a large number of bentonite samples and see how the FPS method works covering a wide range of smectite crystallochemical variability and crystallinity. For thispurpose, nearly 100 bentonites samples were prepared using a spray dryer and X-ray diffraction data collected on a Bruker D8 Advance instrument. The quantification was made using the R package powdR (Butler and Hillier, 2020 in several stages.

The results of the quantification showed that some samples had a good fit and thus a satisfactory quantification. However, there were samples with fit problems that required further adjustments until a satisfactory fit was achieved. Problems with fits are mainly due toreference standards not necessarily being identicaltothe mineralsin the samples. This is due to factors such as the crystallochemical variability of the smectites, not only regarding the 2:1 layer but also the nature of the interlayer cation which influences the position of the basal reflections.

To overcome these problems, a larger number of reference samples are needed to try to cover the mineralogical variability of bentonites, though most common types are adequately covered by a relatively small number of standard reference patterns.

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Bentonites and K-bentonites: Issues in identifying and interpreting ancient tephras

Warren D. Huff

Emeritus, Department of Geology, University of Cincinnati, Cincinnati, Ohio 45221 USA

warren.huff@uc.edu

The Ordovician record of explosive volcanism consists of examples of both near-vent pyroclastic flows and ignimbrites and distal sequences of altered fallout tephras known as K-bentonites. Questions frequently arise as to whether a particular clay-rich bed might be an altered volcanic ash fall in the form of a bentonite or K-bentonite. These beds are often datable using fission track and U/Pb dating of zircons, K/Ar, and Ar/ Ar of amphibole, biotite and sanidine. Due to their unique composition, they provide an indispensable tool when correlating sections. The criteria for recognizing such beds are varied, but fall into two broad categories, field criteria and laboratory criteria. Ideally, one would want both, but often that is not possible. Here we will examine some of the key features to look for in each case that can aid in reliable identification.

Control mechanisms of special bentonites as highly effective buffer material for nutrients and salts in peat-reduced and peat-free growing media

Matthias Schellhorn[1,*], Jana Michaelis[2], Uwe Hilmer[2], Ralf Diedel[1], Franz Sperhake[3], Kevin Kaps[3], Stefan Dultz[3]

[1]Stephan Schmidt KG, 65599 Dornburg, Germany
[2]Detlef Hegemann Umwelttechnik GmbH, 28309 Bremen, Germany
[3]Institute of Soil Science, Leibniz Universität Hannover, 30419 Hannover, Germany

*matthias.schellhorn@schmidt-tone.de

Clays and especially bentonites are an important additive used in peat-based growing media forornamental plant cultivation, aiming at constant supply of K, P, micronutrients, pH-buffering, improvement of rewettability and cohesion of growing media. Specific clays allow buffering of plant nutrients such as K and P, but also elements harmful to plants such as Mn (Binner et al., 2017; Binner & Schenk, 2013; Schellhorn et al., 2013. The increasing demand in peat- reduced and peat-free growing media poses new challenges, because peat substitutes and biogenic waste materials, e.g., coir/wood fibers and compost, respectively, usually contain high nutrient and salt loads and, compared to peat, have relatively low sorption capabilities. Bentonites in general might be suitable to buffer high salt contents of alternative raw materials for peat-free growing media and avoid overdosage of nutrients as well. Tackling the need for regulating nutrient balance at start of the crop and keeping it constant during cultivation in peat-free growing media by using bentonites has not yet been considered in detail, although it showsgreat promise. Here the identification of suitable bentonites is a prerequisite for cultivation safety.

19 different clays and bentonites were determined in batch experiments on their buffering capacity for K and P for identifying highly efficient clays for stabilizing the chemical propertiesof peat-reduced and peat-free growing media. The influence of clays on nutrient buffering was determined in a plant experiment using a peat-free growing media. Sorption isotherms were established. Clay mineralogy, oxalate-soluble Fe and specific surface area were determined.

The clays differ clearly in their K and P buffering capacities, which can be explained by the clay properties determined to some part only. For P buffering it is assumed that the surface of Fe oxides differs widely as this factor did not fully explain the observed variability. As a result, the performance of some special ben-tonites is outstanding in comparison to the other used claysin this study.

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Crystallochemical characterization of bentonites used on treated wines

Fernando Rocha[1,*], Sofia Catarino[2], Cristiana Costa[3]

[1]GeoBioTec, Department of Geosciences, Aveiro University, 3810-193 Aveiro, Portugal
[2]LEAF, Higher Institute of Agronomy, Lisbon University, 1349-017 Líbon, Portugal
[3]Technological Center for Ceramics and Glass, 3025-307 Coimbra, Portugal

*tavares.rocha@ua.pt

Bentonite is a technological aid widely used in winemaking to remove or reduce the concentration of undesirable constituents. Bentonite nature, composition and structure influences the adsorption capacity. The effects of bentonite addition to wine have been mostly studied in order to assess the depletion of proteins, amino acids, bioamines, polyphenols, and aroma compounds. Previous study (Catarino et al., 2008 was carried out to evaluate the release of contaminant elements from several bentonites to wine, and to understand the effects of their physical and chemical characteristics. Six different bentonites (B1, B3, B4, B5, B8, and B9 supplied by four companies (in Portugal were studied. Mineral constitution of bentonites (silt and clay fractions was assessed by XRD. External specific surface area was determined by the indirect method BET. Chemical composition was assessed by flame atomic absorption spectrometry (FAAS and by inductively coupled plasma mass spectrometry (ICP-MS.

For the present work, same set of samples was studied to assess their crystallochemical features. Morphological and pseudototal chemical analysis of individual particles was assessed using a Tescan scanning electron microscope with energy dispersive spectroscopy (SEM-EDS VEGA LMU mode. Powder samples of clay fractions were also analyzed by XRD to compute d(060 values.

XRD results show that smectites are mainly of dioctahedral type but on 2 samples (B3 and B4trioctahedral ones are present. SEM results allowed to compute smectites structural formulas. There are significative differences between samples; beidellites are predominant followed by montmorillonites and nontronites. These results stress previous ones obtained by Catarino et al. (2008, indicating the importance of detailed assessment of physical and chemical characteristics of bentonites used on wine treatments, thus suggesting the need for more information about the trademark products.

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Experimental study of dissolution reaction of palygorskite: effect of solution pH

F.J. Huertas[1*], A.E.S. Van Driesche[1], M. Bentabol[2], M.D. Rodríguez-Ruiz[2]

[1]Instituto Andaluz de Ciencias de la Tierra (CSIC-University of Granada), 18100 Armilla, Granada, Spain
[2]Departamento de Qumica Inorgnica, Cristalografa y Mineraloga. University of Mlaga.Campus de Teatinos. 29071 Mlaga, Spain

*javier.huertas@csic.es

The unusual crystal structure of palygorskite is largely responsible for its unique physico- chemical properties such as surface area, porosity, high-temperature phases and active sorption centers. Some of these properties give rise to a markedly different behavior compared to other industrial clays, and confers palygorskite with a high added value for a wide range of industrial applications such sorptive, rheological or catalytic material. Despite the extensive (potential) use of both raw and composite palygorskite products, surprisingly little is known about the intrinsic reactivity and stability of these clay particles.

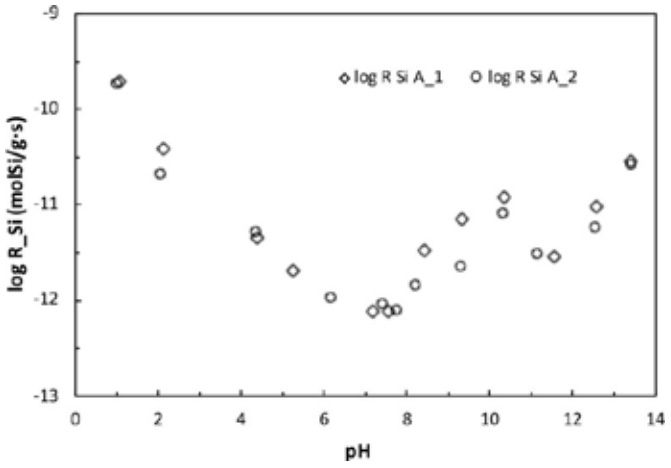


Figure 1. Variation of the palygorskitedissolution rate (R_Si) with the pH of the alteration solution. Two replicates are included.

Reactivity and stability of palygorskite from Senegal was investigated in electrolyte solutions with pH ranging from 1 to 13 at 25°C. Palygorskite (0.5 g/L) was reacted with solutions for 4 to 100 days in bath reactors. Peri- odically, solutions were sampled and analyzed for pH and Si, Al, and Mg concentrations. Dissolution rates (R) were derived from the temporal evolution of Si concentration. The log_R_Si vs pH (Fig.1) showed two mini- ma, at pH 7-8 likely associatedto Al sites dissolution, and at pH 11-12 associated to Mg sites and carbonation.

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Mineralogy, geochemistry, and genesis of lithium-bearing argillaceous sediments associated with the Neogene Bigadiç borate deposits, western Anatolia, Turkey

Selahattin Kadir[1,*], Tacit Külah[2], Hülya Erkoyun[1], Cahit Helvacı[3], Muhsin Eren[4], Burak Demiral[1]

[1]Eskişehir Osmangazi University, Department of Geological Engineering, 26040 Turkey
[2]Kütahya Dumlupınar University, Department of Geological Engineering, 43100 Turkey
[3]Dokuz Eylul University, Department of Geological Engineering, 35160 Turkey
[4]Mersin University, Department of Geological Engineering, 33343 Turkey

* skadir.icc@gmail.com

The lithium-bearing claystone, marl, carbonate, and siliceous carbonate are associated with the Miocene Bigadiç borate deposits in the lacustrine environment of western Anatolia (Turkey). The materials forming these rocks were provided by the alteration of rhyolitic and dacitic volcanic rocks in the area. The lith- ium-bearing claystone and bituminous shale locally coexisted with nodular borate. However, no detailed mineralogical or geochemical characterizations of this economic, strategical, and technological important lithium-bearing clay (hectorite, saponite) has not been clearly performed previously. The present study was undertaken to close this gap. Texturally, sanidine and plagioclase crystals were altered, biotite and hornblende Fe-oxidized, locally opacitized, and chloritized in a sericitized, argillized, locally carbona- tized, and zeolitized glassy matrix of the rhyolitic and dacitic tuffs. The claystone is composed of abun- dant smectite associated with minor to accessory illite, volcanogenic quartz, feldspar, mica, hornblende, and occasionally calcite, aragonite, dolomite, and gypsum/anhydrite, along with realgar and orpiment in some locations. The well-ordered hectorite and rarely saponite were identified by sharp basal reflections at 14.23–14.56 Å and 11.98–12.73 Å, respectively, and nonbasal at 4.56 and 1.52–1.53 Å. The lithium values increase up to 2380 ppm in the hectorite-rich claystone and marl units and up to 449 ppm in the volcanic rocks. Micromorphologically, hectorite and saponite typically have a webby to crenulated form with irregular margins edges volcanic materials and coexists with rhomboidal calcite, blocky gypsum/anhydrite, and Fe-(oxyhydr)oxide phases. These minerals and phases are also evidenced by their individual sharp EDX spectrum of Si/Mg, Ca/C, Ca/S, and Fe, respectively. Local enhancement of Ba and Ti values are detected. The Li standard is absent in the EDX system thus it is not determined. The positive correla- tion of REE vs. each of SiO_2 and Al_2O_3; Li vs. MgO, SiO_2 vs. each of Rb, Th, and Zr; negative correla- tion of Li vs. each of Al_2O_3, SiO_2 and K and increase of MgO+CaO, Sr +Rb, Li, LREE/MREE+HREE ratio; negative Eu anomaly and high values of As and S suggest that the alteration of feldspar, biotite and hornblende originated from the Miocene volcanic and pyroclastic materials and presence of orpiment, realgar, and gypsum/anhydrite during the hydrothermal alteration activities were the main sources for the formation of hectorite and saponite.

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Influences of micropores and water molecules in the palygorskite structure on the color and stability of Maya blue pigment

Guanzheng Zhuang[1,*], Li Li [2,3,4], Mengyuan Li [2,3,4], Peng Yuan [2,3]

[1]Inst. of Resources Utilization and Rare Earth Development, Guangdong Academy of Sciences, Guangzhou 510650, China
[2]CAS Key Laboratory of Mineralogy and Metallogeny, Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[3]CAS Center for Excellence in Deep Earth Science, Guangzhou 510640, China
[4]University of Chinese Academy of Sciences, Beijing 100049, China

*sizhoutufei@163.com

Maya blue is an ancient hybrid pigment composed of indigo and microporous palygorskite, with a fantastic hue and outstanding stability. Its color-causing and stabilization mechanism are unsolved problems. Previous work implied that water molecules in clay micropores might be related to the formation of Maya blue pigment. However, the influences of different water molecules and micropores on the color and stability of Maya blue have not been clarified.

In this work, palygorskite materials contained different water molecules were obtained by heating at 180, 300 and 570°C. Maya blue-like pigments were prepared from these palygorskite materials and solid indigo by grinding. The microporous structure of palygorskite and the status of inside water molecules were investigated by thermal analysis, X-ray diffraction, Fourier transform infrared and microporous analysis. The color properties, chemical resistance and photostability of pigments were characterized by reflectance spectra, CIE color parameters and color differences after the attack of concentrated nitric acid, dimethyl sulfoxide, and visible light exposure equaling to about 100 years.

It was confirmed that the greenish-blue and stable hybrid pigment could only be prepared when indigo molecules were inserted into the micropores of palygorskite. Zeolitic water molecules inside the micropores should be removed because they hindered the insertion of indigo molecules. The key to immobilizing indigo molecules inside micropores was hydrogen bonds between indigo and coordinated water (C=O·····H—OH). This study emphasized the important role of micropores and hydrogen bonds in the synthesis of organic-inorganic hybrid pigments.

Periodic DFT study of the crystal structure and physical properties of the monoclinic polymorph of palygorskite mineral determined by Periodic DFT

Francisco Colmenero[1,*], Ana María Fernndez Diaz[2], Vicente Timn[3]

[1]Complutense University of Madrid, Department of Chemical Physics, 28040 Madrid, Spain
[2]Centro de Investigaciones Energéticas, Medioambiéntales y Tecnológicas (CIEMAT), 28040 Madrid, Spain
[3]Instituto de Estructura de la Materia (IEM-CSIC), 28006 Madrid, Spain

*francolm.ucm.es

Palygorskite is a hydrated 2:1 type phyllosilicate clay mineral with a fibrous-like morphology found in a wide variety of geological settings having numerous commercial applications in pharmaceutical, fertilizer and pesticide industries. Palygorskite occurs as fine-grained material with poor crystalline mases. This feature as well as its fibrous morphology hinders the determination of its full crystal structure including the positions of hydrogen atoms. In this work, the hydrogen atom positions are determined using first-principles methods based on Periodic Density Functional Theory (DFT) using plane waves and pseudopotentials (Payne *et al.,* 1992) for a prototypical structure of monoclinic dioctahedral monoclinic palygorskite with formula, where □ is the octahedral vacancy. These methods were highly efficient for this purpose in previous works (Colmenero *et al.,* 2019). From the calculated structure, the powder X-ray diffraction pattern is determined and compared with that derived from the experimental crystal structure reported by Chiari *et al.* (2003). Similarly, from the computed crystal structure, the infrared (IR) spectrum of monoclinic palygorskite was theoretically determined and compared with the experimental spectrum recorded from a sample from Torrejón el Rubio, Cáceres, Spain (Fernández *et al*., 2013). The agreement is satisfactory, giving support to the computed crystal structure. Since the bands in both spectra showed a high degree of consistence, a normal coordinate analysis of the theoretical spectrum is carried out to assign all the bands in the observed spectrum. The elastic tensor, mechanical properties, equation of state and thermodynamic and optical properties are also obtained. In conclusion, first-principles theoretical methods are highly successful to determine the full crystal structure of the monoclinic polymorph of palygorskite, for the interpretation of its infrared spectrum, and for the prediction of its mechanical, thermodynamic and optical properties.

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Tunisian smectitics clays

Fakher Jamoussi[1], Emna Fakhfakh[1], Islem Chaari[2], Samir Mefteh[1], Imen Khiari[1] , Ali Sdiri[3]

[1]Georessources Laboratory, Water Researches and Technologies Center (CERTE), Tunisia, BP 273, 8020 Soliman, Tunisia
[2]National Center of Researches in Material Sciences, BP 73, 8027 Soliman Tunisia
[3]National School of Engineers of Sfax, ENIS km 4 road Soukra, Sfax 3038

fakher.jamoussi@certe.rnrt.tn; fakherjamoussi@gmail.com

The mineralogical prospection of clays in Tunisia along the outcropping stratigraphic series from the Permian to the Quaternary carried out by Jamoussi et al., 2000 and Jamoussi 2001 reveal the abundance of smectite from the Upper Cretaceous.

Tunisia's clay imports reached almost 60 million dinars (18 million €) in 2019 corresponding to 203,000 tons of imported clay. These imports include 16,000 tons of Bentonite and bleaching earth, a priori smectitic or palygorskitic, the rest of the imports correspond to kaolinitic clays.

The only exploited smectitic clay deposit is probably near El Hamma in southeastern Tunisia dating from the Coniacian Santonian. Common clays are exploited in deposits around brick manufacturing units, mainly in the Center East of Tunisia.

The compilation of the results of the mineralogical analysis of hundreds of samples from the different paleogeographic domains carried out by Jamoussi et al., 2003, leads to a synthetic log. We can thus distinguish that the Upper Cretaceous is dominated by smectite (20-89%) over kaolinite and illite, always accompanied by fibrous minerals in the southern Atlas. There is thus a predominance of smectite in the Upper Cretaceous, Paleogene and Neogene. The smectites of the sediments studied are alumino-ferriferous beidellites (Jamoussi and Srasra, 1992; Jamoussi, 2001), which supports the hypothesis of a continental heritage, since these beidellites are precisely characteristic of the soils and alterations of a hot and dry climate (Paquet, 1970).

Coniacian to Miocene-aged smectitic clay deposits outcropping in the southern Atlas of Tunisia have been fully characterised, including their mineralogical and chemical compositions. These natural materials have been proposed to be used in different industrial applications, for example, in production of lightweight aggregates (Fakhfakh 2006, Fakhfakh et al. 2007), retention of pollutants (Chaari et al., 2007, 2008, Sdiri et al., 2013), clarification of oil, clarification of phosphoric acid, retention of organic matter (Jamoussi, 2001), cosmetic and pharmaceutical products (Fakhfakh, 2006, Mefteh, 2017, Khiari, 2017), as well as other health care products such as peloids (Chakroun et al. 2013, Mefteh et al., 2014, Khiari et al., 2019).

Smectitic clays are used in Tunisia in the field of drilling, thalassotherapy, foundry. Common clays containing varying levels of smectite, illite and kaolinite are used by brick manufacturing units.

TS08 + TS20 Sepiolite, Palygorskite and Bentonite

POSTER PRESENTATIONS

Adsorption of bioactive compounds on clays

Konstantinos Safakas[1], Katerina Katerinopoulou[1], Athanasios Ladavos[1,*], Iro Giotopoulou[2], Nektaria-Marianthi Barkoula[2], Archontoula Giannakopoulou[3], Haralambos Stamatis[3], Ioannis Ropoulos[4]

[1]University of Patras, Department of Business Administration of Food and Agricultural Enterprises, 30100 Agrinio, Greece
[2]University of Ioannina, Department of Materials Science and Engineering, 45110 Ioannina, Greece
[3]University of Ioannina,Department of Biological Applications and Technologies, 45110 Ioannina, Greece
[4]IPER, Laboratory of Chemical and Microbiological Analysis, 21st February 192, Ioannina, Greece

*alantavo@upatras.gr

Clay minerals are natural materials available in abundance that can be utilized in active food packaging as nano-carriers of bioactive compounds to extend the self-life of food products during storage and retain the food safety and quality. Moreover, clay minerals provide significant contribution to the improvement of barrier and physi- cochemical properties of polymer films. The interest of the food packaging industry in bioactive compounds isbased on their interesting biological properties that include among others antibacterial, antifungal and antioxi- dant properties. Most active food packaging developed so far are based on phenols (carvacrol, tocopherols andthymol), polyphenols and essential oils.

Adsorption of bioactive compounds into or onto clay minerals was afforded by using a simple evaporation/ adsorption process without any use of toxic solvents. Clay-bioactive compounds constituents' hybrids were prepared in powder form, aiming to achieve more applicable materials for use in industry extruders during the preparation of polymer nanocomposite films for food packaging applications. Two types of clay were used, organophilic organo-modified montmorillonite (OrgMt) and hydrophilic Bentonite (Bent) and three bioactive compounds namely carvacrol, thymol and olive leaf extract.

The intercalation of bioactive molecules in the OrgMt interlayer was studied by X-ray diffraction analysis. Thermogravimetric Analysis (TGA) was used to estimate the adsorbed amount of bioactive compounds into Bent and OrgMt clay layers. Evaporation of bioactive compounds from the hybrids occurs at higher temperatures in comparison to the neat bioactive compounds. This result indicates that clay carriers enhance the thermal stability of the bioactive compounds. Antioxidant activity of pure bioactive compounds and clay-hybrids was detected using 2,2-diphenyl-1- picrylhydrazyl (DPPH) assay. The obtained hybrids were analyzed for their antimicrobial activity against bacterial populations of *Escherichia coli* BL21DE3 and *Salmonella enteritis* strains resenting a significant inhibition of the bacterial growth. Clay/carvacrol exhibited excellent and prolonged anti- oxidant and antimicrobial activity in comparison to other two bioactive compounds.

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Characterization of K-bentonite from Dolná Ves deposit (Kremnické vrchy Mts., Western Carpathians, Slovakia – a source of illite-smectite (ISCz-1

Marek Osacký[1,*], Yuqing Bai[1], Peter Uhlík[1], Helena Pálková[2], Ľubica Puškelová[3]

[1]Comenius University in Bratislava, Department of Mineralogy, Petrology and Economic Geology, Bratislava 84215, Slovakia

[2]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, Bratislava 845 36, Slovakia
[3]Earth Science Institute, Slovak Academy of Sciences, Dúbravská cesta 9, Bratislava 840 05, Slovakia

*marek.osacky@uniba.sk

Although mixed-layer illite-smectite is one of the most abundant clay minerals in the Earth crust, the economic accumulations of illite-smectite are rare and only several K-bentonite deposits (i.e. rich in illite-smectite) are mined around the world. In the present study, we investigate K-bentonite samples from the Dolná Ves deposit collected in 2019 – 2020. The Dolná Ves deposit is located in the southwestern part of Kremnické vrchy Mts. The thickness of the productive layer ranges between 10 and 60 m, with the K-bentonite reserves of about 9 Mt. Since the 1990s, the K-bentonite from the Dolná Ves deposit is a part of the Clay Minerals Society Source Clays collection, as a source of illite-smectite (ISCz-1). The previous studies were focused mainly on the investigation of clay-sized fractions of K-bentonite, dominated by illite-smectite. In the present study, we collected different technological types of Dolná Ves K-bentonites and both, whole-rocks and different size fractions isolated from the whole-rock samples were analyzed. The main goals were to better understand the relationships between different technological types of K-bentonites and their properties (mineralogy, chemistry and surface properties) which may result in different possible applications for K-bentonites from Dolná Ves deposit.

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Perlite and kaolinite-rich zones in the marginal part of the Lutila I bentonite deposit, the Western Carpathians, Slovakia

Peter Uhlík[1*], Jozef Hodermarský[2], Jaroslav Lexa[3], Miroslav Pereszlényi[4], Jana Brčeková[1], Marek Osacký[1]

[1]Comenius University in Bratislava, Faculty of Natural Sciences, Department of Mineralogy, Petrologyand Economic Geology, Bratislava 842 15, Slovakia

[2]REGOS, s.r.o., 841 04 Bratislava, Slovakia

[3]Earth Science Institute, Slovak Academy of Sciences, 840 05 Bratislava, Slovakia

[4]PC&G, s.r.o., 842 15 Bratislava, Slovakia

*peter.uhlik@uniba.sk

Bentonite exploitation has increased significantly over the past 10-15 years in Slovakia. With the annual production of more than 200 kt belongs to the world's TOP 15 producers. The most important bentonite deposits in Slovakia are located in the Central Slovakia Volcanic Field, where they associate with rhyolite volcanics in the southern part of Kremnické vrchy Mts. The aim of the study is to characterize samples from recently discovered perlite and kaolinite-rich zones from one of the largest bentonite deposits in Slovakia - Lutila I. Admixture of the both, perlite and kaolinite, decrease quality of the bentonite. On the other hand, presence of high volume of the both could be interesting as source of the other industrial minerals. Perlite is parental rock for bentonite. So the presence of almost unaltered perlite next to bentonite can bring new information about the bentonite genesis.

Light grey, crumbly, porous glassy rocks with porphyritic texture contain 70-80 wt.% of volcanic glass, about 20 wt. % sum of non-clay minerals (feldspars>quartz) and 4-0.3 wt.% of clay minerals (montmorillonite>kaolinite). Significant number of feldspars and quartz phenocrysts decrease quality of expanded perlite. Active perlite deposits in the area contain about 95 wt.% of volcanic glass and 5 wt.% of phenocrysts. It looks that higher number of phenocrysts in primary perlite has also negative limitation for quality of bentonite as a result of perlite alteration. The highest montmorillonite content in bentonite from the Lutila I deposit is up to 80 wt.%.

Light, very crumbly, intensively altered rock contains 40-50 wt.% of kaolinite, 30 wt.% of opal-C/CT and again about 20 wt. % of non-clay minerals (feldspars and quartz).

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Mineralogy and crystal chemistry of Mg-smectites from Turkey

Adrián Lorenzo[1,*], Mefail Yeniyol[2], Andrea García-Vicente[1], Emilia García-Romero[3,4], Mercedes Suárez[1]

[1]University of Salamanca, Department of Geology, Salamanca 37006, Spain.
[2]University of Istanbul-Cerrahpaşa, Department of Geology, Istanbul 34850, Turkey.
[3]Mineralogy and Petrology, Complutense University of Madrid, Madrid 28040, Spain,
[4]Geosciences Institute (IGEO), Spanish Research Council-Complutense University. Spain.

*adrianlorenzo@usal.es

Four bentonitic samples from Turkey C5, YA3, KT4, and YD28 have been studied. They were picked up from southwest and southeast of Eskişehir dolomite-rich sedimentary Neogene sequence where authigenetic Mg-clay minerals are abundant, and from a vein-type magnesite deposit at south of Konya where stevensite is locally found with sepiolite and formed by replacement from magnesite. An in deep study of their mineralogy and crystal chemistry was done by X-Ray diffraction, thermal analysis (thermogravimetric analysis, differential thermal analysis, and differential scanning calorimetry), VNIR-SWIR spectroscopy, and transmission electron microscopy with point analysis by analytical electron microscopy. The samples were analysed in natural conditions and after homoionization with Ca to be sure of the octahedral Mg and interlayer contents.

These samples can be described as bentonites, because their majority mineral are Mg-smectites, with impurities of the minerals from the sepiolite-palygorskite series. The term in the series must be Mg-palygorskite or close to sepiolite according to the thermal analysis. Dolomite is the main non-clay mineral present, and it is a bit more abundant in YA3 sample in which smectite>palygorskite, and small amounts of quartz and serpentine as detrital minerals are found. KT4 contains smectite, and detrital illite and quartz. In general, there are smectites with low crystallinity, especially the sample YD28, which displays no ordering in [001] direction. 060 reflection appears at ~1.52 Å in all samples, which implies that all smectites are trioctahedral.

The reflectance spectra of the samples are very similar, without appreciable bands in the visible wavenumber range, with the exception of C5 sample that has a wide band at ~540 nm related to a higher content of octahedral Fe^{3+}. The spectra show two big absorptions bands in the IR region, the first at 1400 nm due to OH^- vibrations and the second at 1900 nm due to H_2O vibrations. This second band is deeper, as correspond to smectites. Smaller bands due to M-OH vibrations appear between 2200-2400 nm and they slightly vary depending on the octahedral content. Both, the spectroscopic and thermal studies show certain differences among the samples related to the content in sepiolite-palygorskite, other impurities and the octahedral content of smectites.

Crystalchemistry of the smectite particles is complex in all samples, and it cannot be only explained by the possible contamination of fibres. Probably, it also influences the small particles size. In any case, the content in SiO_2 is high for smectite, and the point analysis of the smectite particles show a composition close to fibrous minerals.

Clay mineral assemblages in the Cretaceous Justina bentonite deposit (Neuqun Basin, Argentina): sedimentological and genetic considerations

Gisela Pettinari[1,*], Telma Musso[1], Manuel Pozo[2], Gabriel A. Martínez[3], Rafael González[4]

[1]PROBIEN (CONICET-UNCo), Departamento de Geología y Petróleo, Facultad de Ingeniería, Universidad Nacional del Comahue, 8300 Neuquén, Argentina

[2]Universidad Autónoma de Madrid, Department of Geology and Geochemistry, 28049 Spain

[3]Tolsa Minerales La Patagonia S.A., Cinco Saltos, Argentina

[4]Tolsa S.A., 28031, Madrid, Spain

*gpettina@gmail.com

A new type of sodium bentonite deposit of Cretaceous age has been recognized intercalated with detrital continental facies in the Neuquén basin (Argentina). The bentonite occurs within the Anacleto Formation, the uppermost lithostratigraphic unit of the Neuquén Group (Cenomanian-Campanian). The Neuquén Group comprises a sequence of continental sediments deposited during the initial foreland stage of the Neuquén Basin, conforming three finning-upward fluvial cycles varying in thickness from 500 to 1300 m. Within the study area, the Anacleto Formation contains approximately 70 meters of fine-grained deposits, composed mainly of pelitic and very fine psamitic levels. Pelitic levels are constitute by intercalated massive reddish brown mudstones and siltstones, while yellowish to grayish pink sandstones of medium to fine grained size conform the psamitic facies of the sequence.

Thirty-two samples were collected for the mineralogical study (XRD, SEM and optical microscopy) of the bentonite and associated lithofacies. Bentonite levels are intercalated in siliciclastic facies and are easy to identify due to their grey to pink colors, sometimes with a red lamination, or even red. The beds are horizontal to subhorizontal, 0,21-0,8 m thick (0.60 m average value).

According to the bulk and clay mineralogy, three mineralogical assemblages were established: Assemblage 1. Sodium dioctahedral smectite (montmorillonite) with very low proportion of quartz, feldspars and gypsum. The smectite is relatively well ordered (lower FWHM, larger crystallite size). Assemblage 2. Sodium, calcium or Ca-Na dioctahedral smectite (montmorillonite) with variable proportion of quartz, feldspars, gypsum, mica and analcime. The smectite is poorer ordered than that of assemblage 1 (higher FWHM, smaller crystallite size). Assemblage 3. Mixed layers illite-smectite (50-70% Ca-smectite) (R0), illite and subordinate 7 Å phases (chlorite + kaolinite). In the bentonites, phyllosilicates are dominant (74-98%) with a mean value of 92%. Quartz (0.5-11%) and feldspar (0-19%) occur subordinate with traces of gypsum and analcime (< 2%). In the associated facies located below and upper the bentonite level, phyllosilicates content is variable (43%-81%) and depends on the detrital minerals proportion such as feldspars (6-28%) and quartz (5-23%). In these lithologies is noticeably the presence of analcime reaching up to 7%.

Petrographic examination (thin section) of a representative bentonite sample shows a lamination constituted by laminar mica grains (phlogopite-biotite) and by relict laminae, sometimes broken, with a dirty appearance. Some quartz grains and possible glass fragments are detected. The presence of euhedral opaque crystals is recognized in small aggregates. Secondary fibrous gypsum has been also identified as surface coatings. SEM analysis showed a matrix type microfabric, showing the presence of two groups of smectites with different particle size. The larger smectites have globular morphology, reach a size of 20 µm and seems to originate from the smaller ones. In samples from Assemblage 2 can be identified the presence of small grain-size zeolites (analcime) (<20 µm) infilling porosities. The occurrence of celestine and barite is also outstanding.

The following minerals are interpreted as authigenic: sodium montmorillonite, analcime, barite, gypsum and celestine. The sedimentary environment would be of a lacustrine-palustrine character related to fluvial-alluvial deposits. The smectite could have formed from inherited constituents from both fine fluvial deposits and pyroclastic deposits of tuffs and volcanic glass. The distribution of the bentonite and the differences in the crystallinity of its smectite in different points has allowed a paleoenvironmental reconstruction, showing that the bentonite is mostly developed in the inner zones of the lacustrine environment. The observed association of authigenic minerals is indicative of high pH and salinity conditions in arid climatic conditions within a general humid setting.

Influence of the smectites in the resistivity of the Miraflores Basalt (Panama

Emilia García-Romero[1,2,*], María del Carmen Andrade[3], Eva María Manchado[4], Mercedes Suárez[5]

[1]Mineralogy and Petrology, Complutense University of Madrid, Madrid 28040, Spain
[2]Geosciences Institute (IGEO), Spanish Research Council-Complutense University, Madrid 28040, Spain
[3]CIMNE, Campus Nord C1, Barcelona 08034, Spain
[4]Nucleus, University of Salamanca. Salamanca 37008, Spain
[5]Department of Geology, University of Salamanca. Salamanca 37008, Spain

mromero@ucm.es

The Miraflores basalt is Miocene in age and it outcrops widely around the Pacific side of the Panama Canal. This basalt was used for production of aggregates and sand for the fabrication of the concrete in the construction of the third set of locks of the Panama Canal, which were inaugurated in 2016. It is a tholeiitic basalt with plagioclases and pyroxenes, mainly clinopyroxenes, titanomagnetite, and scarce apatite as primary minerals, together with iddingsite and palagonite as secondary phases resulted of hydrothermal alteration of the basalt. Both iddingsite and palagonite are mainly formed by smectites which also appears filling nano and microcraks and surrounding the plagioclases and pyroxenes in a dense network across the rock (García-Romero and Suárez, 2021). The smectites are Fe-rich beidellites, and their presence influences the mechanical properties of the basalt, as shown by Suárez et al, (2021).

In this work a wide group of representative samples coming from two quarries in the Miraflores Basalt was studied by X-ray diffraction, chemical analysis, optical microscopy, and scanning electron microscopy, and their cations exchange capacity (CEC) and resistivity were determined. The result shown the influence of the presence and amount of smectites both in the CEC and resistivity, and these two properties are negatively correlated between them.

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TS09 Clays and Cultural Heritage

ORAL PRESENTATIONS

The compositional 'fingerprint' of a clay deposit: ceramic provenance studies in the Eastern Mediterranean region

Anno Hein[1,*], Ioannis Iliopoulos[2], Vayia Xanthopoulou[2,3], KaterinaPollatou[1,2], Peter M. Day[1], Vassilis Kilikoglou[1]

[1]Institute of Nanoscience and Nanotechnology, N.C.S.R. "Demokritos", 15310 Aghia Paraskevi, Attica, Greece
[2]Department of Geology, University of Patras, 26504 Patras, Greece
[3]Lab of Electron Microscopy and Microanalysis, University of Patras, 26504 Patras, Greece

*a.hein@inn.demokritos.gr

The manufacture of ceramics from clayey raw materials can be counted among the oldest engineering advancements of humankind. Clays, extracted commonly in the vicinity of the production sites, were processed and often combined to produce a plastic paste, which could be formed into functional shapes, such as storage vessels, transport jars or cooking pots. In the final step of manufacture, the fashioned objects were solidified through the application of high temperatures. Tracing the distribution and trade of ceramics from specific production sites allows for the study of social and economic relations in and between ancient societies. Common approaches for ceramic provenance studies are the analysis of their elemental composition and the investigation of the petrographic fabric. Both approaches are based on the assumption that the original raw materials were distinct in terms of their composition.

The compositional distinctiveness of individual clays from different sources, however, depends on their geological context and the diagenesis of the deposit. Only in the case that the compositions of individual clays can be sufficiently distinguished are the differences expected to have been propagated in the composition of the pottery, which was manufactured from these clays. It must be considered, however, that the direct comparison of ceramics and raw materials potentially used for their manufacture is complicated by the varied practices of clay paste preparation. The general distinctiveness of natural raw material sources, suggested in the 'Provenience Postulate', assumes that compositional intra-source variation is sufficiently smaller than the inter-source variation. In practice, though, even for individual clay types, this assumption has to be verified in each case study, taking into account the compositional parameters determined and the spatial extent assumed for a specified raw material source area.

In the present paper the study of raw material composition will be discussed as an integral part of ceramic provenance studies. Issues such as elemental composition and its relationship to clay type and accessory minerals, clay paste preparation and methodological constraints will be discussed with examples of raw material and ceramic data from the Eastern Mediterranean region. Results of the clay studies are included in the *ceraDAT* an open access database for archaeological ceramics from the region.

Clays in archaeology and archaeometry

Elisabetta Gliozzo

University of Bari, Department of Humanities, 70121 Italy

Elisabetta.gliozzo@uniba.it

The wide availability and the numerous properties of clays have determined their vast and diachronic use as raw material. Ceramic production is only the best known and most studied but it certainly does not exhaust the wide range of applications known in the ancient world. The study of clays in archaeology and archaeometry still primarily regards the study of ceramics, while this contribution intends to broaden the current panorama to areas that have not yet been or sporadically the object of focused investigation.

For example, what were the applications in the cosmetic and pharmaceutical fields? What use was made of clays in the production of textiles? Is there a direct relationship between the distribution of clays and the dynamics of the ancient population? What was the knowledge of clays by the ancients? To what extent did the local availability and the technical properties of this raw material influence the selection of the raw material for artisanal productions?

For the moment, it is only possible to give vague answers to many of these questions, and these limitations imply that a substantial contribution of the applied clay sciences is still necessary and hopeful for significant historical and archaeological reconstruction.

Characterization of byzantine bricks from western Anatolia

Elif Çam*, Elif Uğurlu Sağın

İzmir Institute of Technology, Department of Conservation and Restoration of Cultural Heritage, 35430 İzmir, Turkey

*elifcam@iyte.edu.tr

Fired bricks are among the oldest building materials produced by human knowledge, skills, and possibilities (Bakırer, 1980). The first production of fired bricks occurred in Mesopotamia in the 4th millennium BC and spread from civilization to civilization (Davey, 1961; Bakırer, 1980). They were frequently used in the construction of walls, arches, vaults, and domes during the Byzantine Period (Mango, 2006).

The properties of the bricks differ due to the manufacturing process, such as the type of raw clay, the shaping method, the firing temperature and time (Benavente et al., 2006). Studies on historical bricks provide information about production technologies used by the ancient artisans while examining the properties of bricks. In the scope of the study, Byzantine bricks taken from Anaia Church, Kadıkalesi archaeological site in Kuşadası, Aydın were investigated by means of basic physical and colorimetric properties (standard test methods (RILEM, 1980)), chemical compositions (SEM-EDS), mineralogical compositions (XRD and FTIR), thermogravimetric analyses (TGA) and microstructural properties (SEM).

The analyses revealed that bricks of Anaia Church were produced by using two different clay sources. Both of the raw materials of bricks were determined as calcareous since they contained CaO ranging between 8.6–13.8% and 19.8–23.3%, respectively. Bricks with higher CaO content were found to be denser and less porous than the others. Furtherly, the higher amount of Ca was observed to induce the lighter color on bricks of Anaia Church, since the carbonates inhibit the formation of iron oxides which provide reddish color in brick matrix (Cultrone et al., 2005; Pavia, 2006). The mineralogical compositions of bricks mainly consisted of quartz, plagioclase feldspars, calcite and muscovite, and also new minerals phases occur in higher temperatures which were gehlenite, hematite, and diopside were observed in some samples. The combined results of XRD, FTIR, TGA and SEM images suggested that the firing temperatures of bricks were differentiated and did not exceed 900°C. The firing temperatures differences of the bricks may be due to the inhomogeneous internal temperature distribution of the brick kilns used during the Byzantine Period.

Historical bricks should be accepted as documents reflecting the raw material properties and production methods, as well as the knowledge, skills, and technologies of their period. The brick properties determined by this study should be considered when it is necessary to use new materials for the conservation of the church.

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TS10 Clays and Health

ORAL PRESENTATIONS

Thermodynamic and electrokinetic behaviors of montmorillonite colloid and implications in biotechnology

Jia Hui Liu[1,2], Xi Xi Chen[1,2], Chun Hui Zhou[1,2,*]

[1]Research Group for Advanced Materials & Sustainable Catalysis (AMSC), State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China

[2]Qing Yang Institute for Industrial Minerals, You Hua, Qing Yang, Chi Zhou 242804, China

*clay@zjut.edu.cn

Montmorillonite (Mt) is hydrophilic clay mineral with a high swellability in water and a high cationic exchange capacity (Zhou et al., 2012). Mt is a common ingredient as both the carrier and active substance in biotechnology products. The unfavorable dispersion and swellability of Mt in ethanol/water limited its application in drug delivery systems, tissue engineering, biomaterial, etc (Metz et al., 2015). To improve the dispersion, swellability and rheological property of Mt in ethanol/water remains a challenge. Herein, lithium and lauramidopropyl betaine (LAB-35) were used to co-modify Mt to produce LAB-35-Li-Mt. The structure of LAB-35-Li-Mt were investigated. Li^+ and LAB-35 were successfully introduced into the interlayer space of Mt by ion-exchange. Li^+ partly entered into the framework of Mt nanolayer. The LAB-35-Li-Mt exhibited enhanced dispersion, swellability and rheological property in ethanol/water. The results of XRD indicated that the presence of heterogeneous delaminated structures in ethanol/water. The swellability and dispersibility of LAB-35-Li-Mt swelled in ethanol/water were possibly because ethanol interacts with LAB-35-Li-Mt in the interlayer space through ion-dipole and hydrophobic interaction. Our findings could provide a new way to load poorly water-soluble drug on Mt. In addition, the Mt/ethanol/ water ternary system can lead to environment-friendly paints and cosmetics.

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The occurrences of the rare-earth elements in the coarse fractions of mined Georgia kaolins

W. Crawford Elliott[1,*], Prakash Malla[2]

[1]Department of Geosciences, Georgia State University, Atlanta, GA 30302 USA
[2]Research & Development Department, Thiele Kaolin Company, Sandersville, GA 31082 USA

*wcelliott@gsu.edu

World class kaolin ore deposits are located in the innermost Coastal Plain adjacent to the Fall Line in Georgia and South Carolina. The REE are found in the fine fraction of the mined kaolin ore (< 45 µm, Cheshire et al., 2018). This fraction is processed further for the kaolinite clay product. REE have also been characterized in the coarse fraction considered gangue or mine waste (grit) (> 45 µm; Elliott et al., 2018; 2019). The heavy subfractions of mine waste/coarse fractions of the mined Georgia kaolins contained sizeable concentrations of REE, enriched in the heavy REE, and select trace elements (Zr, Hf, Nb, Ta, U, and Th). The total REE was 5012 ppm for Buffalo Creek Member and 1648 ppm for the Jeffersonville Member (Elliott et al, 2018). The REE were hosted xenotime in these fractions. These REE are considered a possible coproduced resource from kaolins. The sources for the rare-earth containing mineral are open question(s). Monazite belts, saprolite from granite plutons adjacent to the Coastal Plain, phyllite schist, and, generally, Piedmont, Blue Ridge and Appalachian/Grenville terranes (Mertie, 1953; Cheshire et al., 2018; Bern et al., 2017; Dombrowski, 1993; Epperson et al., 2018) are possible sources for the REE-bearing minerals.

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Deciphering the role of surface interactions in the antibacterial activity of layered double hydroxides by atomic force microscopy

Jazia Awassa*, Samantha Soulé, Damien Cornu, Christian Ruby, Sofiane El-Kirat-Chatel

Université de Lorraine, CNRS, LCPME, F-54000 Nancy, France

* jazia.awassa@univ-lorraine.fr

As pristine zinc-based layered double hydroxides (LDHs) are extensively investigated as efficient antibiotic-free antibacterial agents, understanding the mechanisms of interactions between LDHs and bacterial surfaces becomes of great importance. In the present study, the role of surface interactions in the antibacterial activity of zinc-based LDH nanoparticles was investigated. The antimicrobial properties of ZnAl LDH nanoparticles against Gram-positive *Staphylococcus aureus* bacteria were studied using agar disk diffusion and broth microdilution methods. The antimicrobial performance of ZnAl LDH nanoparticles were compared to those of MgAl LDH nanoparticles which served as a negative control. The morphological impacts on bacterial cells caused by treatment with ZnAl and MgAl LDH nanoparticles were examined by atomic force microscopy (AFM) imaging. Cells treated with ZnAl LDH nanoparticles presented irregular features in comparison to those of untreated and treated with MgAl LDHs. Furthermore, silicon nitrides AFM probes were functionalized with ZnAl and MgAl LDHs in order to probe the interactions of LDH nanoparticles with the cell surface by means of AFM-based single particle force spectroscopy (Figure 1), where adhesion force measurements were performed by recording 32 × 32 force–distance curves on areas of 400 x 400 nm on living cells surfaces. The antibacterial ZnAl LDH nanoparticles possessed a specific recognition to *S. aureus* cells with high adhesion frequency in comparison to control non-active MgAl LDH nanoparticles. Such finding suggests the presence of correlation between the specific ability of zinc-based LDHs to adhere on bacterial cell membranes and their possible capability to inhibit the growth of bacteria.

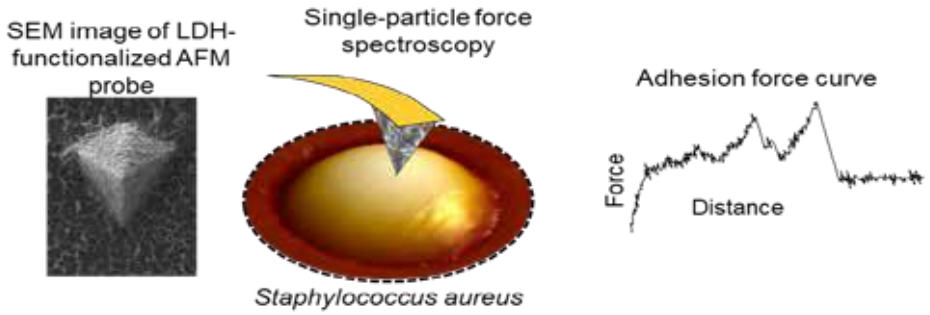


Figure 1. A schematic illustration of the interactions probed between single living *S. aureus* cells and LDH-functionalized AFM tips.

Modify smectites and layered double hydroxides for zearalenone detoxification

Youjun Deng[1,*], ChunChun Hsu[1], Jakub Matusik[2]

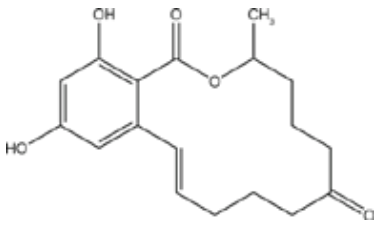
[1]Department of Soil & Crop Sciences, Texas A&M University, College Station, TX, 77843-2474, USA
[2]AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Department of Mineralogy, Petrography and Geochemistry, al. Mickiewcza 30, 30-059 Kraków, Poland

*yjd@tamu.edu

Zearalenone (ZEN) is an endocrine disrupting mycotoxin produced mainly by *Fusarium graminearum* and *F. culmorum*. It is one of the most important mycotoxins in agriculture. Zearalenone contamination occurs commonly in maize, wheat, barley, and sorghum. When ingested, this phenolic resorcylic acid lactone acts as a non-steroidal estrogen, can bind to estrogen receptor and cause estrogenic syndrome and precocious development in various animals, particularly young pigs. Zearalenone has been suspected as the primary initiator of hepatic tumors in some animals. The objectives of this study were to evaluate and to modify smectites and layered double hydroxides as zearalenone binders and therefore to detoxify or inactive the toxin in the contaminate feed. We hypothesize that, as zearalenone is poorly water soluble (0.02 mg/mL) and hydrolysis stable in neutral or acid buffer solutions, it may behavior similarly as aflatoxin B1, another important mycotoxin that can be effectively detoxified by smectites, due to their similar molecular composition, size, and solubility. We expect that hydrophobic interaction would be the key interaction for zearalenone's adsorption in the acidic and neutral pH range. At slightly alkaline pH, the dissociation of the phenol O-H groups may change the molecules to anionic species and therefore enable its adsorption by layered double hydroxides through the anion exchange reactions.

Six smectites with different layer charge densities, and eight different inorganic cations (Li, Na, K, Cs, Mg, Ca, Sr, Ba) saturation and one cationic surfactant treatment on a selected smectite demonstrated large ranges of adsorption capacity (0.2-1.2 mol/kg) for zearalenone. In addition to external surface adsorption, X-ray diffraction analysis after heating the specimens suggested that limited amount of zearalenone accessed the interlayer environment in the organo-smectite and the K-saturated smectite. The experiment on adsorption of zearalenone by layered double hydroxides before and after modification with surfactant is on-going, and the results will be reported at the conference.

The preliminary results implied the potential of the modified clay minerals as binders of zearalenone. their selectivity and efficiency in the real contaminated feed should be further evaluated.



Absorption of pyocyanin by montmorillonite, sepiolite and palygorskite

Bidemi Fashina*, Youjun Deng

Department of Soil and Crop Sciences, Texas A&M University, College Station, TX 77843-2474, USA

tokunbofash@tamu.edu

Pyocyanin is an important virulence factor produced by drug-resistant *Pseudomonas aeruginosa.* Given the importance of pyocyanin in the recalcitrance and resistance of *P. aeruginosa* to antibiotics, the inactivation/deactivation of pyocyanin has been proposed as a novel approach in combating drug-resistant *P. aeruginosa* infections. In this study, the potential of montmorillonite, sepiolite, and palygorskite to bind and degrade pyocyanin was investigated.

A combination of sorption experiments, in-situ variable-temperature x-ray diffraction (VTXRD), energy dispersive x-ray spectrometry (EDS), and UV spectroscopy were employed to investigate the (1) adsorption affinity (K) and capacity (Q_{max}) of clay minerals for pyocyanin, (2) binding sites for adsorption on clay minerals and (3) the degradation/transformation of pyocyanin on clay surfaces. Adsorption experiments were performed at pH3, 4.9, and 7 at which pyocyanin occurred as ~100% protonated, ~50% protonated and zwitterionic, and ~100% zwitterionic species.

Overall, the Qmax was 0.23-0.53 mol/kg for sepiolite, 0.21-0.43 mol/kg for palygorskite, and 0.43-0.68 mol/kg for montmorillonite. The estimated Qmax and K were pH-dependent: pH3 < pH7 for sepiolite, pH3 > pH7 for palygorskite, and pH3 ≈ pH4.9 > pH7 for montmorillonite. At pH < pKa, sepiolite deprotonated some of the pyocyanin molecules while palygorskite and montmorillonite directly adsorbed the protonated pyocyanin. At pH > pKa, sepiolite directly adsorbed neutral pyocyanin molecules while palygorskite and montmorillonite protonated some of the neutral pyocyanin. Pyocyanin molecules were mostly adsorbed in the tunnels of sepiolite, the external surface of palygorskite and, the interlayer of montmorillonite. Adsorbed pyocyanin prevented the folding of tunnels and collapse of interlayer spaces in sepiolite and montmorillonite, respectively. The clays did not degrade pyocyanin, instead, the structure was slightly transformed on the surfaces of sepiolite and montmorillonite.

This study demonstrates the potential of clay minerals in disarming *P. aeruginosa* by binding and transforming pyocyanin in the interlayer of montmorillonite and tunnels of sepiolite. The binding of pyocyanin by clay minerals will reduce the concentration/distribution of pyocyanin while the observed structural transformation could reduce the reactivity of the toxin.

Assessment of some clayey products available on market designed for topicaluse

Carla Marina Bastos[1,2], Fernando Rocha[1,*], Cristina Sequeira[1], Denise Terroso[1]

[1]GeoBioTec, Department of Geosciences, Aveiro University, 3810-193 Aveiro, Portugal
[2]Exatronic, Lda., 3800-373 – Aveiro, Portugal

*tavares.rocha@ua.pt

The establishment of quality requirements of clayey products for medicinal, wellness, andaesthetic purposes are mainly sustained by the good interaction between the clayey formulation and the skin. The release of ionizable elements and their availability to percutaneous absorption should be, ideally, physiologically effective during passive percutaneous absorption. The solubility, molecular mass, depth of penetration, and toxicology of the clay components, while topic vehicle, need to be considered in the percutaneous absorption. Clayey products are promoted in the European market as therapeutic clays or aesthetics, which labeling combine characteristics of medicinal products along with cosmetics. Different countries regulate these products under different legal frameworks.

This study focuses on the mineralogical, chemical, and technological characterization of some clayey products available on the market, designed for topical use, framed in peloids concept, andclaimed as natural products. The main goals are to contribute to the establishment of clayey products quality criteria, as reliable scientific information, aiming the compliance of intended use, the information for the potential health hazards and toxicological effects of clayey products, and the distinction in what concerns therapeutic compliance and aesthetic or wellbeing products certification.

Thirteen clayed products for cosmetic purposes available online and commercial stores together with three thermal peloids were studied. Eight samples were obtained in a semi-solid formulation (paste) and the remaining samples were acquired in the form of powder. All samplesare indicated for dermal application, generally for face masks, cataplasm, or whole-body use. Sixof the samples were formulated with mineral thermal water. The paste samples are specially designed as peloids preparations ‘ready-to-use’. The labeled indications/information commonly included healing, cleanse, detox, absorbent, refreshing, calming, decongesting, and energizing actions. However, we can find that there is no harmonized labeled information as well for the usage and dosage indication. The expected adverse events are centralized in skin reactions and the safety alerts are based on eye and mouth avoidance.

Mineralogical composition of the sixteen studied samples reveals a polymineralic association with the presence of variable quantities of quartz, calcite, and feldspars whereas clay mineralsare predominant and characterized by the presence of a significant clayey fraction content, composed mainly by illite, smectite, and kaolinite in variable amounts and several mineral associations. The clayey products contain median values of 17 ppm As, 315 ppm Ba, 79 ppm Cr,11 ppm Co, 29 ppm Pb, 26 ppm Ni, and 62 ppm Zn. One sample presented 4.1 ppm of Cd.

The studied samples have safety concerns about specific limits of As, Ba, Cd, Cr, Co, Pb, Ni, and Zn which are above the regulated avoidable limits, and samples pH is out of range of skin’s natural pH.

Chemical evaluation of peloid formation with clay and thermomineral water

Ilgaz Nacakoğlu[1,*], Şıh Ali Sayin[2], Mukaddes Bolat[3], Köksal Köse[4], Serap İçöz[5]

[1]TURKAP Association President (Turkey Spa Talasso and Cure Centers Association), İstanbul, Turkey
[2]Clay Sciences Association, ankaya, Ankara, Turkey
[3]Ministry of Culture and Tourism Expert, İstanbul, Turkey
[4]Istanbul Medical Thermal Director and Peloid Producer, İstanbul, Turkey
[5]MTA General Management Office, Mineralogy and Petrographic Coordinator, Ankara, Turkey

*nacak9@hotmail.com

Clay has been used in wound treatment and skin cleansing since ancient times, depending on its physical and chemical structure. In the following periods, especially with the development of mineralogy, clay minerals, which are a raw material in the industrial field, are still used for therapeutic purposes in spas and mud baths. While our country has a rich potential in terms of clay minerals depending on its geological and geomorphic structure, it is also among the first in Europe in terms of geothermal resource wealth.

Peloidotherapy has been practiced empirically for millennia. It is known that natural muds and clays are used for rheumatism, arthritis, muscle and joint diseases, skin diseases, some cosmetic purposes, and it has been revealed in scientific studies that various clays are also consumed by eating. The demand and necessity of applying peloidotherapy in places where the natural mud is using for thousands of years and now a days started with decline or in places where there is no natural mud, has revealed the production of peloid by mixing some known clays with thermomineral waters. These peloids are still used for health and cosmetic purposes. In this study, we aimed to evaluate the result by investigating the chemical structure of the final product, peloid, after examining the chemical structure of the clay and thermomineral water used in the formation of peloid. Thus, we aimed to investigate whether there is any beneficial or harmful transformation in the chemical structure to the human organism.

For this purpose, clay samples taken from Eskişehir Mihalıççık region and thermomineral water sample taken from Istanbul Tuzla Historical İçmeler locality were examined and the results were evaluated by examining the peloid formed as a result of the mixing procedure of both substances.

Molecular dynamics simulation of pyocyanin adsorption on montmorillonite

Bidemi Fashina*, Youjun Deng, Randall T. Cygan

Department of Soil and Crop Sciences, Texas A&M University, College Station, TX 77843-2474, USA

*tokunbofash@tamu.edu

The planar three-ring pyocyanin is an important virulence factor in the resistance of *Pseudomonas aeruginosa* to antibiotics. In our earlier study aimed at inactivating and degrading pyocyanin, montmorillonite effectively adsorbed pyocyanin in the interlayer. However, the structure and the mechanism of pyocyanin—montmorillonite interaction remained unclear. Using molecular dynamics (MD), the structure and dynamics of hydrated (HMP) and dehydrated (DMP) pyocyanin–Na–montmorillonite were investigated.

All MD simulations were carried out with the LAMMPS package using a combination of ClayFF & CVFF as forcefields. The potential energies, radial distribution functions, density profiles, diffusion coefficients were computed for the MD simulations.

Pyocyanin was oriented subparallel to the clay surface resulting in an interlayer expansion of Na–montmorillonite from 9.8 Å to 13 and 13.7 Å for DMP and HMP, respectively. In dry conditions, the interlayer components of montmorillonite primarily interacted with pyocyanin while in moist conditions the dominant interaction is the coordination of Na^+ with water. In DMP, Na^+ was adsorbed close to the ditrigonal hole while pyocyanin molecules were in the midplane of the interlayer space (Fig 1.). The mechanism of interaction between montmorillonite and pyocyanin followed the trend: ion-dipole interactions: Na---O (≈2.5 Å) > Na---N (≈3.0 Å) > H-bonding (≈2.5 Å) between alkyl H and clay basal surfaces. In HMP, the Na^+ and pyocyanin molecules are distributed within the interlayer (Fig 1.). The mechanism of interaction between montmorillonite and pyocyanin followed the trend: Na---O (≈2.6 Å) > H-bonding (≈3.0 Å) between water and hydroxy of pyocyanin > Na---N (≈3.0 Å) > water bridged H-bonding (≈3.7 Å) between alkyl H and clay basal surfaces. The mobility of interlayer Na^+ and water was lower in HMP compared to pristine hydrated Na-montmorillonite.

These results elucidated the bonding mechanism between pyocyanin and the basal surface of montmorillonite and the importance of hydroxy oxygen and amine nitrogen in montmorillonite-pyocyanin interaction.

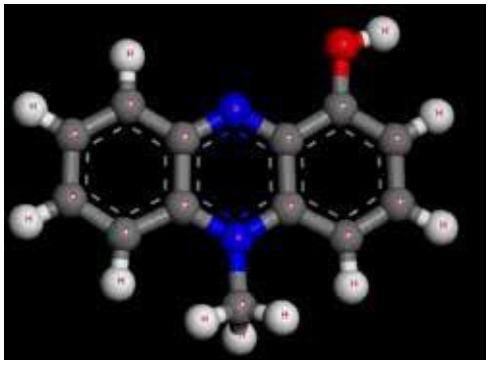


Figure 1. Atomic density profiles of dehydrated and hydrated pyocyanin-montmorillonite.

Hydrotalcite–niclosamide nanohybrid as an anti-SARS-CoV-2 strategy

Goeun Choi[1,2,3,*], Huiyan Piao[1], N. Sanoj Rejinold[1], Seungjin Yu[1,2], Jin-Ho Choy[1,4,5]

[1]Intelligent Nanohybrid Materials Laboratory (INML), Institute of Tissue Regeneration Engineering (ITREN), Dankook University, Cheonan 31116, Korea

[2]Department of Nanobiomedical Science and BK21 PLUS NBM Global Research Center for Regenerative Medicine, Dankook University, Cheonan 31116, Korea

[3]Department of Chemistry, College of Science andTechnology, Dankook University, Cheonan 31116, Korea

[4]Department of Pre-medical Course, College of Medicine, Dankook University, Cheonan 31116, Korea

[5]Tokyo Tech World Research Hub Initiative (WRHI), Institute of InnovativeResearch, Tokyo Institute of Technology, Yokohama 226-8503, Japan

*goeun.choi@dankook.ac.kr

COVID-19 has been affecting millions of individuals worldwide and, thus far, there is no accurate therapeutic strategy. This critical situation necessitates novel formulations foralready existing, FDA approved, but poorly absorbable drug candidates, such as niclosamide (NIC), which is of great relevance. In this context, we have rationally designed NIC-loaded hydrotalcite composite nanohybrids, which were further coated with Tween 60 or hydroxypropyl methyl cellulose (HPMC), and characterized them in vitro. The optimized nanohybrids showed particle sizes <300 nm and were orally administrated to rats to determine whether they could retain an optimum plasma therapeutic concentration of NIC that would be effec- tive for treating COVID-19. The pharmacokinetic (PK) results clearly indicated thathydrotalcite-based NIC formulations could be highly potential options for treating theongoing pandemic and we are on our way to understanding the in vivo anti-viral efficacy sooner. It is worth mentioning that hydrotalcite–NIC nanohybrids maintained a therapeutic NIC level, even above the required IC_{50} value, after just a single administration in 8-12 h. Inconclusion, we were very successfully able to develop a NIC oral formulation by immobilizing with hydrotalcite nanoparticles, which were further coated with Tween 60 or HPMC, in order to enhance their emulsification in the gastrointestinal tract.

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Through the history, traditional use of clays in Anatolia for medicinal purposes

Ilgaz Nacakoğlu

TURKAP Association President (Turkey Spa Talasso and Cure Centers Association), İstanbul, Turkey

nacak9@hotmail.com

For thousands of years, human beings have used various healing waters, plants, and muds from nature for health and beauty purposes.

Nature and return to natural which we observe too often in the world today, has also increased the use of natural products. The use of certain muds for medical purposes is called peloidotherapy. Anatolian lands are the cradle of civilization. When Anatolian history is analyzed, the use of thermo-mineral water, which started in Roman baths in its best-known form, has become widespread in Seljuks and Ottomans and became known worldwide.

These waters and muds have been used for health and beauty in these lands for thousands of years. Soil has been referred as the 'mother earth' and reckoned a living thing and was adopted as a mother, source of abundance, wealth and a habitat of sheltering, feeding and conserving livings. Being regarded as sacred by Turks throughout history, soil was also regarded as a medicine, source of cure and a means of treatment.

In Anatolian Turkish folk medicine, the soil is utilized in the administer treatment methods and techniques in the form of eating, licking, swallowing, drinking or washing by mixing with water, applying, setting foot in or lying on the ground and burying some objects in the ground.

In these, administer treatments by using the soil, besides religious and realistic applications, were utilized to transfer the disease to the soil as a non-living thing or to transfer the healing magical power to the human being through the soil.

Sorption characteristics of Newcastle disease virus with kaolin

Himanshu Yadav[1,*], Shubham Gaurav[2], T.V. Bharat[3], Sachin Kumar[4]

[1]Research Scholar, IIT Guwahati, Department of Civil Engineering, 781039, India
[2]Research Scholar, IIT Guwahati, Department of Bioscience and Bioengineering, 781039, India
[3]Professor, IIT Guwahati, Department of Civil Engineering, 781039, India
[4]Professor, IIT Guwahati, Department of Bioscience and Bioengineering, 781039, India

*yadav18b@iitg.ac.in

Newcastle disease virus can cause infection in more than 250 avian species and can lead to the generation of huge pathogenic waste due to such spread (Miller and Torchetti, 2014). A large number of carcass and infected excreta of avian species can lead to the transmission of pathogens to other species. There is lack of planning in management of such waste. The open dumping (Dersoet al., 2018), on farming burning (Abebe, et al., 2017), and incineration are most common ways fordisposal of such waste. This pathogenic waste also reaches to the municipal solid waste landfill without the knowledge of fate of viral pathogens. The landfilling of such waste one of the most viable option for waste management. The spread of pathogens from generated pathogenic waste canbe minimized by the containment of waste using spray of kaolin slurry. The biomedical waste disposal (BMW) facility can also be designed using kaolin as liner material. The sorption characteristics are most important parameters in designing such facility. The knowledge of sorption characteristics with varying dose of kaolin, and contact time etc. are important parameters. But suchstudies for adsorption of NDV on kaolin surface is not available.

In this study, Batch sorption study was conducted to understand the sorption parameters of kaolinite by varying contact time and dose of kaolin. Various isotherms like Langmuir and Freundlich were also fitted very well with the experimental data. The sorption study shows a high adsorption of viruson kaolin surface, which makes kaolin a suitable material for containment of such biomedical waste.

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TS10 Clays and Health

POSTER PRESENTATIONS

Prodrug system based on hectorite: a multidisciplinary study

Marina Massaro[1,*], Ana Borrego- Sánchez[2], Alberto López Galindo[3], Monica Notarbartolo[1], Paola Poma[1], Rita Sánchez-Espejo[3], C. Ignacio Sainz-Díaz[3], César Viseras Iborra[3,4], Serena Riela[1]

[1]Università degli Studi di Palermo, Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), 90128 Palermo, Italy

[2]Italian Institute of Technology, Center for Human Technologies, 16152, Genoa, Italy
[3]Andalusian Institute of Earth Sciences, CSIC-UGR, 18100 Armilla, Granada, Spain
[4]University of Granada, Department of Pharmacy and Pharmaceutical Technology, Faculty of Pharmacy, 18071, Granada, Spain

*marina.massaro@unipa.it

The development of specific systems able to deliver a chemotherapeutic agent in the target site, decreasing the side effects often associated with its administration, is still a challenging.

Clay minerals possessing interesting properties such as high biocompatibility, suitable particle size and morphology and specific surface area, represent since ancient times nanomaterials that can be safety used in medicine (Massaro et al. 2020). Among them, hectorite (Ht) is a natural layered magnesium-lithium silicate belonging to the smectite group. It is a trioctahedral clay mineral with an ideal chemical formula of $Na_{0.3}Mg_{2.7}Li_{0.3}Si_4O_{10}(OH)_2$. Recent studies have shown the great potentiality of Ht as drug carrier for application in biological field, regenerative medicine, and tissue engineering (Hoppe et al., 2011).

Herein we report the use of Ht as drug carrier system, by its covalent modification with methotrexate for anticancer treatment. To better understand the mechanism of cellular uptake of hectorite, we also report a systematic study of the Ht interaction with a phenanthroline by experimental and theoretical studies, to develop a fluorescent material. The latter was used to study the mechanisms involved in the cellular uptake of Ht by various endocytosis-inhibiting studies and fluorescence microscopy.

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Antitumor effects of nanomaterials based on clay minerals able to delivery chemotherapeutic drugs into different cancer cell lines

Rebecca Ciani[1,*], Marina Massaro[1], Monica Notarbartolo[1], Paola Poma[1], Rita Sánchez-Espejo[2], Riccardo Vago[3], Csar Viseras Iborra[2,4], Serena Riela[1]

[1]University of Palermo, Department of Biological, Chemical and Pharmaceutical Sciences and Technologies (STEBICEF), Palermo 90128, Italy

[2]Andalusian Institute of Earth Sciences, CSIC-UGR, Granada 18100, Spain

[3]San Raffaele Scientific Institute, Neurogenomics Unit, Milan 20132, Italy

[4]University of Granada, Department of Pharmacy and Pharmaceutical Technology, Faculty of Pharmacy, Granada 1807, Spain

*rebecca.ciani@unipa.it

Cancer therapy still presents a lot of issues both in terms of side effects and total recovery. The major drawbacks of systemic chemotherapy include limited drug selectivity, which results in cytotoxicity against rapidly dividing healthy cells, and development of drug resistance. On the other hand, drug penetration in solid tumors is a challenge, particularly due to barriers (Sriraman et al., 2014) and poorly organized vasculature (Minchinton & Tannock, 2006), with the likelihood of sub-therapeutic treatment exposure and, as a result, limited drug efficacy. Natural occurring clays have a variety of morphologies and physico-chemical characteristics that might be useful for drug loading while avoiding the common problem of other synthetic nanocarriers: cytotoxicity. Moreover, the use of clay minerals as drug carriers for cancer therapy can provide several benefits such as: improved drug pharmacokinetic, modified (Taroni et al., 2020) release, and co-delivery (Massaro et al., 2016). Herein we present the development of different carrier systems based on clay minerals (halloysite and hectorite) for the delivery of methotrexate and epirubicin for anticancer therapies. The synthetized nanomaterials were thoroughly characterized both from a physico-chemical and biological point of view. The obtained results suggest that the carrier systems based on clay minerals are promising for the delivery of chemotherapeutic drugs and it is possible to foresee a future application for local solid tumor therapy (Pasquale et al. 2020).

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Preliminary study of thixotropic hydrogels based on laponite and cucurbituril for topical delivery of lipophilic drug molecules

Raquel de Melo Barbosa[1,*], Serena Riela[2], Francesca Maestrelli[3], Marina Massaro[2], Beatrice Nencini[3], Csar Viseras Iborra[1,4]

[1]University of Granada, Department of Pharmacy and Pharmaceutical Technology, Faculty of Pharmacy, 18071, Granada, Spain

[2]Universit degli Studi di Palermo, Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), 90128 Palermo, Italy

[3]Universit di Firenze, Dipartimento di Chimica, 50019, Sesto Fiorentino-Firenze, Italy

[4]Andalusian Institute of Earth Sciences, CSIC-UGR, 18100 Armilla, Granada, Spain

*rbarbosa@ugr.es

In the last years, great technological progresses are achieved in the drug delivery with the goal to enhance several aspects like improving drug dissolution, improving stability, absorption properties, reduction of side-effects, prolonging release and consequent improving patient compliance, reduction of systemic toxicity in case of topical treatments, and so on.

Laponite^{Ò} (LAP) is a swelling and biocompatible synthetic clay (2:1 phyllosilicate), widely used for its ability to form thixotropic hydrogels with a “house-of-cards” structure. LAP hydrogels can interact with several species in different manner according to their nature (ion exchange, hydrogen bonding, van der Waals forces, protonation and ligand exchange at the edges of the crystal and so on) (Bezerra Motta Cmara et al. 2021).

Cucurbiturils (CB) are cyclic oligomers of glycoluril units (6, 7 and 8 that corresponding to CB[6], CB[7], CB[8], respectively) which can exhibit host–guest chemistry like cyclodextrins. In addition, it is known that CB macromolecules form stable organic/inorganic nanomaterials with clay minerals, by interactions both between portal carbonyl groups of CBn and the positively charged alumina groups of clay (via hydrogen bonds formation Al-OH–O=C-) and electrostatic forces between the negatively siloxane groups of clay and the partial dipole of carbonyl groups of CBn (Massaro et al. 2016).

Herein we report a preliminary study of a new hydrogel based on LAP/CBn for topic drug delivery. As drug model, we choose the flufenamic acid (FFA), a class II drug with poor solubility and high permeability (Maestrelli et al. 2016).

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Intercalation of a neuroprotective drug in Laponite and development of cellulose-based materials for its oral administration

Isaac Bravo[1,2], Lucía Viejo[2], Cristóbal de los Ríos[2], Eva M. García-Frutos[1], Margarita Darder[1,*]

[1]Instituto de Ciencia de Materiales de Madrid (ICMM), CSIC, Madrid, 28049, Spain
[2]Instituto Teófilo Hernando, Departamento de Farmacología y Terapeutica, Facultad de Medicina, Universidad Autónoma de Madrid, Madrid, 28029, Spain

*darder@icmm.csic.es

The study of multitarget neuroprotective drugs is a therapeutic strategy for the treatment of neurodegenerative diseases such as Alzheimer's. Multitarget therapies began in the 1990s and, over time, new multitarget drugs with innovative pharmacological actions have been developed, such as the family of indoles and aza-indoles derived from the gramine alkaloid (Lajarin-Cuesta, et al., 2018). In this context, our objective is to design an appropriate formulation for the oral administration of these drugs, developing hybrid and bionanocomposite materials based on clays. In particular, layered clays have been widely studied as drug carriers to facilitate their oral administration and provide controlled drug release (Viseras et al., 2010). In this work, an indole derivative was adsorbed in Laponite® (Lap), using the commercial product Laponite® XLG. X-ray diffraction confirmed the intercalation of the drug in the interlayer region of the clay, and the elemental chemical analysis indicated a loading of 62.3 meq/100 g Lap. This amount is very close to the cation exchange capacity (CEC) of Lap (63 meq/100 g), suggesting a complete exchange of sodium cations in the interlayer space of Lap. Per se toxicity studies of the hybrid in the SH-SY5Y neuronal line were carried out and its neuroprotective effect against okadaic acid, a selective inhibitor of the protein phosphatase 2A (PP2A), was evaluated, observing that it is not toxic and continues to offer neuroprotection similar to that of the non-encapsulated drug. The release tests of the hybrid material carried out in media that simulate the gastrointestinal tract indicated a release of drug in acid medium close to 25%. In order to minimize release in such conditions and provide a sustained delivery in the simulated intestinal fluid, the hybrid was encapsulated in a micro/nanocellulose matrix processed as microbeads with a pectin coating for additional protection. Alternatively, low density materials composed of the hybrid dispersed in a microcellulose/pectin matrix were evaluated as orodispersible tablets to provide an alternative way of administration of the neuroprotective drug.

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Hydrogel based in nanoclay as pharmaceutical carriers of tuberculostatic drug

Raquel de Melo Barbosa[1,2,*], Fernanda P. Santos Reginaldo[3], Rita Sánchez-Espejo[1,2], César Viseras[1,2], Tulio Moura[3], Raquel Brandt Giordani[3], Marina Massaro[4], Serena Riela[4], Fernanda Raffin[3]

[1]University of Granada, Department of Pharmacy and Pharmaceutical Technology, Faculty of Pharmacy, 18071 Granada, Spain

[2]Andalusian Institute of Earth Sciences (CSIC-UGR), 18100 Armilla, Granada, Spain

[3]Department of Pharmacy, Federal University of Rio Grande do Norte, 59010-180 Natal, Brazil

[4]Università degli Studi di Palermo, Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), 90128 Palermo, Italy

*rbarbosa@ugr.es

Recently, hydrogels have attracted increasing attention and have become a major research subject (Aguzzi et al., 2007). They can form depots for localized, sustained release of drug use in biomedical applications, including soft tissue engineering scaffolds, stem cell culture biosensors, tissue fillers. Specifically, Laponite RD (LAP) is a swelling and biocompatible nano-clay composed of layered synthetic phyllosilicates with an octahedral MgO sheet sandwiched between two tetrahedral silica sheets and a chemical formula given by: $Na^{+0.7}[(Si_8Mg_{5.5}Li_{0.3})\ O_{20}(OH)_4]^{-0.7}$. It is widely used as a mechanical cross-linker to create hydrogels with robust mechanical properties. Furthermore, LAP on its own is commonly utilized in the industry as a rheological additive due to its ability to form gels when dispersed in polar solvents such as water, exhibiting negative charges (Tomás et al., 2016). In contrast, the edge charges are pH-dependent, forming a particulate network gel with a house-of-cards structure. This work focuses on the studies of intrinsic properties of hydrogels formed between LAP nanoparticles with isoniazid (INH), an antibiotic used to treat tuberculosis disease. The nanocomposites were prepared by adding different concentrations of LAP (1-3%, w/w) to water under constant stirring and adding INH. After drying, the samples obtained were evaluated by Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), X-ray powder diffraction (XRD), and high-resolution microscopy (HRTEM). Results presented the inclusion of INH in the LAP structure. They can provide a solid basis for designing new sustained-release pharmaceutical formulations based on nanohybrids for tuberculosis treatment.

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Assessment of clay/spring water formulation as thermal mud

Beatrice Nencini[1], Rita Sánchez-Espejo[1], Raquel de Melo Barbosa[1], Fátima García-Villén[1], Imen Khiari[2], Marina Massaro[3], Serena Riela[3], Alberto López-Galindo[4], César Viseras[1,4,*]

[1]University of Granada, Department of Pharmacy and Pharmaceutical Technology, Faculty of Pharmacy, 18071 Granada, Spain

[2]Georesources Laboratory of Water Research and Technologies Center (CERTE), Technopole Borj Cedria, BP273 Soliman, Tunisia

[3]Università degli Studi di Palermo, Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), 90128 Palermo, Italy.

[4]Andalusian Institute of Earth Sciences (CSIC-UGR), 18100 Armilla, Granada, Spain.

*cviseras@ugr.es

Clays are used in various pharmaceutical and cosmetic applications as active ingredients or excipients (Viseras et al., 2007; Moraes et al., 2017). In particular, they are used as a fundamental ingredient of the thermal muds used in medical hydrology. The therapeutic effects of thermal muds have been explained by the combination of thermal, mechanical, and chemical mechanisms. Their main effects are directly related to the conductive heat transfer between the heated applied thermal mud and the skin. As topical semisolid dosage forms, they require a suitable consistency for the application and enough viscosity to remain in contact with the application area. The pH is also important because if it is too acid or basic, it could modify the skin's physiological balance, properties, and physiology.

With these premises, the aim of this study was to formulate and characterize a clay/spring water hydrogel as thermal mud to be used in medical hydrology. To formulated the thermal mud, a purified clay mineral sample (Veegum HS©, montmorillonite) was used as solid phase, and traditional medicinal water from Caldane (Italy) was used as liquid phase. The hydrogel was rheological and thermal characterized at different times. pH was also measured without any change. The studied system showed non-Newtonian, pseudoplastic behavior. Apparent viscosity values were obtained from flow curves. Thermal analyses results were able to assure heat transfer, therefore, the thermal efficacy of the system. The obtained results suggest that the system formulated with VHS clay and Caldane water shows adequate properties as thermal mud.

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TS11 History of Clay Science

ORAL PRESENTATIONS

The counter intuitive behavior of potassium bearing clay minerals regarding the exchange process: Focus on the pioneer experiments performed

Hubert Fabien

IC2MP-Hydrasa, UMR 7285 CNRS, Université de Poitiers, 86022 Poitiers, France

fabien.hubert@univ-poitiers.fr

Clay minerals such as micas (muscovite, biotite, phlogopites), illites or glauconites have been widely studied in Soil Science since the beginning of the 20th century because of their potential ability to provide potassium (K) for plant growth. Cation exchange leading to the transformation of K-bearing clay minerals into swelling clay minerals such as smectite or vermiculite is by far the dominant process mentioned in the literature. Although the mechanism allowing the exchange of interlayer potassium from trioctahedral clay minerals (layer charge decreases by oxidation of octahedral Fe^{2+}) was evidenced, the mechanism at the origin of potassium exchange for dioctahedral K-bearing clay minerals is less clear. For muscovite, interlayer potassium is generally considered as fixed whereas for illite, interlayer potassium can be potentially replaced.

Several laboratory experiments were performed by Professor A.D. Scott and co-workers in the 60's regarding the exchange process of K-bearing clay minerals. They experimentally demonstrate some counter intuitive behaviour of K-bearing clay minerals regarding the exchange process such as: i) the amount of exchangeable potassium from K-bearing clay minerals decrease with the decrease of particle size whatever their crystal chemistry (Scott, 1968); ii) For illites, the total amount of interlayer potassium cannot be exchanged leading to interstratified crystal structures constituted by illite and swelling layers (Smith, 1967); iii) main part of the resulting swelling layers differ from smectite or vermiculite layers and exhibit a specific layer to layer distance of ~12 Å, whatever the exchangeable cation used.

These pioneer experiments will be bringing to the light in order to show their importance to explain past andpresent observations in field or laboratory experiments dealing with K-bearing clay minerals.

Scott A. D. (1968) Effect of particle size on interlayer potassium exchange in micas. In 9th International Congress of Soil Science Transactions, 2, 649–660.

Smith S. J. (1967) Susceptibility of interlayer potassium in illites to exchange. Iowa State University of Science and Technology. Ph.D.

A history of The Clay Minerals Society

Kevin Murphy[1,*], Steve Guggenheim[2], Warren Huff[3]

[1] The Clay Minerals Society, Chantilly, Virginia, USA
[2] Steve Guggenheim, The University of Illinois and Chicago, USA
[3] Warren Huff, University of Cinninnatti at Ohio, USA

*kevin.murphy@clays.org

The Clay Minerals Society was officially founded in 1962. This followed 10 years of 'clay' meetings organized under the auspices the National Academy of Sciences.

It is now a healthy, international membership organization which publishes its journal *Clays and Clay Minerals* in conjunction with publishing partner SpringerNature. It also runs annual meetings, offers generous student grants, awards prizes to leading clay scientists, runs the Source Clays Repository, the Reynolds Cup, the *Glossary of Clay Science*, and is involved in the 'Images of Clay' gallery.

- What prompted the founding of this organization?
- Who have been the leaders of this Society since its inception?
- What were the major developments in the 60 years since foundation?
- How has its existence benefited science?
- What are the many related industries which rely on clay science?
- What role does the Society's work play in environmental remediation?

This presentation will answer these questions and many more about the existence of this leading clay science society.

History of clay science in Turkey

Asuman Günal Türkmenoğlu[1,*], Selim Kapur[2,]**

[1]Middle East Technical University, Department of Geological Engineering, Ankara, Turkey
[2]Çukurova University, Department of Soil Science and Plant Nutrition, Adana, Turkey

*asumant@metu.edu.tr; **kapurs@cu.edu.tr

The use and application of clays in Turkey dates back to prehistorical times as examplified by the manufacturing of clay balls and geometric objects in Çatalhöyük settlement around 10000BC. During the later periods of history, such as the Ottoman period, various clays (e.g.tin-i- mahtum/terra sigillata) were used for medical/healing purposes. Since the early 19th century modern educational institutions and medical schools were found. Istanbul University is the firstpublic research university located in Istanbul, Turkey, re-established in 1846 as the first Ottoman higher education institution based on European traditions. Geology and mineralogy education was first started in 1900 at the Natural Science Department at the İstanbul University.The University was reorganized following the educational reforms and the classes officially began in1933.Since then many universities were found including geology and soil science departments , where courses on mineralogy and clays were thoroughly taught.Establishment ofthe General Directorate of Mineral Research and Exploration (MTA) in 1935 accelerated geological mapping, exploration and laboratory studies of metal, coal, petroleum and industrialmaterials including kaolin, bentonite, bauxite, borate etc. deposits which affected the development of aluminum, glass, ceramic paper and cement industries in Turkey. Likewise soil and land use mapping and subsequent research on soil properties coupled with clay minerals were commenced by the establishment of the General Directorate of Soil and Water Conservation (TOPRAKSU) in the early 1950s and the University of Ankara laboratories since1933. The clay minerals of the soil classes were utilised in interpreting these maps for soil fertility, erosion and irrigation purposes.

Clay Science Society and Soil Science Society of Turkey were founded in 1983 and 1964 respectively, have missions specific to clay-and soil-related issues. They are the representativesof international clay and soil science associations. Their activities mainly include the organization of national and international conferences, symposiums, workshops; make publications related to clay and soil science and applications; contribute the awareness of publicand young scientists on the importance of clays and soils in interdisciplinery research and applied studies.

The need and advancement of clay studies are supported by many universities, governmental and private institutional and research organizations in Turkey. In this presentation the eminentclay and soil scientists as well as the organizations who contributed to the development of teaching, research and applications related to the clays, clay minerals and soils in Turkey are summarized.

From the Groupe Français des Argiles to the Association Internationale Pour l'Etude des Argiles:A subjective journey into the French Clay Group history

Bruno Lanson

Univ. Grenoble Alpes, CNRS, Univ. Savoie Mont Blanc, Univ. Gustave Eiffel, IRD, ISTerre, F-38000, Grenoble, France

bruno.lanson@univ-grenoble-alpes.fr

The French National Center for Scientific Research (CNRS) was created at the dawn of WWII (Oct. 19th 1939) to coordinate scientific activity in France, its activity surging after the post-war reconstruction period. In this period of intense increase and structuring of French scientific activity, Mr. Joseph Peres who then was adjunct to the CNRS director officially established the French Clay Goup (GFA) as a CNRS commission on Feb 28th 1950. Pr. Jean Orcel, a mineralogist from Natural History National Museum (MNHN, Paris) who devoted his early career to the chemical characterization of chlorites and of their H_2O content, was nominated as its first president, Mrs Simonne Caillère (also a mineralogist at MNHN) and Stéphane Hénin (a soil scientist and agronomist) acting as secretaries. Creation of this French Clay Group commission gave an official status to the group of scientists created right after WWII and interested in "clays and clay minerals". Presentations given at these group meetings were published as early as 1949 as proceedings, that became the "Bulletin du GFA" in 1955 and finally Clay Minerals in 1976 when the various publications of European Clay Groups (Belgium, Spain, France, Italy, DTTG, Nordic countries, UK) merged.

In the meantime, the French Clay Group became independent from CNRS (1969) to reach its present sta-tus. 70+ years after its official creation, it is probably time for a (totally subjective) journey in the GFA history and of its evolution towards its present status. I will take advantage of this journey to report on some scientific contributions from its former members and of the influence members of the French clay community have had on the shaping of the international clay community. This influence translates for ex-ample in the French origin of the AIPEA (Association Internationale Pour l'Etude des Argiles) acronym,but more discrete contributions appear in clay mineral nomenclature and or mineral naming.

Activity of The Clay Science Society of Japan (CSSJ)

Toshihiro Kogure

The University of Tokyo, Department of Earth and Planetary Science, Graduate School of Science, 113- 0033, Japan

kogure@eps.s.u-tokyo.ac.jp

The Clay Science Society of Japan (CSSJ, http://www.cssj2.org/english/) is Japan's only academic organization in clay science established for the progress of basic and applied research on clays and clay-based materials, dissemination of the research results, and promotion of communication among members and non-members inside and outside Japan. The origin of CSSJ can be stretched back to 1957, when the first domestic symposium of clay science was held under the leadership of Japanese distinguished clay scientist, Prof. Toshio Sudo. This symposium was followed by the establishment of Clay Research Group of Japan (the predecessor of CSSJ) having Prof. Sudo as the president. After that, CSSJ was established officially in 1963.

The number of CSSJ members at present is about 330, including honorary-, senior-, student-, and supporting-members. According to our policy, the society consists of members with various backgrounds, including geoscience/resource, chemistry/material science, soil science/agriculture, construction/civil engineering, environmental science, etc. Every year we award a regular member, a few young members, etc. to encourage their activities.

Annual meeting (Clay Science Symposium) with two days' period is held in Japan, where more than one hundred members/non-members attend. The meeting includes oral presentations, poster sessions, special symposium, and field excursion.

With respect to publication, CSSJ publishes "Clay Science", a quarterly journal in English mainly issuing original papers from 1960 (http://www.cssj2.org/english/clay_science_e/). All published papers are freely accessible via J-STAGE, an electronic journal platform for science and technology information in Japan (https://www.jstage.jst.go.jp/browse/jcssjclayscience). We publish another journal, "NENDO KAGAKU" written in Japanese, generally three times a year, for issuing original papers, reviews, information for the members, etc. (http://www.cssj2.org/english/nendokagaku_e/). Moreover, we have published a handbook of clays and clay minerals written in Japanese in 1967 (and revisions in 1987 and 2009) to promote clay science in Japan.

As another important activity, CSSJ serves clay mineral samples (CSSJ Reference Clay Samples) which were supplied by domestic companies, for research activities of clay. At present, we are supplying seven samples to researchers inside and outside Japan. More details are available at http://www.cssj2.org/english/reference_clay_e/.

Finally, CSSJ is ready to contribute to the international activity of clay science. CSSJ invited International Clay Conference twice (1969 and 2005) in Japan and organized the first Asian Clay Conference in 2010. We are also managing a foundation to financially support young members or students to attend international conferences related to clay science held in foreign countries.

TS12 Soil Mineral Quantification

ORAL PRESENTATIONS

Improving accuracy of quantitative x-ray diffraction analysis through machine learning

Rachel E. Drapeau[1,*], Barry R. Bickmore[1], Emily J. Evans[2]

[1]Brigham Young University, Department of Geological Sciences, Provo, UT 84602 USA
[2]Brigham Young University, Department of Mathematics, Provo, UT 84602 USA

*mrachele@byu.edu

Quantitative X-ray diffraction analysis (QXRD) is an inexpensive method to quantify the relative proportions of mineral phases in a rock sample. However, the analytical software available for QXRD requires extensive user input to choose phases to include in the analysis. Consequently, analysis accuracy depends greatly on the experience of the analyst, especially as the number of phases in a sample increases (Raven & Self, 2017; Omotoso, 2006). The purpose of this project is to test if incorporating machine learning methods into QXRD software can improve the accuracy of analyses by assisting in the phase- picking process. In order to provide a large enough sample of X-ray diffraction (XRD) patterns and their known compositions to train the machine learning models, we created a dataset of millions of calculated XRD patterns of realistic mineral mixtures. These synthetic XRD patterns were calculated using crystal structure files from the American Mineralogist Crystal Structure Database (AMCSD) with mineral occurrence data from the Mineral Evolution Database (MED) to mimic geologic knowledge used by expert analysts. Using this dataset, we trained and refined a variety of machine learning models to determine which model is most accurate in identifying the correct mineral phases.

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Augmenting the full-pattern summation method for analysis of X-ray powder diffraction patterns with Rietveld calculations

Barry R. Bickmore[1,*], Emily J. Evans[2]

[1]Brigham Young University, Department of Geological Sciences, Provo, UT 84602 USA
[2]Brigham Young University, Department of Mathematics, Provo, UT 84602 USA

*barry_bickmore@byu.edu

Both full-pattern summation and the Rietveld method are popular for applying quantitative phase analysis (QPA) to X-ray powder diffraction (XRPD) patterns of mineral mixtures, but have different attractions. While the Rietveld method generally takes less effort to apply, it is often less useful than full-pattern summation for samples that include amorphous phases, or even poorly crystalline phases like clay minerals. The Rietveld method involves fitting an experimental pattern with a linear combination of synthetic patterns derived from known crystal structures, while simultaneously fitting the parameters of peak-shape functions (and sometimes preferred orientation functions) to the patterns of the individual phases. One advantage of this approach is that no special sample preparation is required, because preferred orientation and differences in particle size distribution are adjusted for in the calculation. Another is that it is easy to find many thousands of archived crystal structure files, including several chemical variations of common (and sometimes uncommon) minerals. However, with XRPD patterns cannot be calculated for amorphous materials, so the most that can be done is to calculate by subtraction the total amount of amorphous material present. And while it is possible to calculate XRPD patterns for clay minerals exhibiting rotational disorder, etc., this would add even more adjustable parameters to an optimization routine that is possibly already overburdened.

Full-pattern summation, by contrast, involves collecting a library of experimental XRPD patterns for pure phases with associated reference intensity ratio (RIR) values, and fitting the XRPD pattern of the mixture (plus an internal standard) with a linear combination of a set of patterns from the library. Amorphous and disordered phases can easily be accommodated, and the optimizations are often more robust than in the Rietveld method, given that they involve far fewer adjustable parameters. However, preparation of both the library of standards and samples requires rigorous procedures to ensure reproducible particle size distributions and random orientation, and it is often impossible to find pure samples of some phases.

We are building software that would perform QPA using the full-pattern summation method, augmented by standards fitted to difference patterns, in cases where certain minerals are suspected to be present, but cannot be easily added to the library of standards. Rietveld calculations will also be used to remove and correct for impurities when preparing standards. This approach will at least partially address the disadvantages of full-pattern summation.

Bentonite XRD powder quantitative analysis using Rietveld refinement: revisiting and updating bulk semiquantitative mineralogical compositions

Jaime Cuevas[1,*], Miguel ngel Cabrera[1], Ral Fernández[1], María Jess Turrero[2], Ana Isabel Ruiz[1]

[1]Universidad Autónoma de Madrid. Geología y Geoquímica, Madrid 28049 Spain
[2]CIEMAT. Avd. Complutense 40, Madrid, 28040 Spain

*Jaime.cuevas@uam.es

Bentonite is a complex mineralogical mixture. It is composed of montmorillonite, illite, and accessory minerals, like quartz, cristobalite, feldspars, carbonates and minor iron oxy-hydroxides. It originates from moderate temperature hydrothermal alteration of intermediate or acidic volcanic rocks. Sources of its heterogeneity are: (1) raw material is extracted in different locations in the same quarry: resulting of different chemistries for the same mineral(feldspars solid solutions); (2) montmorillonite and illite are poorly crystalline phases; montmorillonite change in the type of exchangeable cation and illite can be interstratified within smectite sheets; and (3) hardness and size of accessory minerals are high in comparison of clay minerals, theerefore uniform grinding of bentonite is not possible. FEBEX bentonite is the Spanish reference for research in the confinement of high level radioactive waste. It is very stable under repository conditions (< 100 ºC). Changes in bentonite properties are needed to study in long-term experiments (7-14 years). One example is the hydration of a bentonite block under a thermal gradient generated by heating a disk of iron powder (metal waste canister). The iron-bentonite interaction is studied towards a hydration front forced to ocurr in the opposite direction. The XRD powder profiles of bentonite are very similar and, in order to minimize the bias of semi-quantitative determination methods, Rietveld refinement has been used (BGMN software Profex interface; Döbelin & Kleeberg, 2015). 2-70 $^{0}2\theta$ patterns have been refined using structural models of albite, anortite, calcite, cristobalite, muscovite1Md (illite), smectite_di2w, goethite and hematite. The confidence in quantification of the major phases allow to discuss small changes observed in bentonite, i.e. the presence of hematite in the heated dry iron zone and goethite near the hydration source. Smectite content 72 ± 3% and addition of illite 1Md phase improves hk0 lines profile refinement, consistent with the presence of illite randomly interstratified in this bentonite (Cuadros & Linares, 1995).

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Development and evaluation of a disorder structure model of hydroxy-interlayered smectite (HIS) for Rietveld refinement

Dietel Jan[1,*], Dohrmann Reiner [2,3], Ufer Kristian[2], Kaufhold Stephan[2], Gröger-Trampe Jens[3], Bertmer Marko[4]

[1]LLBB, State Laboratory Berlin-Brandenburg, 12489 Berlin, Germany
[2]BGR, Federal Institute for Geosciences and Natural Resources, 30655 Hannover, Germany
[3]LBEG, State Authority of Mining, Energy and Geology, 30655 Hannover, Germany
[4]University Leipzig, Felix-Bloch-Institute for solid state physics, 04103 Leipzig, Germany

[*]jan.dietel@landeslabor-bbb.de

The process of acidic weathering of soils is a worldwide problem. During this process, Al^{3+} is dissolved from silicates such as feldspars or chlorites by selective dissolution. Al^{3+}, e. g. either precipitates as $Al(OH)_3$ or is transported to swellable clay minerals such as smectite, vermiculite or interstratifications including smectitic or vermiculitic layers. Al^{3+} intercalates replacing hydrated Na^+ or Ca^{2+} Mg^{2+} cations, and polymerizes in the interlayers forming "island-like" structures and the resulting phases are called hydroxyl-interlayered minerals (HIMs). This process is difficult or impossible to reverse. The final stage of this process are acidified soils with drastically reduced cation exchange capacity and water holding capacity. These soils thus lose their buffering capacity and are unusable for many plants and especially agricultural use due to the lack of soil fertility. This process is known for decades but still cannot be described sufficiently using mineralogical methods, especially X-ray diffraction (XRD), which is the most common method for mineral quantification. Due to the lack of crystal structure models, the frequently used method of Rietveld refinement cannot be applied. The goal of this research was to create a disorder structure model for hydroxy-interlayered smectite (HIS) to be able to quantify this phase in soil samples. Firstly, a synthetic HIS sample set was created by treating Milos bentonite with 0.1 mol/L $AlCl_3$ solution with different reaction times and sample-to-$AlCl_3$ ratios. The resulting sample set consists of a continuous series of HIS samples with different degrees of hydroxy-interlayering ranging from 0 to 96 % mol/mol smectite/HIS. These samples were characterized in detail using the following methods: XRD, Infrared spectroscopy, X-ray Fluorescence spectrometry, Fe^{2+}:Fe_{total} determination, Nuclear Magnetic Resonance spectroscopy, Simultaneous Thermal Analysis coupled with mass spectrometry and Cation Exchange Capacity. It was found that hydroxy-interlayering evolved in-situ in the smectite interlayers by polymerization and that hydroxy-interlayering consists of a number of small oligomers (mono to pentamers) instead of a few large oligo- or polymers. Subsequently two structure models for hydroxy-interlaye red smectite (HIS) were created, one for the air-dried condition (collapsed, one water, to water hydration state) and one to describe the ethylene-glycol saturated condition. Both models are able to describe both, preferred oriented patterns and powder patterns including the turbostratic disorder typical for smectite and HIS. The models were evaluated using the synthesized samples and the calculated and the refined values for the degree of hydroxy-interlayering were compared. Four out of eight samples were chosen to create synthetic mixtures with clinochlore, muscovite, quartz, and albite to prove the correctness of the quantification results. The outcome of this study is a new structure model which opens the possibility to characterize and quantify HIS in acidicly weathered soils using XRD and the Rietveld refinement technique.

Dietel, J., Gröger-Trampe, J., Bertmer, M., Kaufhold, S., Ufer, K., Dohrmann, R. (2019) Crystal structure model development for soil clay minerals – I. Hydroxy-interlayered smectite (HIS) synthesized from bentonite. A multi-analytical study. *Geoderma*, https://doi.org/10.1016/j.geoderma.2019.03.021

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TS13 Clay Geochronology

ORAL PRESENTATIONS

Extracting radiometric ^{4}Ar-^{39}Ar ages in a three-component system: an example from the Tatra Mountains, Poland

Artur Kuligiewicz[1,*], Marek Szczerba[1], Michał Skiba[2], Chris M. Hall[3]

[1]Institute of Geological Sciences, Polish Academy of Sciences, 31-002, Krakow, Poland
[2]Institute of Geological Sciences, Jagiellonian University, 30-387 Kraków Poland
[3]Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48109-1005, USA

*ndkuligi@cyf-kr.edu.pl

Interpretation of the ^{40}Ar-^{39}Ar dating results for a clay-bearing rocks is a complicatedtask, especially when working with material what can possibly contain more than two populations of K-bearing phases. Such a situation can arise when dating fault-related rocks, such as clay gouges, from the areas with a history of multiple reactivation episodes.

In order to resolve some issues connected with dating of multiphase mixtures, a new interpretative concept is introduced, which allows the extraction of ^{40}Ar-^{39}Ar or K-Ar age values in a three- component system (3C). The approach was tested on ^{40}Ar-^{30}Ar data coming from a clay gouge samplefrom the Tatra Mountains, Poland. The results werecompared against Illite Age Analysis (IAA), which is a well-established interpretative concept (Pevear,1992) (Figure 1).

The newly developed method produced results comparable with IAA approach. Both methods returned very large uncertainties for the calculated age values, which was caused by the small range ofillite polytype contents among the dated size-fractions.

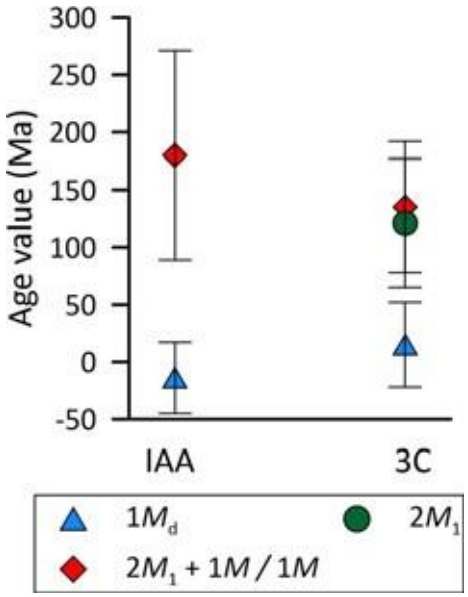


Figure 1. Comparison of age values obtained for different illite polytypes with IAA and 3C approaches.

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Validation of a procedure for high-precision determination of $^{40}Ar^{*}/K$ in clay

J. M. Wampler*, W. Crawford Elliott

Georgia State University, Geosciences Department, Atlanta, GA 30302, USA

*marionwampler@earthlink.net

Since the inception of the conventional K-Ar geochronologic method around 1950, the K content used for an age calculation has, with few exceptions, been determined on a different test portion than the one from which Ar was extracted for isotopic analysis. As others have noted, weighing errors and sample inhomogeneity contribute to the uncertainty of an age value obtained in this way, and weighing error precludes accurate dating of very small samples. One of several advantages of the ^{40}Ar-^{39}Ar method over the conventional K-Ar method is that, in the former, K and $^{40}Ar^{*}$ from a single test portion are determined simultaneously, so weighing error and sample inhomogeneity do not contribute analytical error to calculated age values.

Because clay particles are very small, most of the Ar within them is released quickly as they are heated at temperatures less than 1000°C. Argon can be extracted from clay held within copper-foil capsules (melting temperature about 1050°C) by heating the capsule and its contents to about 1000°C, and the capsule then can be recovered for determination of the K therein. Validation of this approach to K-Ar dating requires demonstration that, in such a process, essentially all of the radiogenic Ar and virtually none of the K in the encapsulated clay leaves the capsule while it is heated. For some years, this single-test-portion procedure has been used for K-Ar dating of clay in Atlanta (first at Georgia Institute of Technology and later at Georgia State University). Validation data have been included in several published papers (Stephens et al., 2007; De Man et al. 2010; Stroker et al., 2013; Vandenberghe et al., 2014), but none of these includes the complete set of available data for different clay minerals.

That essentially all radiogenic Ar is released from glauconite pellets by heating for at least 10 minutes at or near 1000°C has been confirmed by several demonstrations that repeated heating under the same conditions releases radiogenic Ar in an amount less than 1% of the originally released amount. The same is true for clay samples containing discrete illite and illite-rich illite-smectite. Final confirmation of this aspect of the work is to be done by isotopic analysis of Ar released by complete fusion of the residue from 1000°C-heating of some old, highly illitic clay samples. That virtually all of the K from 1000°C-heated glauconite and illite remains within the copper-foil capsules has been confirmed by K measurements of HF-extracts of the interiors of fused-quartz tubes that held capsules as they were heated. The amounts of K in many such extracts show that much less than 1% of the K in these clays leaves the capsules during heating.

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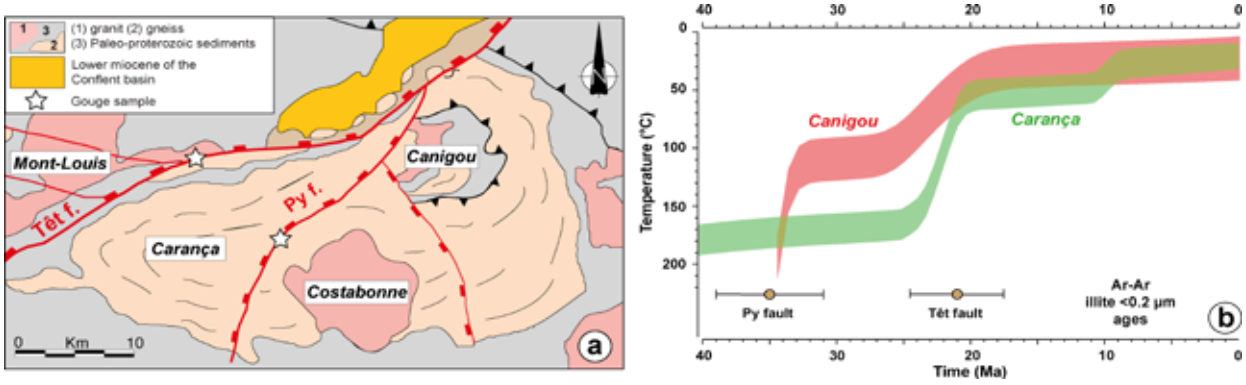
Dating fault activity in the Eastern part of the Pyrenees: a combined approach low temperature thermochronology and $^{40}Ar/^{39}Ar$

Gaétan Milesi[1,*], Delphine Charpentier[1], Patrick Monié[2], Henri Leclre[1], Philippe Mnch[2], Aoutmane Bouaoudi[1], Martine Buatier[1], Pierre Trap[1], Roger Soliva[2], Arthur Iemmolo[2]

[1]Chrono-Environnement, UMR 6249-CNRS, Université Bourgogne Franche-Comté, Besançon, France
[2]Géosciences Montpellier, Université de Montpellier, CNRS, Université des Antilles, Montpellier, France

*gaetan.milesi@univ-fcomte.fr

Eastern Pyrenees relief is inherited from both the Eocene collision between the European and Iberic plates and from the Neogene extension link to the Gulf of Lion opening. In this study area, the Têt and Py faults are two major regional faults which allow the exhumation of the Canigou and Carança massifs (Fig. a). To better understand the tectonic evolution of the eastern Pyrenees thermal evolution of different massifs have been modelled using thermochronological data (Maurel et al. 2003; Milesi et al., 2020). The new thermal modelling (Fig. b) reveals a Priabonian (35-32 Ma) cooling stage only record in the Canigou massif. During the upper Oligocene and lower Miocene (26-19 Ma) an important cooling event is recorded in both massifs and a late Serravalian-Tortonian (12-9 Ma) cooling stage occurred in the Carança massif. The outcrops of the Têt and Py faults show metric scale core zone, suggesting importantdisplacement on the fault. XRD and SEM analyses performed on these gouges make in evidencethe presence of newly formed illite < 0.2 µm. Different granulometric fractions have been datedwith $^{40}Ar/^{39}Ar$ method to highlight period of fault activity under brittle regime associated to illite formation. Illite ages obtained are respectively of 35 ± 4 Ma for the Py fault and 21 ± 3.5 Ma for the Têt fault. These results are consistent with the regional main cooling phases recorded by the low temperature thermochronology. Results obtained open new questions about the extent of faultmovement and the temperature conditions necessary to the generation of illite in the fault zone.



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Crystallinity, K-Ar dating and stable isotopic analyses of clay alteration in the Patterson Lake Corridor, Athabasca Basin, Saskatchewan, Canada

Jeanne B. Percival[1,*], Jeremy W. Powell[1], Kenzie Gracequist[2], Igor Bilot[1], Alain Grenier[1]

[1]Geological Survey of Canada, Natural Resources Canada, Ottawa, ON, Canada K1A 0E8
[2]Department of Earth Sciences, Carleton University, Ottawa, ON, Canada K1A 5B6

*Jeanne.Percival@NRCan-RNCan.gc.ca

The Patterson Lake corridor (PLC) along the southwestern margin of the Paleoproterozoic Athabasca Basin contains high-grade uranium deposits entirely within crystalline basement rocks. A suite of clay alteration samples was collected from a series of deposits and prospects across this exploration corridor. The samples represent hydrothermal alteration associated with mineralized shear zones and alteration haloes surrounding the deposits. Various silt and clay-size fractions were separated using centrifugation and then mineralogy, K-Ar dates and stable isotopes were determined. The goal is to assess the evolution of hydrothermal alteration in the region pre-, syn- and post-mineralization.

Samples from the non- to weakly-mineralized zones are dominated by muscovite/illite with subordinate sudoite. Samples derived from mineralized zones generally consist of abundant muscovite/illite and minor clinochlore, kaolinite and tourmaline. Comparison with Crystallinity Index Standards (Kbler Index, KI) for illite show that alteration halo silt-size fractions plot near the epizone-anchizone boundary and chlorite plots along the anchizone--diagenetic boundary (Fig. 1). However, mineralized samples plot within the diagenetic zone. Trends between KI and grain-size are mirrored by a decrease in K-Ar dates within progressively finer fractions. The δ^2H results show alteration halo and mineralized samples have distinct fluid histories which is supported by the younger ages of mineralized samples shown in Fig. 1.

The younger K-Ar dates reflect polygenic clay authigenesis whereas older K-Ar dates include crystalline metamorphic micas. These results support a hypothesis in which the highest-grade ore zones and larger tonnage deposits represent sustained fluid pathways that channeled hydrothermal solutions episodically since the Mesoproterozoic.

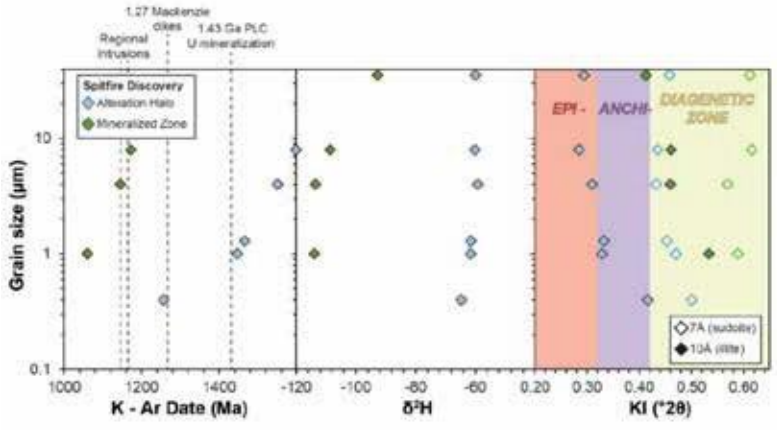


Fig.1. K-Ar dates, δ^2H and KI for two samples from the Spitfire uranium discovery plotted as a function of grain size. Timing of regional tectono-thermal events, and the KI range corresponding to diagenetic to low-grade metamorphic conditions are displayed for reference

Paleozoic ferruginous duricrust formation in Malawi: new insights from the (U-Th)/He geochronological, geochemical and mineralogical investigations

Maximilien Mathian[1,*], Guillaume Baby[2], Jean-Noël Ferry[3], Patrick Rafiki N. Chindandali[4], Cécile Quantin[1], Rosella Pinna-Jamme[1], Cécile Gautheron[1]

[1]GEOPS, Université Paris Saclay, UMR CNRS 8148, 91405 Orsay, France
[2]IPGP, Univ. Sorbonne Paris Cité, UMR CNRS 7154, 75005, Paris, France
[3]Total R&D, Total Scientific and Technical Center Jean Féger, 64000, Pau, France
[4]Malawi Geological Survey Department, M3, Zomba, Malawi

*maximilien.mathian@unc.nc

Earth's landscapes evolution is driven by physical erosion and chemical weathering, two processes influenced by tectonic and climatic changes. Dating studies of tropical regoliths have demonstrated that some of these objects could be particularly old (up to the Mesozoic). They also demonstrated that they are able to record within their mineralogy the traces of distinct paleoclimatic and/or geodynamic events, making them invaluable archives of the Earth history. However, the timing of formation of ferruginous and aluminous duricrusts, the type of events that can be recorded in their mineralogy and the extent through time of such record are still open questions.

To provide some keys to solve these scientific issues, we studied two lateritic ferruginous duricrusts from a high plateau located in Northern Malawi, the Nyika Plateau (Malawi, 2200 m), considered as a relic from an ante-Mesozoic paleolandscape. We crossed mineralogical and geochemical analyses with (U-Th)/He dating of hematite and goethite on these objects. If one of the studied samples is a goethite-rich pisolithic duricrust, with a Quaternary age, the second one displayed a structural organization pointing to the detrital origin of its main clasts, cemented by goethite. These clasts however have a complex mineralogy, revealed either by single grain XRD analyses and SEM observations. The (U-Th)/He ages range from the Devonian to the Quaternary, with a combination of ages and chemical index highlighting a mixing between old partially dissolved iron oxides generations and younger ones. It demonstrated the ability of detrital duricrusts to host a large record of traces of events that drove their local landscape evolution. But also, those samples provide strong implication about Devonian tropical climatic conditions.

TS15 Clays, Organics, Hybrid Materials

ORAL PRESENTATIONS

Effective utilization of montmorillonite surface for adsorption of aromatic compounds revealed by molecular dynamics simulation

Masaya Miyagawa*, Fumiya Hirosawa, Hiromitsu Takaba

Kogakuin University, Department of Environmental Chemistry and Chemical Engineering, Hachioji, Tokyo 192-0015 Japan

*miyagawa@cc.kogakuin.ac.jp

It is known that the hydrophobic interlayer of organoclay can adsorb aromatic compounds. However, rational design of the interlayer has not yet been achieved because the interlayer structure is not revealed thoroughly by experiment. We herein show results of molecular dynamics (MD) simulation of montmorillonite modified with octadecyltrimethylammonium ion or methylviologen (Mont-C_{18} and Mont-MV) and their nanocomposites containing anthracene or phenol (Mont-(C_{18}•Ph_3) and Mont-(MV•Ph_{OH})). Nanostructures of Mont-C_{18}, Mont-(C_{18}•Ph_3), Mont-MV, Mont-(MV•Ph_{OH}) were modelled by the method we reported previously (Miyagawa et al., 2021; Miyagawa et al., 2022). In brief, all Na^+ ions were substituted with C_{18} or MV, followed by NPT-MD simulation. Ph_3 or Ph_{OH} was placed in the interlayer of Mont-C_{18} or Mont-MV, followed by the NPT-MD simulation. Atomic interactions of C_{18}, MV, Ph_3 and Ph_{OH} were calculated by PCFF, while that of Mont was calculated by INTERFACE (Heinz et al., 2013). Figure 1(a) and (b) show snapshots of Mont-(C_{18}•Ph_3) and Mont-(MV•Ph_{OH}). Ph_3 forms a bimolecular layer in the interlayer, while Ph_{OH} forms a unimolecular layer. This difference is ascribed to the organocation: C_{18} forms pseudotrimolecular layer, resulting in enough gallery height for Ph_3 to form the bimolecular layer. In contrast, the interlayer is too narrow for Ph_{OH} because MV is almost flat, leading to formation of the unimolecular layer. Considering that the siloxane surface plays a role of the adsorption site, the formation of the bimolecular layer is preferable because both the upper and lower Mont layers are available. Therefore, effect of the organocation on the adsorption amount was revealed by the MD simulation.

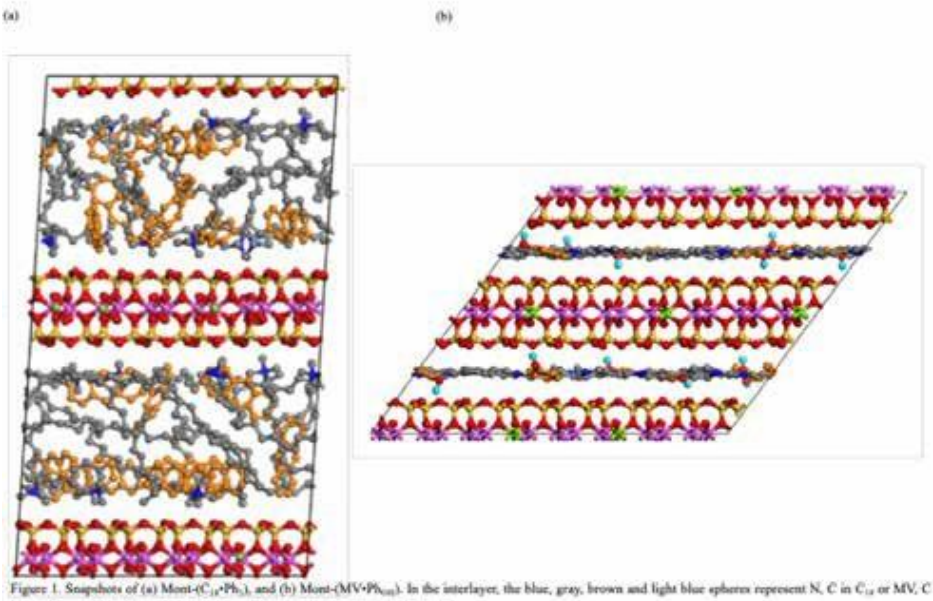


Figure 1. Snapshots of (a) Mont-(C_{18}•Ph_3), and (b) Mont-(MV•Ph_{OH}). In the interlayer, the blue, gray, brown and light blue spheres represent N, C in C_{18} or MV, C in Ph_3 or Ph_{OH}, and hydroxy H atom in Ph_{OH}. The other H atoms are not displayed.

Starting stoichiometry, keys parameters, in the microstructural and functional properties of synthesized hybrid nanocomposites chitosan/montmorillonite/metal oxide type

Malek Lahbib, Walid Oueslati, Chadha Mejri*, Abdsslem Ben Haj Amara

University of Carthage, Faculty of Sciences of Bizerte, LR19ES20: Resources, Materials and Ecosystems (RME), 7021 Bizerte, Tunisia

*chadha.mejri@fsb.ucar.tn

The combination of polymer, clay and metallic oxide aims to improve intrinsic performances of nanocomposites. In this work, the effect of starting stoichiometry variation on the microstructural and functional proprieties of synthesized hybrid nanocomposites chitosan/montmorillonite/ZnO (NPs) is investigated. Nanocomposites are Synthesized by the solution blending method. Analysis is assured by a correlation of results issue from respectively, XRD, FTIR, TEM, EDX, Impedance spectroscopy IS, UV-VIS. The microstructural analysis shows the achievement of nanocomposites synthesis regardless of starting stoichiometry rate (Wang et al., 2005). In fact, a real structural change (e.g., intensity and sharpness) was observed, along with the XRD characteristic reflection, in the case of starting and synthesized complexes indicating probably accomplishment of the elaboration process. The appeared structure aberration, related to the stoichiometry variation, characterized by a reflection position shift and a variable intensity strength is in accordance with (Mostafa et al., 2020) works. Results from the IS, in the case of the optimized stoichiometry, indicate that the nanocomposite has a semiconductor behavior and as a dielectric material, the sample is dispersive with a power loss for some frequency range. The optical proprieties are studied using UV-VIS spectrophotometry which determines the absorption along with the UV range of the synthesized samples. Moreover, the functionality (photocatalytic activity) of the synthesized nanocomposite is examined by the application of methylene blue absorption, which is influenced by the starting stoichiometry of the nanocomposite (Fatimah et al., 2011).

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Comparative study of alkylammonium- and alkylphosphonium-based analogues of organo-montmorillonites

Jana Madejová*, Martin Barlog, Ľuboš Jankovič, Michal Slaný, Helena Pálková

Institute of Inorganic Chemistry, SAS, Dúbravská cesta 9, 845 36 Bratislava, Slovakia

*jana.madejova@savba.sk

The organo-montmorillonites are highly attractive materials because of their wide application potential. In this work the basic structural and vibrational characteristics of the samples from two series of structurally analogous alkylammonium- and alkylphosphonium-montmorillonites are reported. The first series consisted of the organo-montmorillonites prepared from tetramethyl-(Me4-N/P), tetrabutyl-(Bu4-N/P) and tetraoctyl-(Oc4-N/P) analogues, while the second series was prepared from tributylalkyl cations with the fourth chain of the increasing length (Bu3-N/P-C*X*, *X* = 4, 8, 12, 16). The XRD analysis revealed that for both series, when comparing the equivalent pairs of the surfactants, slightly higher expansion of the interlayer space was observed for phosphonium-based than for ammonium-based montmorillonites. Difference in the d_{001} values was in accordance with a higher ionic radius of P(III) than N(III). The impact of the different central atom (N/P) of the cation head-group was also studied by the IR spectroscopy in the middle and near region. As a result of differences in the charge density of the nitrogen and phosphorus cationic centers the positions of the C-H bands (stretching and overtones) of phosphonium-Mt were shifted to lower wavenumbers compared to their ammonium counterparts. The effect of the central atom of the head-group was significant for smaller cations, but gradually decreased with increasing size of the ammonium and phosphonium surfactant.

Adsorption of methane and carbon dioxide by water-saturated clay rocks

Denys I. Grekov[1,*], Jean-Charles Robinet[2], Bernd Grambow[3]

[1]IMT Atlantique, GEPEA, UMR CNRS 6144, F-44307 Nantes, France
[2]Andra, R&D Division, Transfer Migration Group, 92298 Chtenay-Malabry, France
[3]SUBATECH, (IMT Atlantique, CNRS -IN2P3, Nantes Université), F-44307 Nantes, France

*denys.grekov@imt-atlantique.fr

Understanding of the effects of water on gas adsorption in geological media is of high importance in order to efficiently control numerous subsurface engineering process operating at gas/rock interfaces. The mechanism of gas adsorption in presence of water is complex and strongly depends on the type of porous media, the amount of water it contains, pressure and temperature conditions. In several cases, the geological media such as clay rocks exist under nearly-saturated state, so their pore body is completely filled with water (due to its preferentialadsorption), which greatly reduces their capacity to adsorb gases (Merkel, 2015).

In order to quantitatively describe CH_4 and CO_2 adsorption by hydrated clay minerals, we rely on the mechanism of gas uptake by dissolution in pre-adsorbed water. This approach is employed to characterise water-saturated porous media of increasing complexity: mesoporous silica with different pore sizes and geometry, isolated clay phases and natural clay-rich rock inpowdered and crushed states. It was found that the solubility in water can reliably explain the CO_2 uptakes by hydrated pore systems regardless of their nature as well as the CH_4 uptakes, but only for solids with large mesopores and montmorillonite clay. A so called adsorption enhanced gas uptake in pore water for CH_4, exceeding its solubility in bulk water by a factor of 5-8, was observed for the systems with narrow pore sizes, highlighting the impact of surface energy on gas solubility and the occurrence of the interaction of weakly-soluble methane with the surface, promoting its uptake in comparison to pure dissolution (Coasne, 2019).

This study thus confirms the feasibility of simplistic approach relying on a solubility to assess the uptake of gases (especially of CO_2) by saturated with water clay minerals but also highlightsthe importance to take into account textural properties for accurate evaluation of the adsorptioncapacity in case of methane.

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Temperature dependence of intercalation capacity of kaolinite

Fevronia T. Andreou[1,*], Eirini Siranidi[1], Arkadiusz Derkowski[2], Georgios D. Chryssikos[1]

[1]Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vas. Constantinou Avenue 11635, Athens, Greece

[2]Institute of Geological Sciences, Polish Academy of Sciences, Research Centre in Cracow, Senacka 1, 31-002 Kraków, Poland

*fandreou@eie.gr

The self-assembly of small molecules (such as urea, formamide, DMSO) in the interlayer of kaolinite, known as intercalation, is a process of fundamental and technological importance. The properties of kaolinite determine the rate and extent of intercalation in a manner that is not fully understood, despite efforts (Fashina and Deng, 2021 and references therein). Recent studies have shown that the amount of non-reactive kaolinite in otherwise pure samples is larger than previously estimated (Andreou et al., 2021). Elevated temperatures (60-80 °C) are commonly employed to accelerate the reaction but the effect of temperature on the intercalation capacity of kaolinite is controversial and rarely addressed.

This is the first systematic investigation of the intercalation capacity of three kaolinites (CMS reference KGa-1b, KGa-2 and Hywite from Imerys) by vibrational spectroscopic monitoring as a function of temperature. Sealed slurries of kaolinite with 5x excess N-methylformamide (NMF) were measured *in situ* by FT-near infrared spectroscopy (NIR) while intercalating over long time periods (up to 1 week) and at different temperatures in the 5-100 °C range. A temperature-independent indicator of the degree of reaction was based on the amplitude of the 2nd derivative 2vNH mode of the intercalating NMF molecules normalised by the corresponding intensity of the 2v inner OH mode of kaolinite. In all kaolinites investigated, increasing temperature was found to accelerate the reaction, as expected, but also to decrease very significantly the final NMF uptake. The latter unexpected finding was confirmed by independent thermogravimetric analysis (TGA) of the final intercalation products.

Additional experiments showed that stepwise changes from higher to lower temperatures caused the stepwise increase of intercalation capacity to the levels reached by the corresponding single-temperature experiment. However, increasing the temperature of pre-intercalated systems did not cause deintercalation, indicating that once intercalated the NMF molecules were no longer in equilibrium with the surrounding fluid. The hindering of intercalation at higher temperatures is discussed in light of the interlayer energetics and the partition of NMF between the liquid and the edges of the mineral particles.

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Enhanced fluorescence of hybrid systems based on layered silicates and cyanine dyes

Peter Boháč[1,2,*], **Šimon Budzák**[3], **Juraj Bujdák**[1,4]

[1]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, SK- 845 36, Slovak Republic
[2]Centre of Excellence for Advanced Materials Application, Slovak Academy of Sciences, Bratislava, SK- 845 11, Slovak Republic
[3]Department of Chemistry, Matej Bel University, Banská Bystrica, SK-974 01, Slovak Republic
[4]Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Bratislava, SK-842 15, Slovak Republic

*peter.bohac@savba.sk

Interaction of organic dyes with layered silicates can cause various changes in properties of the dyes, such as metachromasia (change in color), fluorescence quenching, resonance energy transfer, or even fluorescence enhancement. Most of these phenomena are caused by the molecular aggregation of the dyes. The present study studied the photophysical properties of three cyanine dyes (PIC, OxCy, ThCy) in colloidal dispersions of three smectites (saponite, hectorite, and montmorillonite). Using a different type of smectite and dye/smectite loading enables control of the dye aggregation and the photophysical properties of the hybrid systems. A detailed analysis of the absorption spectra by the chemometric methods revealed the formation of two main oblique aggregates exhibiting light absorption in both H- and J-bands and its effect on the final photophysical properties of the systems. In addition, the samples of hybrid systems of all dyes with synthetic saponite in the lowest loadings of 0.01 mmol g^{-1} exhibited unusual fluorescence enhancement. Theoretical calculations found that the PIC molecule in solution exists in several possible conformations: cis, *trans*-isomer, and different relative orientations of the ethyl side chains can also be observed. According to our calculations, the global minimum is represented by a *trans* structure with an opposite orientation of ethyl chains. The dihedral angles between pyridine subunits are symmetrical and equal to ≈ 26°. This geometry caused nonradiative deactivation of the excited state of the molecule. Adsorption of the PIC on the saponite surface caused the change of the dihedral angles between pyridine subunits to ≈ 10°, which shows the hindering on nonradiative deactivation channel and possible radiative deactivation can take place. This behavior confirmed that fluorescence enhancement is not related to dye aggregation. Similar behavior was confirmed in other cyanine dyes as well.

Acknowledgement: This work was performed during the implementation of the project Building-up Centre for advanced materials application of the Slovak Academy of Sciences, ITMS project code 313021T081 supported by the Integrated Infrastructure Operational Programme funded by the ERDF. The work was supported by the Slovak Research and Development Agency under contract No. APVV-20-0322, APVV-18-0075, and APVV-19-0487. Support from the VEGA grant agency 1/0227/20 is also gratefully acknowledged.

Effect of nonionic surfactant for adsorption behavior of benzyl acetate on montmorillonite in water

Kanji Saito[1,2,*], Kazuchika Hashimoto[1], Régis Guégan[3], Masataka Ogasawara[1], Sumio Kato[1]

[1]Department of Materials Science, Graduate School of Engineering Science, Akita University, 1-1 Tegatagakuen-machi, Akita, 010-8502, Japan

[2]Kagami Memorial Institute for Materials Science and Technology, Waseda University, 2-8-26 Nishiwaseda, Shinjuku-ku, Tokyo 169-0051, Japan

[3]Global Center for Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

*saitok@gipc.akita-u.ac.jp

Fragrance is used in wide application such as food, cosmetics, air fresher and aromatherapy. Many fragrance compounds are volatile and unstable toward oxidation, thus controlled release of fragrance is an important topic in the mentioned applications. A promising way for addressing this issue is to encapsulate a fragrance by different materials. In addition to polymers, supermolecular materials such as cyclodextrin and inorganic nanomaterials including layered double hydroxide (Markland at al., 2011) have been applied to a host material.

Smectites have attracted considerable and ever increasing interest as a host material that accommodate versatile guest species. As a way for efficient introduction of a guest organic molecule into organically modified smectites, formation of micelle based on interactions between a target guest and a surfactant has been reported to be promising (Polubesova et al., 2005; Oliveira et al., 2016). In this study, intercalation of benzyl acetate (BA), which is known as a component of jasmine fragrance, into montmorillonite (Mt) in water was investigated. While showing a poor affinity to raw Mt, BA adsorption was considerably enhanced through the use of pentaethylene glycol dodecyl ether ($C_{12}E_5$) nonionic surfactant as carrier phase, leading to the co-intercalation of the surfactant and BA into the interlayer space of the organo modified clay composite.

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Effect of humic acid on lysozyme interaction with montmorillonite and kaolinite

Yan Li[1,*], Luuk K. Koopal[2], Wenfeng Tan[3], Chuanqin Huang[3]

[1]Institute of Environment Resource and Soil Fertilizer, Zhejiang Academy of Agricultural Sciences, Hangzhou 310021,China
[2]Physical Chemistry and Soft Matter, Wageningen University and Research, Stippeneng 4, 6708 WE Wageningen, The Netherlands
[3] College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China

*liyann0410@163.com

Humic acid (HA) as a soil organic matter (NOM) can participate in the interaction between proteins and clay minerals, depending on clay type, HA and protein content, and solution conditions [1-2]. The effect of HA on the interaction of lysozyme (LSZ) with kaolinite (Kao) and montmorillonite (Mont) was investigated at (initial) pH_i 5 and 8. LSZ adsorption on clays in the presence of HA is dominated by adsorption of HA/LSZ complexes. The HA/LSZ mass ratio ($f_{IEP,pH}$) at the iso-electric point (IEP) is pH dependent. At $f < f_{IEP,pH}$ the HA/LSZ complexes are positively charged and adsorb well to the negatively charged Mont and Kao surface fractions. The adsorption levels on Mont are considerably larger than on Kao, which is mainly due to the much larger area fraction of modestly hydrophobic basal plates of Mont. The presence of HA increased the plateau adsorption of LSZ on Kao and Mont for both pH_i values, and the LSZ adsorption increased with increasing HA content and pH_i values. At pH_i 8 complications arised for low initial LSZ concentrations, for $f < f_{IEP,pH}$ the HA/LSZ complexes were only weakly positive and formed dispersed aggregates and for $f > f_{IEP,pH}$ the HA/LSZ complexes were negative, both conditions caused relatively high equilibrium concentrations of LSZ in solution that decreased with increasing initial LSZ concentration. The present results enhance our insight in protein soil interactions for the case that clay particles are brought in contact with aqueous solutions that contain modest amounts of both NOM and protein and stress the importance of the NOM/protein mass ratio and solution pH.

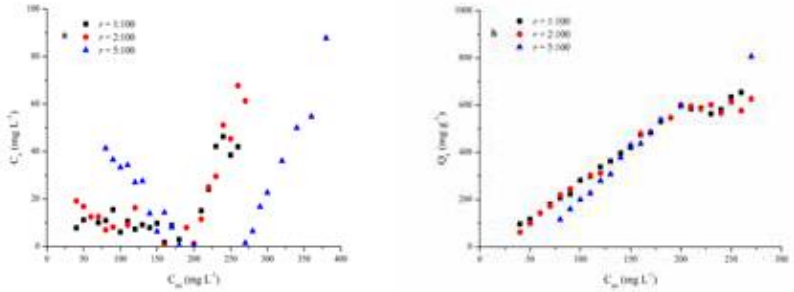


Figure 1. LSZ adsorption on montmorillonite at at pH_i 8 with different HA/clay mass ratios *r*.

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Occurrence of organic matter in hydroxy-interlayered clay mineral (HIM of red earth and its mechanism of carbon sequestration

Dong Liu[1,2,*], Mengyuan Li[1,2], Peixin Du[3], Peng Yuan[1,2]

[1]CAS Key Laboratory of Mineralogy and Metallogeny / Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, CAS Center for Excellence in Deep Earth Science, CAS, Guangzhou 510640, China
[2]University of Chinese Academy of Sciences, Beijing 100049, China
[3]State Key Laboratory of Lunar and Planetary Sciences, Macau University of Science and Technology, Macau, China

*liudong@gig.ac.cn

Hydroxy-interlayered clay mineral (HIM) is one of the most important pedogenic minerals in red earth, playing a crucial role in the migration and cycling of key nutrient elements, such as carbon, in the soil (Bortoluzzi et al., 2008; Yin et al., 2013; Churchman et al., 2020). However, the structure and surface properties of this HIM remain unclear, and the interaction between HIM and organic matter in red earth is not well understood. This knowledge gap hinders our understanding of the carbon cycle in red earth (Hong et al., 2020).

In this study, high-resolution transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) with a nanometer spatial resolution were combined to identify the HIM and investigate the interlayer organic matter in HIM in red earth in southern China. The results show that (i) hydroxy-Al occurs in this HIM, (ii) one HIM layer transforms into two kaolinite layers, and (iii) carbon is present in the interlayer space of HIM. In this case, the intercalated hydroxy-Al in HIM might eventually transform into kaolinite. The organic matter in HIM, associated with interlayer hydroxy-Al, would be protected against microbial decomposition. Therefore, the occurrence of organic matter in HIM interlayer space is an important mechanism of carbon sequestration in red earth. The results of this investigation provide insights into the structure and properties of HIM in red earth, and the role of minerals in terrestrial organic carbon sequestration.

Acknowledgment: National Natural Science Foundation of China (Grant No. 41972046).

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Amorphous clay minerals and soil acidity control organic carbon sequestration in humid tropical soils of India

Ranjan Paul*, Duraisamy Vasu, Pramod Tiwary, Shabana Sheikh, Padikkal Chandran, Shiocharan S. Gaikwad

Division of Soil Resource Studies, ICAR-National Bureau of Soil Survey and Land Use Planning, Maharashtra, India

*ranjan.reliance@gmail.com

Organic carbon (OC) sequestration in soils is generally associated with clay minerals of both crystalline and amorphous nature (Chatterjee et al., 2013; Feng et al., 2013; Datta et al., 2015). In highly smectitic, non-acidic and calcareous soils of the semi-arid tropical (SAT) climate of India, OC content in the top 30 cm seldom exceeds 1% despite long-term organic matter additions (Datta et al., 2018; Paul et al., 2021). However, in acidic soils with the dominance of kaolin (a 0.7nm mineral interstratified with HIS/HIV) and hydroxy-interlayered smectite/vermiculite (HIS/HIV) of humid tropical (HT) climate, OC content ranges from 1.5 to 2% (Bhattacharyya et al., 2005; Chandran et al., 2005). Such preliminary and limited observations apparently suggested an insignificant role of crystalline clay minerals in the stabilization of OC in SAT soils. In contrast, enrichment of OC with a decrease in clay CEC, and an increase in soil acidity and hydroxy-interlayer in smectite, vermiculite and kaolin was observed in the humid tropical soils (Pal, 2017). Therefore, a systematic study was carried out to determine the role of soil acidity and amorphous minerals in OC sequestration, using three spatially associated clay enriched soils viz., (a) Vertisols (Typic Haplusterts, P1), Alfisols (Typic Haplustalfs, P2) and Mollisols (Vertic Argiustoll, P3), located > 1000 m above MSL and developed from weathered basaltic parent material of the Deccan plateau area under HT climate. These soils are under fodder crop, grassland, and broad-leaved forest, respectively. The pH of P1 was higher (7.1-7.3) than the other two soils (5.98-6.96). Mollisols have higher OC (1.22 %, in the surface 30 cm) than Vertisols (1.02 %) and Alfisols (1.09 %). Soil CEC is higher in Vertisols (53-70 cmol p^+ kg^{-1}) than the Mollisols (30-46 cmol p^+ kg^{-1}) and Alfisols (18-20 cmol p^+ kg^{-1}). The Vertisol clays of P1 are dominated by partially hydroxy-interlayered smectite and vermiculite whereas that of P2 (Alfisol) and P3 (Mollisol) by kaolin (HIS/K). The results showed that OC is increasing with a decrease in soil pH, which causes the breakdown of the crystalline clay minerals into amorphous oxides that are trapped in the interlayers of smectite and vermiculite to make them as HIS and HIV. HIS, HIV and kaolin become more active minerals than the crystalline clay minerals to stabilize the OC in the soils. Further, the results indicate that the soil acidity is higher in the rhizosphere of the grassland and forest soils than the soils under fodder crops. This study indicates that the OC sequestration in humid tropical soils under profuse vegetation is more strongly influenced by the amorphous minerals than the crystalline minerals. This knowledge on the fundamental pedogenic processes related to OC sequestration will help in devising management protocols in enhancing OC in SAT soils.

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Electrochromic nanocomposites of Fe(II-based metallo-supramolecular polymer and a layered inorganic–organic hybrid

Kazuko Fujii*, Manas Kumar Bera, Dines Chandra Santra, Masayoshi Higuchi

National Institute for Materials Science, Electronic Functional Macromolecules Group, Tsukuba, 305-0044 Japan

*FUJII.Kazuko@nims.go.jp

Electrochromic (EC) materials have received considerable attention as an important material used in electrochemical glass tinting, i.e., smart windows and antiglare rearview mirrors in cars[1]. Fe-based metallo-supramolecular polymer (polyFe), composed of Fe(II) ions and bis(terpyridyl)benzene, is known as a good EC material[1]. The aim of this study is to create novel and useful nanocomposites of EC metallo-supramolecular polymer (MSP) and layered material to achieve superior EC properties, such as large optical contrast (ΔT) or long optical memory.

We choose a layered inorganic–imidazoline covalently bonded hybrid (LIIm) [2] as the layered material. Imidazoline moieties are covalently immobilized between inorganic layers in LIIm. We simply mixed LIIm with Fe-based metallo-supramolecular polymer (polyFe) in methanol to prepare blue-purple polyFe/LIIm composites. The prepared samples were characteraized by scanning electron microscopy (SEM), X-ray diffraction (XRD), ultraviolet-visible (UV-vis) spectroscopy, cyclic voltammogram (CV), and so on.

SEM and XRD revealed characteristic structural features of polyFe/LIIm composites. UV-vis spectroscopy measurements demonstrated that light absorption close to 600 nm was attributed to metal-to-ligand charge transfer (MLCT) from the Fe(II) ion to the bisterpyridine ligand and was influenced by LIIm in the composites. The composites exhibited a pair of redox waves, assigned to the redox between Fe(II) and Fe(III), in the cyclic voltammograms. Thin composite films demonstrated reversible EC changes, triggered by the redox reaction of the metal.

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Adsorption of some anions by sepiolite belongs to Eskişehir (Sivrihisar) region and its surface active agents-modified forms

Sedef Dikmen[1,*], Gülgün Yilmaz[2]

[1]Eskişehir Technical University, Science Faculty, Department of Physics, 26470, Turkey
[2]Eskişehir Technical University, Porsuk Vocational School, Department of Construction Division, Program in Building Inspection, 26150, Turkey

*sdikmen@eskisehir.edu.tr

In this research, firstly a natural clay mineral, which is sepiolite, was transformed into Na-sepiolite forms and then Na-sepiolite was modified by hexadecyltrimethylammonium (HDTMA) bromide [$CH_3(CH_2)15N(CH_3)_3Br$]. The characterization studies by using different methods (BET, XRF, XRD, SEM, FT-IR, TG/DTA, immersion heat, and zeta potential measurement) were also carried out to identify the modification of natural sepiolite with HDTMA-Br and its adsorption behavior. Then, the adsorption of hazardous anions, which are present in wastewater or underground water with HDTMA-sepiolite were investigated in batch technique. In this manner, the effects of adsorbent dosage, contact time, and pH were investigated for the adsorption of nitrate, sulfate, and phosphate anions onto HDTMA-sepiolite. Adsorption kinetics and isotherm parameters were deduced by using experimental data. Pseudo-first-order, pseudo-second-order, and Weber-Morris models and Langmuir and Freundlich isotherms were applied to the experimental data to obtain adsorption kinetics and adsorption equilibrium, respectively. According to this, the adsorption of phosphate anion data fits well with the pseudo-second-order kinetic model (with high correlation coefficients).

Since the adsorption of these anions on Na-sepiolite is almost nonexistent, these data are not included in the results. The obtained results can be summarized as follows:

- In order to modify the Na-sepiolite surface with HDTMA, an adsorption isotherm was obtained at ~30 °C and in its natural environment. While the amount of adsorbed substance (Q, mol/g) increased very rapidly at low equilibrium concentration (C_e, mol/l) values, it was observed that there was no increase in adsorption after ~ mol/g. It is possible to say that the adsorption of HDTMA on sepiolite occurs mainly through cation exchange and dipole-dipole interaction.
- In the determination of the adsorbent amount in HDTMA adsorption on Na-sepiolite, a constant HDTMA concentration of M was studied. The maximum adsorption amount was determined as M at 5% adsorbent ratio.
- It can be said that pH does not have a significant effect on the amount of adsorbed substance as a result of the tests performed at the concentration of C_i:3×10^{-2} M in order to examine the effect of changes in the pH of the environment on HDTMA adsorption. This shows that cation exchange and dipole-dipole interactions are more common in adsorption as well as electrostatic interaction.

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TS15 Clays, Organics, Hybrid Materials

POSTER PRESENTATIONS

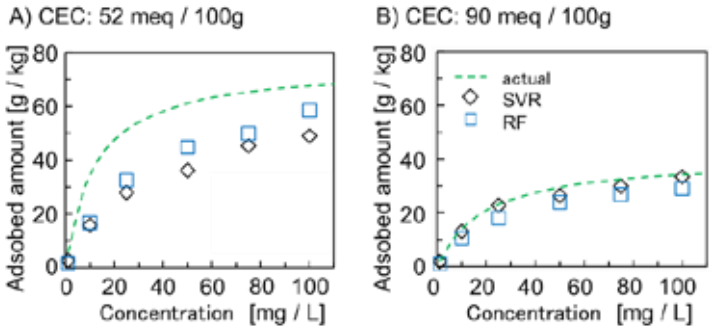
Prediction of adsorption amount of aromatic compounds inorganoclay by machine learning

Hayato Shobuke*, **Masaya Miyagawa, Hiromitsu Takaba, Takumi Matsumoto**

Kogakuin University, Department of Environmental Chemistry and Chemical Engineering, Hachioji, Tokyo 192-0015 Japan

*s318035@ns.kogakuin.ac.jp

Organoclay is a promising material for adsorbing aromatic compounds dissolved in water. From a view point of adsorption capacity and selectivity, combination of host clay and cationic guest molecule must be considered carefully (Ogawa et al.,1997). However, the oretical optimization of the combination is not realistic because adsorption occurs based on interactions among the organoclay, solvent and adsorbate at molecular level. In- contrast, machine learning can predict physical propertyfrom features of material components and search target property efficiently. In the present study, we collected 84 data on adsorption isotherm of aromatic compounds, and constructed model to predict the adsorption amount by the machine learning. Support vec- tor regression (SVR), randomforest (RF), and gradient boosting decision Tree(GBDT) were used as regression methods. In the dataset, 74 data were used for training to construct the model, and therest was used for test. The model was constructed in concentration of 1, 10, 25, 50, 75 and 100 mgL^{-1} individually by applying the rawdata to Langmuir or Freundlich adsorption model. In the test data, RF and SVR show smaller mean absolute error (MAE) than GBDT. Relative error is specifically small in the region of 50~100 mgL^{-1}. Figure1shows predicted results of toluene adsorption in organoclay modified by trimethylphenylammonium (TMPA) with different CEC. In Fig. 1A, prediction accuracy in the small concentration region is relatively low, but within the MAE. In contrast, the actual values are reproduced well in the entire region. It is true that this difference is ascribed to less data of the low CEC in the training data, but the adsorption amount is found to be estimated even inthe low concentration bythe SVR and RF method as long as the number of the training data is sufficient.It is concluded that correction of data by applying the adsorption model is effective to estimate the adsorption amount in organoclay.



Inter layer structure of organ oclay saturated with water bymolecular dynamics simulation

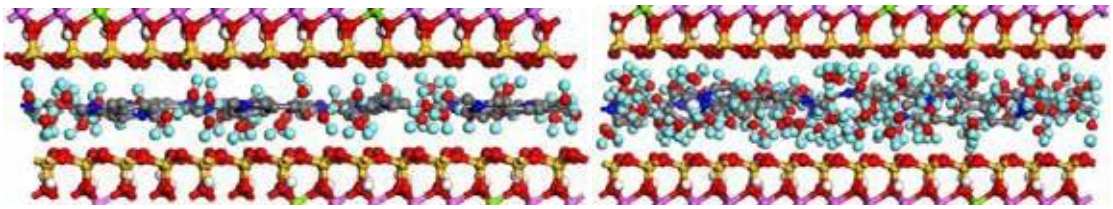
Shoma Nishimura*, **Fumiya Hirosawa, Masaya Miyagawa, Hiromitsu Takaba**

Kogakuin University, Department of Environmental Chemistry and Chemical Engineering, Hachioji, Tokyo192-0015 Japan

*bm21037@ns.kogakuin.ac.jp

Montmorillonite modified with organocation is a promising adsorption material for aromatic compounds, and usage of methylviologen is a good example because phenol is adsorbed by the nanocomposite (Mont-MV) [T. Okada et al., 2002]. In aqueous solution, the adsorption is dependent on the interlayer structure of organoclay, where large number of solvent molecules arepresentaswellastheorganocationan- dadsorbate. However, it is difficult to investigate the structure experimentally due to limit of spacial resolu-tion. In this point, molecular dynamics (MD) method has an advantage. We herein conducted MD simulation of water-saturated Mont-MV (Mont-(MV•H_2O)) and the nanocomposite containing phenol.

Mont-MV was modelled by the method we reported recently [M. Miyagawa et al., 2021]. In brief, all Na^+ions in the interlayer were substituted with the MV cation, followed by the MD simulation with NPT ensemble. Mont-(MV•H_2O) was modeled by inserting H_2O by Monte Carlo method, followed by the NPT-MD simulation. Atomic interactions of MV and H_2O were calculated by PCFF, while that of Mont was calculated by INTERFACE [H. Heinzetal.2013]. Basal spacing of Mont-MV is well consistent with the experimental value [T. Okada et al., 2002], and MV is orientated horizontally. Fig.1(a) and (b) shows snap shots of Mont-(MV•H_2O). The H atoms of H_2O are faced to the Mont layers. MV is almost flat in Fig. 1(a). In Fig. 1(b), however, MVgets twisted because the interlayer swells by the further intercalation of H_2O. The interlayer separation is ca. 5 in Fig. 1(b), comparable to the size of the phenol molecule. In the presentation, we show the nanostructure of phenol intercalated into Mont-(MV•H_2O), and we want to discuss relation with result of energy analysis.



(a) (b)

Figure 1. Snapshots of Mont-(MV•H_2O) containing H_2O at (a) 4 wt% and (b) 10 wt%. The blue, gray, red and light blue spheres represent N, C, O, H in H2O. The other H atoms are not displayed.

Effect of representative clay minerals on methane hydrate nucleation: Insights from molecular dynamics simulation study

Yun Li[1,2,*], Hongzhe Song[1], Peng Yuan[1], Dong Liu[1]

[1]CAS Key Laboratory of Mineralogy and Metallogeny, Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Institutions of Earth Science, Chinese Academy of Sciences (CAS), Guangzhou 510640, China

[2]Shenzhen Key Laboratory of Natural Gas Hydrates, Academy for Advanced Interdisciplinary Studies, Southern University of Science and Technology, Shenzhen 518055, China

*liy39@sustech.edu.cn

Methane hydrate (MH) is an ice-like crystalline formed by methane and water molecules under low-temperature and high-pressure conditions. The mineral composition is an important factor affecting the occurrence of MH. Clay minerals (i.e., montmorillonite (Mt), illite, kaolinite (Kaol), mixed-layer mineral, etc.) are widespread in marine sediments (Guggenheim et al., 2003). The layered structure and surface properties of clay minerals can potentially affect MH nucleation. Therefore, exploring the nucleation mechanism of MH in clay minerals would greatly improve our understanding of the role of clay minerals in the formation and occurrence of MH.

Here we investigate the effect of two representative clay minerals (*i.e.,* Kaol and Mt) on MH nucleation by molecular dynamics simulation. For the Kaol-MH system, MH nucleation with different surface contacts (i.e., siloxane and hydroxyl surfaces) was significantly different from that of the bulk phase. MH was mainly distributed in the bulk solution away from the Kaol surface. Methane molecules could adsorb on the siloxane surface to form clathrate-like structures, promoting the growth of MH. On the external surface of Mt, Na^+ and K^+ counterions respectively form outer- and inner-sphere hydration structures. Methane cannot penetrate these hydration structures to form cages. This analysis provides an important theoretical basis for understanding the nucleation of MH on the surface of clay minerals. It seems likely that the structural and surface properties of clay minerals play a key role in the MH formation in marine sediments.

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Adsorption and aggregation behavior of tetra cationic porphyrins on clay and titania nanosheets

Yugo Hirade*, **Koki Fukushima, Tetsuya Shimada, Tamao Ishida, Shinsuke Takagi**

Department of Applied Chemistry, Tokyo Metropolitan University, Tokyo 192-0397, Japan

*hirade-yugo@ed.tmu.ac.jp

Clay nanosheets obtained by dispersive exfoliation of synthetic clay minerals (saponite) in water have a uniform negative charge on the surface and can adsorb cationic dyes with matching inter-charge distances in high density and without aggregation (Size-Matching Effect) [1]. Using this phenomenon, various photo- functionalities of dye/clay nanosheet composites have been studied. On the other hand, many nanosheetswith semiconducting functions have been reported in recent years [2]. In order to construct a new photo-chemical reaction system using semiconductor nanosheets as a host material, it is essential to control theadsorption behavior of cationic dyes on anionic semiconductor nanosheets.

In this study, we investigated the adsorption behavior of three cationic dyes (tetramethyl-pyridiniumporphyrin, TMPyP) with different intramolecular positive charge distances on semiconducting titania nanosheets (TNS). For example, *p*-TMPyP shows a maximum absorption wavelength (λ_{max}) of 422 nm in aqueous solu- tion, where as in TNS dispersion, λ_{max} is red-shifted by adsorption on TNS and shows λ_{max}=455n mat 1%vs. CEC (CEC = Cation exchange capacity). The red shift of $\lambda_{max}$is due to the change in the dihedral angle between the porphyrin and pyridinium rings upon adsorption [3]. As the adsorption density is further increased, λ_{max} further shifts to longer wavelengths until the saturated adsorption capacity of 40% vs. CEC. This phenomenon was not observed on clay nanosheet [1]. In contrast, when *p*-TMPyP was adsorbed on the TNS mono layer film prepared by the Langmuir-Blodgett method, the same long wavelength shif to fλ-max was observed as in the TNS dispersion. However, there was no further shift in the spectrum with increasing adsorption density. These results suggest that the phenomenon observed in the TNS dispersion is the aggregation of the dye through the nanosheet layer.

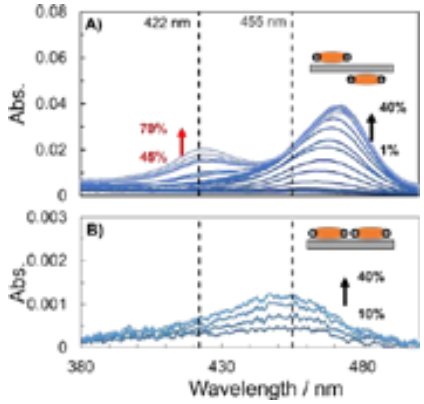


Figure1. Absorption spectra of p-TMPyP/TNS: A) Dispersion ([TNS]=1.27×10^{-5}M, [p-TMPyP]=1~70% vs CEC); B)LB-film([p-TMPyP]=10~40% vs CEC)

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“On surface synthesis” on saponite surface: A novel organic reaction pathway of azonia [5] helicene by interaction with saponite surface

Kyosuke Arakawa*, Tetsuya Shimda, Tamao Ishida, Shinsuke Takagi

Tokyo Metropolitan University, Department of Applied Chemistry, Tokyo 192-0397, Japan

*arakawa-kyousuke@ed.tmu.ac.jp

In recent years, research incorporating a flat solid surface into an organic synthesis reaction has attracted attention as “On surface synthesis”. From the viewpoint of synthetic organic chemistry, a flat surface promotes the reaction when the product has a flat structure with high sp^2 properties compared to in solution, and the reaction proceeds by a different route from that in solution (Shiotari et al., 2017). Flat solid surfaces are an interesting and novel reaction field. However, the solid surface in this field means metal surfaces such as Au (111) or Cu (001). Thus, this unique reaction fields lack generality and ease of handling.

The purpose of this study is to generalize “On Surface Synthesis” by using the surface of saponite. Saponite is i) cheap and low toxicity, ii) stable in heat and solution, iii) has a high specific surface area, iv) is transparent in the ultraviolet / visible light region. It can be said that it is a material suitable for this purpose. In this study, we focused on the photo-closed ring reaction of azonia [5] helicene becauseof the electrostatic interaction with anionic saponite surface and of the product is planar (Sato et al., 2017). Surprisingly, the photoreaction pathway changed between saponite layers and more flat product was obtained. It is considered that the novel organic reaction pathway was caused by the steric interactionof the flat saponite surface.



Figure 1. Photoreaction of azonia [5] helicene in solution and between saponite layers.

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Quantitative assessments of organic matter uncoupling from clay surfaces in presence of salinity

Yanfu Wei[1,*], **Pengcheng Chen**[2], **Honghai Wu**[3], **Hongling Bu**[4]

[1]National Observation and Research Station of Coastal Ecological Environments in Macao, Macao Environmental Research Institute, Macau University of Science and Technology, Macao SAR 999078, China

[2]School of Environmental Science and Engineering & Analysis and Test Center, c, Guangzhou 510006, China

[3]Guangdong Provincial Key Laboratory of Chemical Pollution and Environmental Safety & MOE Key Laboratory of Theoretical Chemistry of Environment, South China Normal University, Guangzhou 510006, China

[4]Guangdong Institute of Eco-Environment and Soil Sciences, Guangzhou 510650, China

*yfwei@must.edu.mo

Most terrestrial organic matter (OM) is released from clay surfaces when the clay-organic complexes enter saline ocean margins. The saline seawater with high cation concentrations balances the negative surface charge of both the OM molecules and the clay minerals, resulting in the flocculation and sedimentation of OM molecules. However, it remains uncertain how salinity would affect the uncoupling process of adsorbed OM on clay surfaces. Here we show that the specific position of OM on the clay surfaces influenced its fate in saline solutions. The OM adsorbed on the outer surface of the clay seldom desorb in the presence of salinity, while the OM in the interlayer was stripped through cation exchange with sodium ions. Spectroscopy characterization revealed that the aromatic protein, fulvic acid-like organics, microbial byproduct, and humic acid-like substances were the main active components likely to adsorb on the clay surface under saline conditions. These results indicated that the clay-terrestrial OM association is strong in saline estuaries, and the terrestrial OM is unlikely to break away from clay surfaces. These results enabled a better understanding of OM immigration from clay-OM complexes in the saline estuary.

TS17 Advanced Microscopy in Clays

ORAL PRESENTATIONS

Atom probe tomography: A unique technique for the investigation of clay minerals at the nanoscale

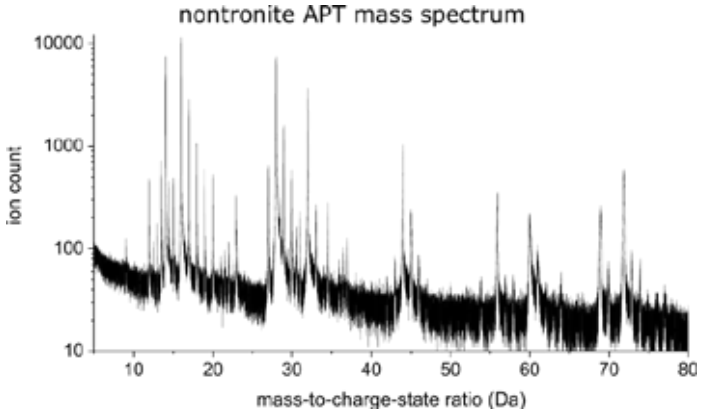
Chiara Cappelli*, Alberto Pérez-Huerta

The University of Alabama, Department of Geological Sciences, Tuscaloosa, AL 35487 USA

*ccappelli@ua.edu

Among the high-resolution microscopy techniques, atom probe tomography (APT) has recently proven to be a powerful technique for the compositional and structural characterization of minerals (Reddy et al., 2020). The unique feature of the APT is its ability to provide simultaneously the 3D spatial reconstruction and chemical composition of the analyzed sample by an advanced system that uses the coupled effect of high voltage and a laser pulse allowing the evaporation of atoms from the surface of a needle-shaped mineral specimen. The recent advances in the APT application on non-conductive (geological) materials, thanks to the laser-assisted mode implementation, have paved the way for the application of this technique to clays and clay minerals (Cappelli et al., 2021). The high spatial resolution (nominal lateral resolution >1 Å) and good detection sensitivity (up to 100 ppb) make APT a useful tool for elemental identification, including the estimate of isotopic ratios, and the assessment of element's association and spatial distribution in clays.

Analyzing highly anisotropic minerals as clays by APT proved challenging and optimization of the FIB-SEM protocol for specimen preparation and of the experimental parameters have demonstrated to be paramount for a successful outcome. The APT analysis of the trioctahedral mica biotite is compered here with that of the micaceous illite and the smectite nontronite. Preliminary data on these clays are promising and place the technique in a point of interest for geoscience disciplines and other broad field of study such as biosciences and materials sciences.



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A multi-technique approach to probe cations in birnessite and their hydration state

R. Coustel[1,*], D. Cornu[1], E. André[1], L. Pérez Ramírez[2], J.-J. Gallet[2,3], F. Bournel[2,3], C. Ruby[1], C. Carteret[1], F. Rochet[2]

[1]Université de Lorraine, CNRS, LCPME, F-54000 Nancy, France
[2]Sorbonne Université, CNRS, LCPMR, UMR 7614, 4 Place Jussieu, 75005 Paris, France
[3]Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 4891192 Gif-sur-Yvette Cedex, France

*romain.coustel@univ-lorraine.fr

Birnessite is a ubiquitous natural Mn layered oxide. The layers of the triclinic form have been described as an alternation of two $Mn^{IV}O_6$ rows and a $Mn^{III}O_6$ one (Lanson et al. 2002; Silvester, Manceau, et Drits 1997), leading to negative charges of the layers that are compensated by the presence of hydrated cations (Na^+, K^+, Ca^{2+}…) in the interlayer space.

The evolution of the structural and vibrational properties of birnessite was studied for various cations and with increasing hyration. Powder X-ray diffraction and Fourier-transform infrared spectroscopy measurements were carried out on Na-birnessite, K-birnessite and Ca-birnessite from secondary vacuum to ambient condition. The cation vibrational modes in the far-infrared domain differs depending on the inserted element. Both structural and vibrational results will be discussed and compared to simulations performed at a DFT level of theory using a periodic approach.

Recent improvements in X ray photoelectron spectroscopy allow measurements up to ~10 mbar (near ambient pressure XPS, NAP-XPS) by taking advantage of synchrotron light brightness. NAP-XPS opens the way to characterize compounds in operando conditions (Boucly et al. 2018; Tissot et al. 2016). Data collected at the TEMPO beamline (SOLEIL synchrotron facility) provides a unique insight into the electronic structure of hydrated birnessite.

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Interlayer structure of dehydroxylated chlorite examined by HR-TEM

Toshihiro Kogure*, **Takuya Umezome**

Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Japan

*kogure@eps.s.u-tokyo.ac.jp

It is well known that the brucite-like interlayer sheet in chlorite is dehydroxylated at a high temperature around 550°C in air but the interlayer spacing is almost not changed, still forming ~ 14 Å reflection. Moreover, this 14 Å reflection is significantly intensified by dehydroxylation, whereas other high-order basal reflections are weakened, which can be used as an examination of the coexistence of 7 Å phase such as berthierine in specimens. Guggenheim & Zhan (1999) determined the interlayer structure of this "modified chlorite" transformed from chromian clinochlore by X-ray structure analysis: dehydroxylation of the interlayer produced two quasi-planar sheets of cations (Mg, Fe, Cr) and anions parallel to the 2:1 layers. However, it is not certain whether a pair of these sheets really exists or appeared statistically in the D-Fourier map at the interlayer region. Moreover, it is not clear whether other (for instance, iron-rich) chlorites than clinochlore also form the same interlayer structure by heat-induced dehydroxylation. In the present study, we attempted to observe the interlayer structure after dehydroxylation of several chlorites using HR-TEM/STEM.

The specimens investigated were clinochlore (Fe/(Mg+Fe) = 0.17), chamosite (Fe/(Mg+Fe) = 0.72). For dehydroxylation, these specimens were powdered and heated in air, in a furnace elevating the temperature at the rate of 10°C/min and keeping for 2 hours at 650°C. The basal spacing was decreased from 14.34 to 14.11 Å for clinochlore and 14.29 to 13.84 Å for chamosite. Mössbauer spectra from the specimens showed that all Fe(II) in the chlorites were changed to Fe(III) by heating. Moreover, the XRD pattern and Mössbauer spectrum from the dehydroxylated chamosite indicated the formation of hematite.

High-resolution TEM imaging with point resolution of ca. 0.2 nm at 200 kV from the dehydroxylated clinochlore showed contrast which is corresponding to the two quasi-planar sheets reported by Guggenheim & Zhan (1999) at almost all interlayer regions. On the other hand, the observation of such contrast was limited locally in the structure of dehydroxylated chamosite. Considering of the formation of hematite in this specimen, it is suggested that the interlayer structure of the two quasi-planar sheets is formed only with magnesium but not with ferric iron.

Input of Transmission Electron Microscopy and electron diffraction to investigate the smectite crystal structure

Anne-Claire Gaillot[1,*], Eric Gautron[1], George Christidis[2]

[1]Institut des Matériaux de Nantes Jean Rouxel (IMN), 44322 Nantes, France
[2]Technical University of Crete, School of Mineral Resources Engineering, 73100 Chania, Greece

*Anne-Claire.Gaillot@cnrs-imn.fr

Smectite is a dioctahedral 2:1 clay which constitutes the main constituent of bentonites. The most common available techniques used to investigate the crystal structure and crystal chemistry of smectite include powder X-ray diffraction (XRD) together with Infrared spectroscopy. Within this context theoretical models of XRD patterns were indeed specificallydeveloped to describe the disordered stacking of the 2D-layers. However, these methods are bulk and the information obtained refers to the entire sample. Transmission Electron Microscopy (TEM) is a very efficient technique to investigate the structure of individual particles that has been used extensively in clay minerals. However, dueto its poorly ordered structure, characterization of smectite by TEM is often rather limited to the study of the smectite aggregates morphology or to smectite particle imaging in the directionparallel to the layers, to observe the interlayer spacing and allow its in situ identification in rockspecimens. Due to the turbostratic stacking of the layers, the electron diffraction has seldom been used to investigate the structure of 2:1 dioctahedral layer as it requires to isolate single layer particles, and information obtained was often limited by the resolution of the microscopeand its detectors.

The introduction of advanced TEM microscopes, with their far greater spatial resolution, but also the extremely high sensitivity of the camera developed in the recent years offer now new opportunities to investigate the structure of single layer or thin multi-layer smectite flakes. Some examples of SAED, HRTEM and HRSTEM data obtained on a Themis-Z TEM will be presented, together with limitations that still need to be overcome. A comparison with conventional TEM will also be presented and possible implications will be discussed.

Application of advanced electron/ion microscopy in nano clay research

Wen-An Chiou

Advanced Imaging and Microscopy Laboratory (AIM Lab), Maryland NanoCenter, University ofMaryland, College Park, MD 20742-2831, U.S.A.

wachiou@umd.edu

Characterization of particle size/shape (morphology), texture/microstructure, and chemical composition is a critical aspect of clays/clayey materials research. Despite numerous reported techniques, the precise measurement of clay properties, especially for the fundamental individual nano-clay particle, remains a challenge due to the miniscule size but diversity of shapes, surface activities, and analytical methods. Instrumentation capable of simultaneous microstructure determination (imaging and diffraction), microchemistry (spectroscopy), and properties measurement in high resolution is essential for clay characterization.

Recent developmen ts in ultra-high-resolution electron microscopy, especially aberration corrected TEM/STEM and attached analytical equipment, enable imaging of the lattice of 40 pm and determination of elemental composition from an area of less than 1 nm. Furthermore, the combination of SEM with focus ion beam (FIB) technology (FIB/SEM) and associated spectroscopy equipment has resulted in powerful and indispensable tools. These advances can facilitate the preparation of ultra-thin specimens from a specific sample site for microscopy (TEM/STEM) study at atomic-scale and sample modification for specific experiments. Associated technology (SIM, SIMS, and ToF-SIMS) can further provide additional valuable information from different perspectives that enhance clay research.

In-situ observation and operando experiments using different special sample holders/stages such as heating, cooling/cryo, wetting/liquid, in an electron/ion microscope not only provide dynamic observation and imaging at the nanoscale, but can also precisely measure the samples' properties before/after the chemical reaction. The *in-situ*/operando experiment is becoming crucial in understanding the interactive and reactive processes, either natural and/or simulated, of clays and clayey materials in different environments. Using advanced software with high-speed computing, 3D renderings of clay particles or assembly can be reconstructed, which promises to increase our understanding and application of nano clay materials.

Examples of applying advanced electron/ion microscopy and related technologies for *in-situ* observation/experiments of nano clay research will be presented and discussed. These experiments signify an opening of new opportunities in fundamental clay research.

TS17 Advanced Microscopy in Clays

POSTER PRESENTATIONS

The composition and growth mechanism of coexisting complex polytypes of 2:1 type clayminerals into biotite in rhyolite

Jiaxin Xi[1,*], Hongping He[1], Yiping Yang[1], Huifang Xu[2]

[1]Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[2]Department of Geoscience, University of Wisconsin-Madison, 1215 West Dayton Street, Madison,WI 53706, USA

*xijiaxin@gig.ac.cn

The polytypism of clay minerals has been well investigated in a wide range of geological settings (Alain Meunier, 2003). As representative 2:1 type phyllosilicate with various polytypes, mica minerals can have complex stacking sequence. And the frequency of occurrence of mica polytypes has been shown to be a function of crystallization environments (Smith and Yoder, 1956; Ross et al., 1966; Bailey, 1984; Xu and Veblen, 1995). However, the coexistence of basic- and complex-period polytypes in the same occurrence is extremely rare (Ross et al., 1966; Pignatelli et al., 2016), and the origin of this coexistence is poorly understood.

This work is therefore aimed to clarify the origin of coexisting biotite polytypes and their growth mechanism, as well as to analyse the relationship between crystallized environment and polytypism of 2:1 type clay minerals. The biotite phenocrysts from rhyolite of the Long Valley Caldera, California, USA, were investigated for the objectives. Micro-X-ray diffraction (μXRD), transmission electron microscopy (TEM) and related techniques were used. The μXRD analyses characterized various polytypes, and TEM observations revealed that common polytypes (e.g., 1*M*, 2M_1, and 3*T*) and rare polytypes (e.g., 4M_2 and 4A_8) coexist within biotite monocrystals. The two 4-layer polytypes of Fe-rich biotite, 4M_2 and 4A_8, were identified via selected-area electron diffraction (SAED) and high-resolution scanning transmission electron microscopy (HRSTEM) at the atomic resolution, with unique stacking sequences ([0222] for 4M_2 and [002 2 false] for 4A_8). Energy-dispersive X-ray spectroscopy (EDS) results showed differences in their chemical compositions, especially Fe and K. The 4A_8 polytype is reported for the first time. According to these observation and results, the study suggests that environmental changes, such as rapid cooling and inhomogeneous compositional distribution, led to chemical and structural oscillations and complex nucleation of the two 4-layer polytypes. Screw dislocations producing spiral growth enhance polytype stability and form ordered long-period/complex polytypes.

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Characteristics of growth layered structures in hydrogenetic ferromanganese nodule

Junming Zhou[1,2,3,*], Toshihiro Kogure[2], Taiga Okumura[2], Yoshio Takahashi[2], Peng Yuan[3]

[1]Southern Marine Science and Engineering Guangdong Laboratory (Guangzhou), Guangzhou 511458, China
[2]The University of Tokyo, Department of Earth and Planetary Science, Tokyo 113-0033, Japan
[3]Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

*zhoujunming0109@163.com

Ferromanganese nodules and crusts have been the focus of extensive researches, due to their potential as resources for many critical and base metals, and their ability in recording the history of oceanic and climatic conditions. They generally exhibit the growth layer structures of sub-micron to micron orders. However, the characterization of these structures seems not complete yet. Here we attempted to elucidate mineral phases in the growth layer structures of a hydrogenetic ferromanganese nodule and their relationship with composition and valence state, using advanced microscopy.

The specimen is a hydrogenetic ferromanganese nodule of a few centimeters in diameter, from the Central Pacific Ocean (13°00.6′S, 159°17.6′W). Thin cross-sections of the nodule were prepared for micro X-ray fluorescence (μ-XRF), scanning electron microscopy (SEM), and micro X-ray diffraction (μ-XRD) to understand the composition, structure, and mineral phases in the nodule. Moreover, to characterize at a finer scale, focused-ion-beam (FIB) was used to prepare thin-film specimens from the areas of interest, for transmission electron microscopy (TEM) with energy-dispersive X-ray spectrometry (EDS) and electron energy-loss spectrometry (EELS).

Visual and SEM observation of the thin cross-section identified approximately three different structures: micro-nodule, stromatolite-like layered structure, and laminated rim of the whole nodule. These three structures exhibit two types of growth layers: indistinct and distinct layers. μ-XRD indicated that the mineral of indistinct layers is Fe-vernadite with poor crystallinity and the minerals of indistinct layers are 10 and 7 Å phyllomanganates. TEM observation showed that the growth layer structures mainly consist of alternate distribution of dense and porous layers. Although the mineral phase in the adjacent porous and dense layers is the same and their chemical compositions are similar, the crystal size and valence state of Mn in these two layers are different according to the TEM and EELS analysis. These findings are significant to understand the formation of the growth layer structures and reconstruct the redox environment of the paleo-ocean.

TS18 Layered Double Hydroxides

ORAL PRESENTATIONS

Synthesis of layered double hydroxide/chitosan composites used for a reversible trapping of water pollutants

Abi. Khalil[1,2,*], S. Betelu[1], S. Delpeux[2], F. Muller[2], A. Seron[1]

[1]BRGM, 3 av. Claude-Guillemin, 45060 Orléans Cedex 2, France
[2]ICMN, 1B Rue de la Ferollerie, 45071 Orléans Cedex 2, France

a.abikhalil@brgm.fr

Various industries such as metals surface treatment industries, food industries, and many others generate effluents polluted by anionic and cationic inorganic trace and major elements such as (CrO_4^{2-}, Ni^{2+}, Cu^{2+}, Zn^{2+}, HPO_4^{2-} SO_4^{2-}, …) and non-biodegradable heavy metals. Major elements are frequently highly concentrated in industrial effluents. Both must therefore be treated before water release to the environment. The synthesis of universal composite material for the trapping of both cation and anion pollutants is thusof prime interest for the conservation of water resources.

The present study is based on the development of innovative composites involving layered double hydroxides (LDHs) dispersed in a chitosan matrix, as binder, to capture concomitantly anion and cation pollutants. Beads composite shaped were designed for the obtainment of homogeneous macroscopic properties in terms of shape, diameter, composition and formulation. The trapping performances of the synthesized materials were studied and correlated to the porosity and physico-chemical properties of the adsorbent. Zn^{2+}, Al^{3+}, SO_4^{2-}, NO_3^-, NO_2^-, and HPO_4^{2-} were selected as targeted pollutants.

Co/Fe LDHs with different cation ratios, in the range from 2/2 to 10/2, were synthesized using co-precipitation at varying pH value method, in order to further investigate the selectivity of anion capture. The synthesized LDHs were characterized using different techniques: X-Ray diffraction, to determine the purity and crystallinity of LDHs, Fourier Transform Infrared spectroscopy and Atomic Absorption spectroscopy to identify the interlayer anions and to quantify the cationic ratios. The structural and morphological properties were characterized using Transmission Electron Microscopy and Scanning Electron Microscopy. These techniques showed the synthesis of pure and crystalline Co/Fe-CO_3 LDH phases with the meant desired ratios. The obtained particles are hexagonal. However, have Co/Fe heterogeneous ratios; that will be discussed.

Concerning the chitosan/LDH composites, chitosan powder was first dissolved in acetic acid solution and LDH precursors (metal salts solution) were then added and vigorously mixed to the weekly cross-linked chitosan gel. It was added drop wisely into an alkaline solution (NaOH) under controlled conditions to form the desired beads. The difference in pH between the formed chitosan gel and the alkaline solution allows the gel to pull up together and form elastic and resistant beads. The formation of colloidal beads was chosen in order to get easily handled composites with the same macroscopic morphology: shape and diameter, composition, and adsorbents formulation. The formation of LDH phases in the composites was controlled using XRD analysis on freeze-dried and grinded beads.

Cryogenic electron microscopy was then used to characterize the homogeneity of the LDHs dispersed in the chitosan beads. Trapping capability anions and/or cations were investigated using each elementary component (LDH and Chitosan) and then composite beads.

DH-containing materials derived from minerals: from technical aspects of synthesis to the application in As(V removal

Karolina Rybka[1,*], Jakub Matusik[1], Michal Slan[2,3]

[1]AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, al. Mickiewicza 30, 30-059 Krakow, Poland

[2]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dbravská cesta 9, 845 36 Bratislava, Slovakia
[3]Institute of Construction and Architecture, Slovak Academy of Sciences, Dbravská cesta 9, 845 03 Bratislava, Slovakia

*krybka@agh.edu.pl

Layered double hydroxides (LDH) are considered as promising materials for the removal of anionic forms of pollutants. However, their application on an industrial scale may be limited by the cost of production (Rybka et al., 2021). The final cost of the material obtained with co-precipitation is determined by the price of chemical reagents used as substrates as well as the energy and time expenditure. Therefore, the goal of this work was to (i) substitute the chemical reagents with widely available and relatively cheap minerals as sources of metals building the LDH structure, (ii) optimize the co-precipitation synthesis methodology in terms of time and energy reduction, and (iii) compare their adsorption efficiency toward As(V).

Magnesite (M) and dolomite (D) were used as divalent metal (M^{II}) sources, and halloysite (Hall) and hematite (Hem) were used as trivalent metal (M^{III}) sources. Prior to the LDH co-precipitation, the extraction of the metals was performed by the dissolution of mineral substrates. No pretreatment was necessary, and no interactions occurred between the substrates. Therefore, the extraction step can be limited to one stage. Because the dissolution of substrates was incomplete, two approaches were considered. In the first one, the formed solution was separated from the undissolved residues (-C). In the second one, the suspension of residues in the solution was further used (-UC). This was followed by co-precipitation with NaOH.

Both procedures led to precipitation of the LDH phase in all samples. Some of the -C samples exhibited admixtures, while undissolved residues were present in the -UC samples. The materials showed structural and chemical differences in terms of the interlayer anion arrangement and chemical composition. Despite that, the materials showed high efficiency, which was found in the range of 614.7 ±11.4 to 1633.5±11.7 mmol/kg. As compared to similar LDH-containing materials obtained from industrial wastes or minerals, the studied materials showed similar or better performance.

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Rybka K., Matusik J., Slan M. (2021) Technical aspects of selected minerals transformation to LDH-containing materials: The structure, chemistry and affinity towards As(V). *Journal of Environmental Chemical Engineering*, 9, 106792

Preparation of Zn based layered double hydroxide using epoxide method for efficient photodegradation of Bisphenol A

Marwa Bouebdellah*, **Marcello Brigante, Gilles Mailhot, Claude Forano, Vanessa Prevot**

Clermont Auvergne University, Institute of Chemistry of Clermont-Ferrand, 63000 Clermont-Ferrand, FRANCE

*Marwa.bouebdellah@uca.fr

Photocatalysis is still receiving considerable interest for pollution control due to its low cost and environmental process. Among a new generation of heterogeneous photocatalysts, LDHs are a very promising photocatalytic materials, that can be used in catalysis, photocatalysis, and as catalyst support. They can serve also as precursors to generate a variety of MMOs, semiconducting oxides with adjustable catalytic properties and a high surface area (Ju, 2017).

This presentation will bring together the main results concerning the structural and the physico-chemical proprieties of ZnGa and ZnAl LDH obtained by epoxide method. The effect of the synthesis conditions on the purity and properties of these materials was investigated thanks to a multi-technique approach (XRD, IR, microscopy, and solid state NMR...). The efficiency of the as obtained LDH phases were tested as photocatalysts for the photodegradation of Bisphenol A in aqueous solution.

LDH nanoparticles were prepared using “the epoxide route” (Victor, 2013) which corresponds to the use of an epoxide in hydro alcoholic solution that induce a spontaneous increase of the pH in the reaction medium leading to the hydrolysis and condensation of metal complexes to form hydroxide networks. (Victor, 2013; Tokudome 2016). Concerning the photodegradation efficiency, the influence of parameters such as the pH, the photocatalyst concentration, and the temperature of calcination allowed to fix the best conditions. Interestingly, the addition of oxidant boosted the photodegradation. Finally, to highlight the mechanism of photodegradation involved, various scavengers were added to the medium.

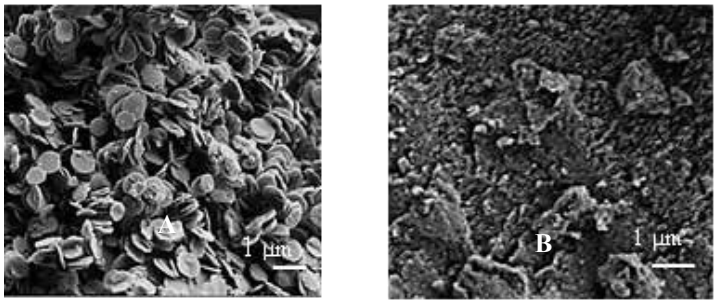


Figure 1. SEM images of LDH matrices prepared by epoxide route A) Zn_2Ga-Cl, B) Zn_2Al-Cl

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ayered Double Hydroxide Gels: Contrast Agents for X-Ray Computed Tomography Imaging of Vascular Structures

Yasuaki Tokudome[1,*], Gowsihan Poologasundarampillai[2], Koki Tachibana[1], Hidenobu Murata[1], Atsushi Nakahira[1]

[1]Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

[2] School of Dentistry, University of Birminghan, Edgbaston Birmingham B15 2TT, United Kingdom

*tokudome@mtr.osakafu-u.ac.jp

X-ray microcomputed tomography (μ-CT) provides detailed images of internal microstructure of organs such as bone, heart and blood vessels with a high spatial resolution [1]. Acrylic-based polymerizable resins are widely adopted for the contrast agent to prepare pathological specimens for imaging of vascular structures. For imaging of vascular structures at higher resolution, it is promising to develop inorganic contrast agents with higher X-ray attenuation coefficient as well as low viscosity, homogeneity, minimum shrinkage, curable (gellable) for replication, and low cost.

In this study, a novel inorganic sol–gel system based on concentrated colloidal dispersion of NiAl layered double hydroxide (LDH) nanoparticles is described towards imaging of vascular structures at high resolution. The LDH nanoparticles with a particle diameter of ~8 nm [2] were employed and integrated with a silicon alkoxide-based sol-gel reaction. NiAl LDH acts as nanofiller and alkaline catalyst to form a silica/LDH monolithic material with homogeneity from the nanoscale. Moreover, NiAl LDH nanoparticles contribute to the strong enhancement of the X-ray attenuation. As a proof-of-concept, X-ray μ-CT imaging of the developed contrast agent in glass capillaries and of blood vessels of a human placenta and murine liver is demonstrated [3].

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Simple and cost-effective mass production of nitrate type MgAl layered double hydroxide: titration from concentrated solution

Soontaree (Grace) Intasa-ard[1], Makoto Ogawa[2,*]

[1]School of Molecular Science and Engineering
[2]School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, 555 Moo 1 Payupnai, Wangchan, Rayong 21210, Thailand

*makoto.ogawa@vistec.ac.th

Mass production of nitrate type Mg/Al layered double hydroxide was examined by the titration of concentrated solution of metal salts with ammonium hydroxide under ambient atmosphere. The influence of the suspension pH and post precipitation aging on the products was studied. Over five grams of single-phase nitrate type Mg/Al layered double hydroxide was obtained from a hundred milliliter suspension (initial concentration of metal salt solution of 1.6 M), which corresponded to 97 % yield from the metal ion consumption. Well-defined platy particles of nitrate type Mg/Al layered double hydroxide was obtained by applying post precipitation aging at 80°C under ambient atmosphere. The sample preparation has been carried out without any caution to remove carbonate contamination to obtain nitrate type Mg/Al layered double hydroxide.

Preparation of anisotropic crystals of β-Ni(OH)$_2$ grown along stacking direction using Ni-diamine complexes

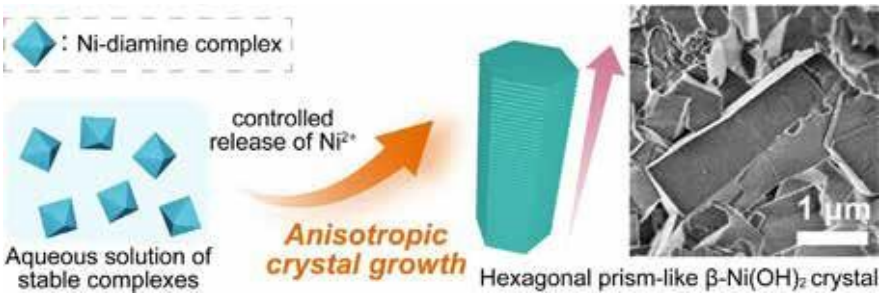
~~Keisuke Muramatsu~~[1,#,*], Mina Jimba[1], Hiroaki Wada[1,2], Atsushi Shimojima[1,2], Kazuyuki Kuroda[1,2]

[1]Waseda University, Faculty of Science and Engineering, Tokyo 169-8555, Japan
[2]Waseda University, Kagami Memorial Research Institute for Materials Science and Technology, Tokyo 169-0051, Japan
[#](Presentaddress) Shinshu University, Research Initiative for Supra-Materials (RISM), Nagano 386-8567, Japan

*kei_muramatsu@shinshu-u.ac.jp

Brucite-type layered metal hydroxides and layered double hydroxides are structurally analogous and important classes of materials with a wide range of applications. Various attempts have enabled the preparation of layered metal hydroxides with diverse crystal shapes; however, the synthetic chemistry to promote the anisotropic crystal growth along the stacking direction is not mature. Here, we report the preparation of β-Ni(OH)$_2$ anisotropically grown along the stacking direction under the presence of dipodal amine ligands (Scheme 1). We successfully prepared hexagonal prism-like β-Ni(OH)$_2$ crystals with an aspect ratio of the thickness to the lateral size larger than 1. A systematic investigation focusing on the molar ratio of aminelig and sto Ni^{2+}, the concentration of Ni-diamine complexes,and stability constants of the complexes re- vealed that anisotropic growth was promoted when the supersaturation at the growth stage was relatively high and was maintained for a longer time. Amine ligands act as Ni^{2+} reservoirs to control supersaturation through the controlled release of metal ions from stable complexes.

This study provides important insights for developing general synthetic chemistry for various layered compounds to control the aspect ratio.



Insight into the role of physico-chemical conditions on the phosphate-Layered Double Hydroxides controlled release properties

Alexandra Jourdain[1,*], Kamilla Thingholm Bünning[2], Ulla Gro Nielsen[2], Vanessa Prvot[1], Claude Forano[1]

[1]Université Clermont-Auvergne, CNRS, Clermont Auvergne INP, Institut de Chimie deClermont-Ferrand, ICCF, 63178 Aubire, France

[2]Southern Denmark University, Department of Physics, Chemistry and Pharmacy, 5230 Odense, Denmark

*alexandra.jourdain@doctorant.uca.fr

Phosphorus (P), Nitrogen (N) and Potassium (K) are essential nutrients and a deficiency of thosewill inhibit plants growth. Therefore, fertilizers are applied on soil in large excess to favor intensive production. This practice leads to the eutrophication of natural water bodies by leaching. To avoid this environmental issue and to preserve P resources, the research works were set to shift to controlled and sustainable fertilizers (Withers, 2015). Among the different strategies explored, the use of Layered Double Hydroxides (LDH) appeared promising. (Everaert, 2016; Borges, 2019). These 2D clay materials are indeed good candidates for this application du to their properties in anion intercalation and their versatility of compositions, synthesis ways and formulations.

The objective of this study was to obtain a better understanding on the controlled phosphate release from Mg_2Al-LDH matrices. Intercalated phases were prepared using different phosphorous sources, LDH precursors and anionic exchange conditions were characterized in detail by a multi technique approach (XRD, SSNMR, FTIR, microscopy, ICP-AES) to highlightthe influence on structural properties. Then, HPO_4^{2-} release kinetics were studied in batch experiments by varying parameters such as solid/liquid ratio, pH, temperature and interfering chemicals. In order to accurately describe the release mechanisms, characterizations of the solid phases before and after release have been performed, showing in particular that the release capacity is strongly reduced for a high solid/liquid ratio.

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Everaert, M., Warrinnier, R., Baken, S., Gustafsson, J.-P., De Vos, D., Smolders, E. (2016)., *ACS Sustainable Chemistry & Engineering*, 4, 4280−4287.
Withers, P. J. A., van Dijk, K. C., Neset, T. S. S., Nesme, T., Oenema, O., Rubæk, G. H., Schoumans, O. F., Smit, B., Pellerin, S. (2015)., *Ambio*, 44, 193–206.

Synthesis and characterization of a new monometallic layered double hydroxide based on Mn

D. Cornu[1,*], R. Coustel[1], G. Renaudin[2], G. Rogez[3], P. Durand[4], A. Renard[1], C. Carteret[1], C. Ruby[1]

[1]Université de Lorraine, CNRS, LCPME, F-54000 Nancy, France
[2]Université Clermont Auvergne, Clermont Auvergne INP, CNRS, ICCF, F-63000 Clermont-Ferrand, France
[3]Université de Strasbourg, CNRS, IPCMS, F-67000 Strasbourg, France
[4]Université de Lorraine, CNRS, CRM2, F-54000 Nancy, France

*damien.cornu@univ-lorraine.fr

Monometallic Layered Double Hydroxide (LDH) are synthesized using only one element for the divalent and trivalent metallic cations. Iron and cobalt monometallic LDHs are well known for their potential applications for nitrate reduction or as capacitors, respectively. However, due to the large reduction potential of Fe^{III}/Fe^{II}, nitrate ions are overreduced by Fe-LDH into ammonium instead of the targeted N_2.

Due to the lower reduction potential of Mn^{III}/Mn^{II}, monometallic Mn-LDH is expected to present milder reductive properties. For the first time, Mn-LDH was synthesized with sulfate ions in the interlayer region (Cornu 2020). XRD measurements and Rietveld refinement demonstrate that this compound presents similar structure (Figure 1) as its Fe analog Fe-LDH (green rust). Mn-LDH was further characterized through Raman and X-ray photoemission spectroscopies. Magnetic properties were studied using SQUID and showed ferromagnetic ordering below 17 K.

The reactivity towards nitrate of the Mn-LDH seems to be limited. However, the synthesis conditions can be modified to obtain Fe-Mn-LDH. Adjusting the Mn/Fe ratio could allow to finely tune the reactivity of the solid. These materials were additionally characterized by ^{57}Fe Mössbauer spectrometry.

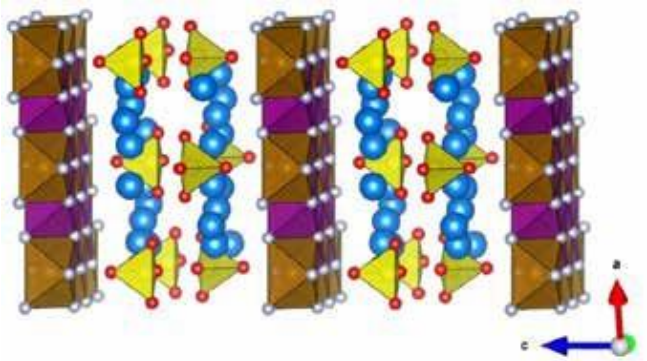


Figure 1. Crystal structure of $[Mn^{II}_2Mn^{III}_2(OH)_6][½SO_4 \cdot 4\ H_2O]$. Brown and purple icosahedrons are Mn^{3+} and Mn^{2+} cations surrounded by hydroxides, blue spheres are water molecules and yellow pyramids are sulfate anions.

Cornu D, Coustel R, Renard A, Durand P, Carteret C, Ruby C. (2020), Synthesis and Characterization of a New Monometallic Manganese Layered Double Hydroxide with Unique Redox Properties, *ChemRxiv*, https://doi.org/10.26434/chemrxiv.13033718.v1

Divalent metal release and antibacterial effects of Layered Double Hydroxides

Jazia Awassa*, Damien Cornu, Samantha Soulé, Cedric Carteret, Christian Ruby, Sofiane El- Kirat-Chatel

Université de Lorraine, CNRS, LCPME, F-54000 Nancy, France

*jazia.awassa@univ-lorraine.fr

According to World Health Organization, about 700,000 global deaths take place per year due to antimicrobial resistance. Recent studies proved that unmodified pristine Layered Double Hydroxides (LDHs) could act as efficient antibiotic-free antimicrobial materials. The partial dissolution of pristine LDHs into their constituents M^{2+} aqueous ions might constitute one possible mechanism explaining their followed antibacterial activity (Figure 1). The partial dissolution of different synthetic LDHs $M^{II}Al^{III}$ (M= Zn, Cu, Ni, Co, Mg) was studied in Lysogeny Broth (LB) and Tryptic Soy Broth (TSB), growth media of *Escherichia coli* and *Staphylococcus aureus* bacteria, respectively. The influence of several physicochemical parameters (crystallinity, M^{II}:Al^{III} ratio, type of intercalated anion {CO_3^{2-}, Cl^-, NO_3^-, ClO_4^-} and nature of M^{II} cations) was investigated. The post-synthetic hydrothermal treatment for $Zn^{II}Al^{III}$ LDH decreased the release of Zn^{2+} ions by 6 times. The opposite effect was observed upon increasing Zn^{II}:Al^{III} molar ratio to 3 : 1 and exchanging carbonate anions with other anions having lower intercalating affinities. Finally, the antimicrobial effect of the studied LDHs was linked in the first place to the nature of constituent divalent metal itself, and to the amount of released M^{2+}ions into the culture media in the second place. This effect was more easily identified in $Zn^{II}Al^{III}$ LDHs whose minimum inhibitory concentration decreased significantly when higher amounts of Zn^{2+} ions were released [1].

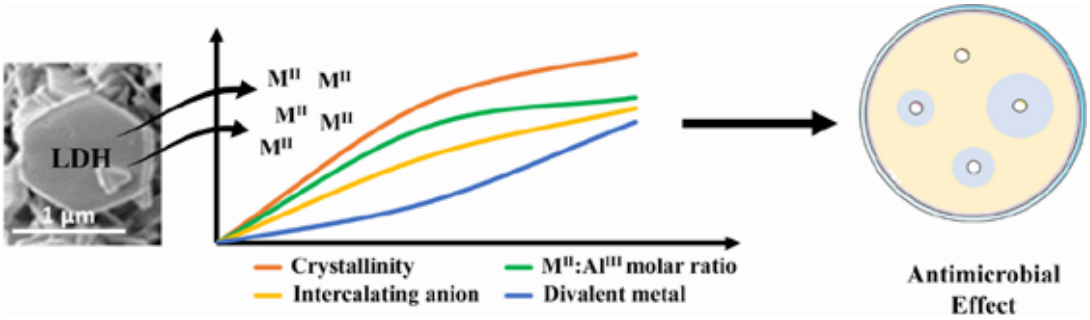


Figure 1. A schematic representation of antibacterial mechanism of pristine LDHs by partial release of divalent metallic ions (M^{II}) initially controlled by their different physicochemical parameters.

[1] Awassa, J.; Cornu, D.; Soulé, S.; Carteret, C.; Ruby, C.; El-Kirat-Chatel, S. Divalent Metal Release and Antimicrobial Effects of Layered Double Hydroxides. *Applied Clay Science* 2022, 216, 106369

Allantoin-zinc layered simple hydroxide biohybrid as antimicrobial active phase in cellulosic bionanocomposites for wound healing

Esther Marugan[1], Ediana P. Rebitski[1], Margarita Darder[1,*], Gustavo del Real[2], Pilar Aranda[1]

[1]Instituto de Ciencia de Materiales de Madrid (ICMM), CSIC, 28049, Madrid, Spain
[2]Instituto Nacional de Investigación y Tecnologa Agraria y Alimentaria (INIA), 28040, Madrid, Spain

*darder@icmm.csic.es

Nowadays, the use of wound dressings to protect wounds or burns is no longer just a barrier mechanism against infection, but a component that actively participates in the healing process (Boateng et al., 2008). Thus, wound dressings loaded with antimicrobial agents are being developed for this purpose, mainly based on biopolymers as biocompatible supports (Lisuzzo et al., 2020; Darder et al., 2022). In the current work, cellulosic materials loaded with a novel zinc layered simple hydroxide (LSH) with allantoin in its structure (allant-ZnLSH) have been developed for potential application as wound dressings. The goal is to develop materials that can exhibit antimicrobial and skin regenerative properties provided by the presence of zinc ions and allantoin, respectively. The allant-ZnLSH biohybrid was synthesized by slow addition of a zinc chloride solution to an aqueous solution of allantoin, while adding a NaOH solution dropwise to maintain a controlled pH. The recovered precipitate was characterized by XRD, FTIR and chemical analysis. The allant-ZnLSH material was further incorporated in polymeric matrices derived from cellulose, such as hydroxypropylmethylcellulose (HPMC), carboxymethylcellulose (CMC) and cellulose nanofibers (CNF), due to their biocompatibility and biodegradability. The mechanical properties, transparency and permeability of these bionanocomposite films were studied, as well as their properties related to the release of allantoin and zinc ions. Their antibacterial action was evaluated against *E. coli* and *S. aureus* in agar plates.

Acknowledgement: The authors acknowledge financial support by project PID2019-105479RB-I00 (AEI, Spain).

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Lisuzzo, L., Wicklein, B. Lo Dico, G., Lazzara, G., del Real, G., Aranda, P., Ruiz-Hitzky, E. (2020). Functional biohybrid materials based on halloysite, sepiolite and cellulose nanofibers for health applications. *Dalton Transactions,* 49, 3830–3840.

Structure and ionic conductivity for Layered Double Hydroxide gel

Noriyuki Sonoyama*, Kohei Ogata, Genki Yamaguchi, Katsuhiro Yamamoto, Katsuhiro Yamamoto

Department of Life and Applied Chemistry, Nagoya Institute of Technology,
Gokiso-cyo, Showa-ku, Nagoya,466-8555 Japan

*sonoyama@nitech.ac.jp

The value of the hydroxide ion conductivity of powder layered double hydroxides (LDH) is at most 10^{-3} Scm^{-1} [1]. On the other hand, the conductivity of single nanosheet LDH is reported to be as high as 0.1 Scm^{-1} [2], suggesting that the conductivity of LDH itself is high, but the high resistance for grain boundary inhibits fast ion migration. Recently, the synthesis of LDH sol by the sol-gel method has been reported [3]. By optimizing the metal ion contents and pH value, we stabilized the gel containing nano-sized LDH.In this study, we analyzed the structure of the obtained gel and measured the ionic conductivity.

No clear peak was observed in the XRD measurement of LDH gel, but a broad LDH-specific diffraction peaks were obtained in the measurement of dried powder. The particle sizes are estimated to be 9.7, 19.7, and 260 nm for Mg-Al, Ni-Al, and Zn-Al LDH, respectively. Figure 1 shows the temperature dependence of the conductivity of various LDH gels. The conductivity of the gel depends on the type of LDH, and the gel with smaller particles showed higher the conductivity. Owing to the high viscosity of the gel, it is speculated that hydroxide ions are moving between the clustered LDH nanoparticles.

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Meta-layered hydroxides: a new 2D material with anion exchange and tunable electronic properties

Víctor Oestreicher[1,*], Diego Hunt[2], Alvaro Seijas-Da Silva[1], Gonzalo Abellán[1]

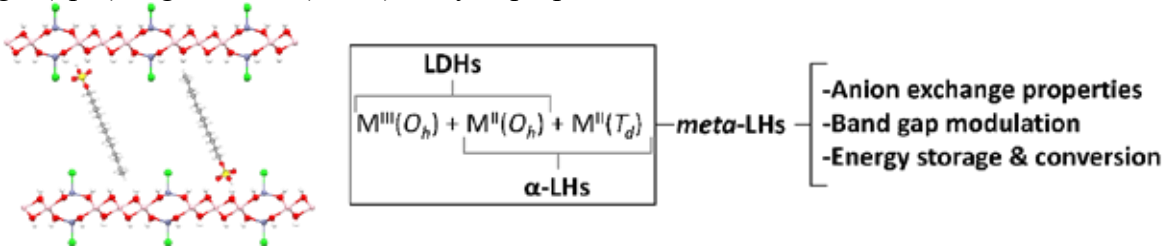
[1]Instituto de Ciencia Molecular (ICMol), Universitat de València, Valencia, Spain
[2]Instituto de Nanociencia y Nanotecnología, Buenos Aires, Argentina

victor.oestreicher@uv.es

In the realm of clay materials, layered double hydroxides (LDHs) represent without any doubt the most famous member of the layered hydroxides (LHs) family. At the beginning being known for their anion exchange properties -reason why they are known as "anion clays"-, they have become an interesting member in the two-dimensional (2D) and layered materials family, representing one of the few examples of positively-charged sheets. Furthermore, their chemical stability at alkaline medium, in addition to their chemical versatility, position them in a prime position in the field of energy storage and conversion. However, one of the main LDHs' drawback is their inherent low conductivity affecting the electrochemical performance. In this line many strategies have been carried out, *e.g.*: carbon matrix hybridization. Nevertheless, due to the intrinsic electrostatic nature that governs the anion-layers interaction, the LDHs' electronic properties are mainly based on the nature on the pristine inorganic host.

In other to overcome this situation, we have intensively worked on the design and synthesis of α-layered hydroxides (α-LHs), another member of the LHs family where the covalent anion-layers interaction allows to control the electronic properties resulting in the modulation of both electrical and magnetic properties (Oestreicher *et al.* 2019 & 2020, Hunt *et al.* 2020). Herein we will introduce our last finding along the investigation of α-LHs with interest on energy storage and conversion, and furthermore we will present the features of a new LHs' member: the *meta*-layered hydroxides (*meta*-LHs), which possess both covalent and electrostatic anion-layers interaction. While the former are based on tetrahedral M^{II} that controls the electronic properties, the later ones are related to the presence of M^{III} allowing the well-known anion exchange properties. Finally, we will discuss the electrochemical results of *meta*-LHs in comparison with their analogs (α-, β-LHs and LDHs) in term of oxygen evolution reaction (OER) at alkaline and neutral conditions.

In overall, our presentation will introduce the main differences between the LHs family members and how *meta*-structures could lead a new pathway for the development of layered hydroxides material for anion exchange, (opto)magnetic and (eletro)catalytic properties.



Hunt, D.; Unveiling the Occurrence of Co(III) in NiCo Layered Electroactive Hydroxides: The Role of Distorted Environments. Chem. Eur. J., 26, 17081–17090.
Oestreicher, V.; et al. (2019) Halide-Mediated Modification of Magnetism and Electronic Structure of α-Co(II) Hydroxides: Synthesis, Characterization, and DFT+U Simulations. *Inorg. Chem.,* 58, 9414−9424.
Oestreicher, V.; et al. (2020) The Missing Link in the Magnetism of Hybrid Cobalt Layered Hydroxides: The Odd–Even Effect of the Organic Spacer. *Chem. Eur. J.,* 27, 921–927.

Introducing Fe-clustering as relevant factor in the design of layered double hydroxides for energy conversion

Alvaro Seijas-Da Silva*, Víctor Oestreicher, Eugenio Coronado, Gonzalo Abellán

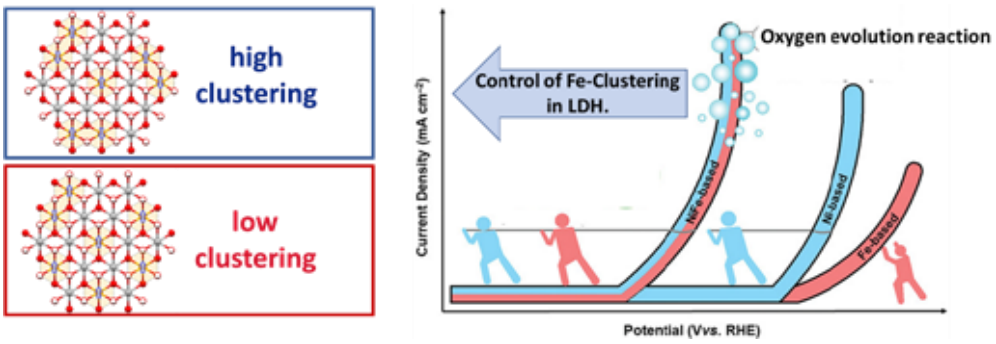
Instituto de Ciencia Molecular (ICMol), Universitat de València, Valencia, Spain

*alvaro.seijas@uv.es

Among the clay materials family, layered double hydroxides (LDHs) represent a distinguished member due to their anions exchange capacity as well as their chemical versatility. Specially, those Fe-based LDHs stand out as one of the best oxygen evolution reaction (OER) electrocatalysts in alkaline conditions (Yi *et al.* 2021). In this context, the important role of Fe centres on the catalytic behaviour has been demonstrated by several in situ techniques as such as X-ray absorption (XAS), Raman and Mssbauer spectroscopies, to name a few (Zhou *et al.* 2021). However, despite all these considerable efforts, there is no information related to the specific role of the atomic distribution of Fe centres (*i.e.*: Fe-clustering) along the LDHs sheets in the OER activity.

Hence, to shed light on the influence of Fe-clustering on this topic, firstly, we have selected MgFe-based LDHs phases as model systems to decipher whether the Fe-clustering exert an effect on the OER performance. By an optimization of hydrothermal method based on triethanolamine different Fe-clustering degree has been achieved, and thanks to the diamagnetic behaviour of Mg, a simple magnetic characterisation allows us to identify the Fe-clustering degree. Nevertheless, both samples behave identically in terms of OER performance when glassy carbon electrodes are used. Surprisingly, when the samples are tested on the most employed electrode, nickel foam, striking differences arise. Specifically, sample exhibiting the lower Fe-clustering behaves as a better electrocatalyst with a reduction of the overpotential values of more than 50 mV to reach 100 mA/cm^2, as a consequence of a favoured surface transformation of MgFe-LDHs phases into more reactive oxyhydroxide NiFe-based ones during the electrochemical tests. Given this scenario, we extended our analysis to NiFe-LDHs where the Fe-clustering is monitored by SQUID and Mssbauer techniques, and furthermore by *in-operando* X-ray absorption (XAS) to assess the transformation of LDHs into the oxyhydroxide catalytic phase.

In overall, our study introduces Fe-clustering as a key parameter to improve the electrocatalytic performance on LDHs.



Yi H.; et al. (2021). Recent Advance of Transition-Metal-Based Layered Double Hydroxide Nanosheets: Synthesis, Properties, Modification, and Electrocatalytic Applications. *Advanced Energy Materials*, 11, 2002863.
Zhou D.; et al (2021). Layered double hydroxide-based electrocatalysts for the oxygen evolution reaction: identification and tailoring of active sites, and superaerophobic nanoarray electrode assembly. *Chemical Society Reviews*, 50, 8790–8817.

An *in-situ* study of the transformation of hybrid layered hydroxides into metallic nanocomposites with interest in energy storage systems

Camilo Jaramillo*, **Víctor Oestreicher, Eugenio Coronado, Gonzalo Abellán**

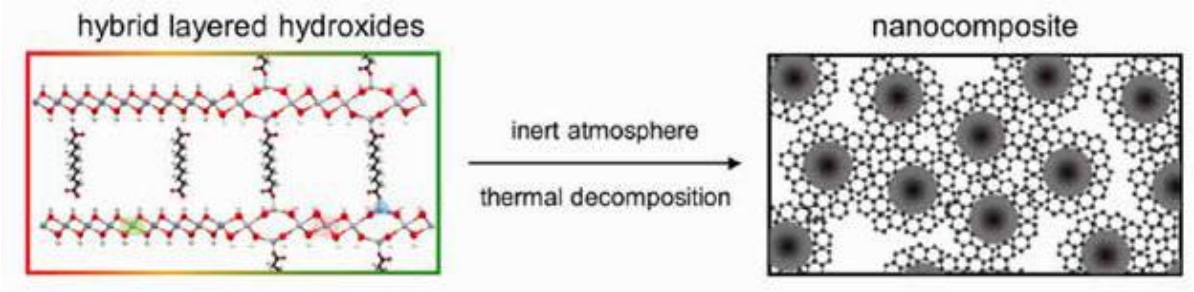
Instituto de Ciencia Molecular (ICMol), Universitat de València, Valencia, Spain

*camilo.jaramillo@uv.es

The high increase of energy demand in recent decade and the necessity of reduce the fossil fuel consumption have triggered the interest of the scientific community in the search of 'green' alternatives. Due to the characteristic intermittence of solar and wind technologies, there is a huge effort on the development energy storage systems. Among them, hybrid capacitors (HCs) are promising materials due its high energy and power density values, in comparison with Li-ion batteries, that make them ideal for industrial and automobile applications. Nanocomposites (NCs) based on metallic nanoparticles (working as *pseudo*-capacitor based in redox reactions) and carbon matrix (working as electric double layer capacitors) are key HCs systems. Typically, these NCs are obtained by the thermal decomposition of hybrid materials under inert atmosphere, as it has been demonstrated for the case of layered double hydroxides (LDHs) and metal organic frameworks (MOFs) (Romero *et al.* 2019; Lopez-Cabrelles *et al.* 2019). However, there is a lack of information in terms of the role of the hybrid in the final NCs, as well as how the thermal transformation takes place.

In this work, we present for the first time an *in-situ* X-ray absorption spectroscopy (XAS) and powder X-ray diffraction (PXRD) study to observe the growth of NC through the thermal decomposition of hybrid layered hydroxides. For that, different hybrids are analyzed: (*i*) the layered hydroxide structure and the anion-layer interactions (LDHs vs α-LHs + electrostatic vs covalent), (*ii*) the metallic composition (metallic ratio and cation nature), and (*iii*) the identity of the organic linkers, to name a few. For instance, in the case of α-LHs, while the LHs structure defines the thermal decomposition (Oestreicher *et al.* 2020), the organic molecule length controls the quality and quantity of the final carbon matrix at the NCs. Interestingly, in all the cases non-changes on the final Co oxidation state have been observed.

In overall, this work introduces fundamental knowledge on the rational design of hybrid layered hydroxides and the subsequent nanocomposites.



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Fabrication of Au@Zn-Al Layered Double Hydroxide-based non-enzymatic electrochemical sensor for lactate sensing

Mohamed Amine Djebbi[1,2,*], Saber Boubakri[3], Mohamed Braiek[4], Nicole Jaffrezic-Renault[4], Philippe Namour[2], Abdesslem Ben Haj Amara[1]

[1]Laboratory of Ressources, Materials & Ecosystem (RME), University of Carthage, Faculty ofSciences of Bizerte, Bizerte, 7021 Tunisia

[2]INRAE, UR RiverLy, Centre de Lyon-Villeurbanne, CS 20244, Villeurbanne, 69625 France
[3]National Institute for Research and Physico-chemical Analysis, BiotechPole Sidi-Thabet, Ariana, 2020 Tunisia
[4]Institute of Analytical Sciences, University of Lyon, Villeurbanne, 69100 France

*med-djebbi@hotmail.fr

Lactate monitoring in the body is of utmost importance in clinical diagnostics. It is a vital biomarkerin the anaerobic metabolic pathway of humans, its elevation may lead to respiratory or hepatic failure and many more diseases and physiological fatigue. In this research, we propose a low-cost and high-performance non-enzymatic electrochemical sensor aimed at the detection of lactate. Thesensor was fabricated by assembling ZnAl layered double hydroxide (LDH) nanosheets along withgold nanoparticles (AuNPs) onto boron-doped diamond electrodes (BDD). The as-prepared materials were characterized by X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FT-IR), UV–visible spectrophotometry (UV–vis), transmission (TEM), and scanning (SEM) electron microscopy, while the modified electrode was characterized by cyclic voltammetry(CV) and electrochemical impedance spectroscopy (EIS). The electrochemical measurements for lactate binding were performed using square wave voltammetry (SWV), revealed high sensitivity of 13.9 µA/µM/cm^2, broad detection ranges of 0.1–30 µM and low detection limit up to 0.1 µM. Besides, the proposed lactate sensor possessed excellent long-term stability, good reproducibility, repeatability, and selectivity. The response currents of detection in biological samples were also close to the standard solutions. Therefore, the developed sensor is promising to be used in clinical practice.

Layered Double Hydroxides for electroanalysis

Isacco Gualandi*, Elisa Musella, Federica Mariani, Danilo Arcangeli, Erika Scavetta, Domenica Tonelli

University of Bologna, Department of Industrial Chemistry 'Toso Montanari', Viale Risorgimento 4, 40136 Bologna, Italy

* isacco.gualandi2@unibo.it

Layered double hydroxides (LDH) have been thoroughly studied as active materials for the design and development of electrochemical sensors. Chemical tenability, as well as the use of earth-abundant elements underpin the use of LDH in different fields ranging from medicine to catalysis. The large surface area, the ions exchange ability and the electrocatalytic behavior of LDHs containing redox active metals are the key features that allow to improve the performances of electrochemical sensors through a boosted charge transfer between the analytes and the electrode surface and/or the analytes pre-concentration. Moreover, the layered structure can host active molecules, such as enzymes, for the selective sensing based on a bio-recognition element.

This contribution summarizes the work of Tonelli's group on LDHs based sensors (1995 - now) focusing on the last advancements. The device preparation is mainly carried out by electrochemical deposition to obtain thin LDHs films that are well adherent to the electrode surface. The most employed sensing strategy is based on redox mediators such as Ni and Co centers that can electrocatalyze the oxidation of different compounds in alkaline environment. The use of Al as trivalent cation is preferred because it hinders the oxygen evolution reaction with a consequent widening of the useful potential range for analytical determinations. Electrodes modified with these materials have been proposed and tested for the quantification of a variety of oxidizable analytes (Tonelli et al, 2012). A recently developed electrosynthetic procedure allows the production of composite materials that exhibit improved electrical conductivity, charge transfer and stability. The composites based on a Ni-Al LDH and various carbon based nanomaterials have been tested for glucose electrooxidation, which was exploited for the fabrication of a sensor with high sensitivity (2.6 A M^{-1} cm^{-2}) and low limit of detection (0.6 µM) (Gualandi et al., 2019). Finally, a new approach based on organic electrochemical transistors (OECT) has also been proposed. It has enabled the design two sensors for glucose and lactate, which exploit an electrode modified with a Ni/ Al LDH entrapping glucose oxidase or lactate oxidase (Mignani et al. 2006). The amperometric current is used for the transduction, it is amplified (400 times) by the transistor architecture. The biosensor detects glucose in the concentration range 0.1–8.0 mM, with a limit of detection of 0.02 mM. For lactate, the biosensor response is linear in the concentration range 0.05–8.0 mM, with a LOD value of 0.04 mM (Gualandi et al. 2020).

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Layered Double Hydroxides for energy applications

Domenica Tonelli*, Isacco Gualandi, Elisa Musella, Erika Scavetta, Sergio Zappoli

University of Bologna, Department of Industrial Chemistry 'Toso Montanari, Viale Risorgimento 4, 40136 Bologna, Italy

* domenica.tonelli@unibo.it

LDHs containing transition metals with redox activity are considered as one of the most promising electrode modifiers in the field of the electrochemical applications in virtue of their high electrocatalytic activities and thanks to a large surface area. Several synthetic methods can be found in literature for LDHs preparation, whose major drawbacks are the long time needed for the reaction to occur and the poor adhesion to the support material when the LDH acts as a coating. Among the different synthesis strategies, electrodeposition has enormous potential because it merges the step of synthesis with the modification of the electrode with a well adhered film by a simple, low-cost, green and rapid procedure.

In 2004 our group proposed the potentiostatic electrodeposition of LDHs and, more recently, a potentiodynamic approach has been applied which results in a better reproducibility of the deposited material (Musella et al., 2019). Furthermore, it allows to synthesise LDHs, as such or intercalated with carbon nanomaterials, with defined Me(II)/Me(III) ratios.

The electrocatalytic features were particularly investigated for LDHs containing Co or Ni as bivalent cation, and Al or Fe as trivalent one. In the field of energy storage and conversion all the synthesised LDHs were investigated by our group as water splitting catalysts to gain more insight on the effect of the substitution of Al with Fe as trivalent metal on their catalytic performance for OER (Vlamidis et al., 2016), and a more in-depth study on the same materials was carried out to estimate the effect of the different trivalent cation on the specific capacitance (Vlamidis et al., 2017)

Composites LDHs/carbon nanomaterials exhibit a boosted charge transfer between the active centre of the LDH and the electrode surface, and a larger active area. These composites were also successfully applied for the development of supercapacitors with an improved specific capacitance and long life (Musella et al., 2021). Very recently our group has started a study on the performances of LDHs based on three metals (Co, Ni and Fe) for OER, investigating different metals ratios which have been established by a chemometric approach and very interesting results have been already obtained.

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Preparation of glass-bead filter disk coated by layered double hydroxide

Shingo Machida*, **Ken-ichi Katsumata, Atsuo Yasumori**

Tokyo University of Science, Department of Material Science and Technology, 125-8585 Tokyo

*shingo.machida@rs.tus.ac.jp

Adsorption of ions/molecules from water has been investigated in various fields including environmental purification. A bulk state adsorbent is relatively collectible. When a bulk substance possesses low adsorption capability, the support of inorganic particle with adsorption capabilities is feasible. Here, we report the deposition of layered double hydroxides (LDHs) on a glass-bead filter (GBF) disk, a spherical glass-beads sintered body with filtration property (Shashini et al., 2019). Notably, GBF has been utilized to the circulated filtration system (Shashini et al., 2019). GBF is thus the best candidate in term of no clogging filter that is advantageous for an adsorption experiment. This study conducted the homogeneous precipitation using urea hydrolysis (Ogawa and Kaiho, 2002) of magnesium and aluminum type LDH (MgAl-LDH) in the presence of a GBF disk (Machida, et al., 2021) (Fig. 1). After the reaction, the bulk filter product was never collapsed. The scanning electron microscope image of the product illustrated the vertically-aligned plate-like particles on the GBF surface. The X-ray diffraction pattern for the product showed the 0.76 nm diffraction line due to the basal spacing of MgAl-LDH (Ogawa and Kaiho, 2002). The Fourier-transform infrared spectrum of the product exhibited the weak shoulder at around 1483 cm^{-1} which was assignable to CO_3^{2-} stretching band (Ogawa and Kaiho, 2002). Furthermore, the resultant bulk filter was applied to the adsorption experiments with methyl orange (MO) in both bath and flow systems, resulting in the drastic color change the product from white to orange. These results indicated the successful coating of Mg-Al LDH on the GBF disk.

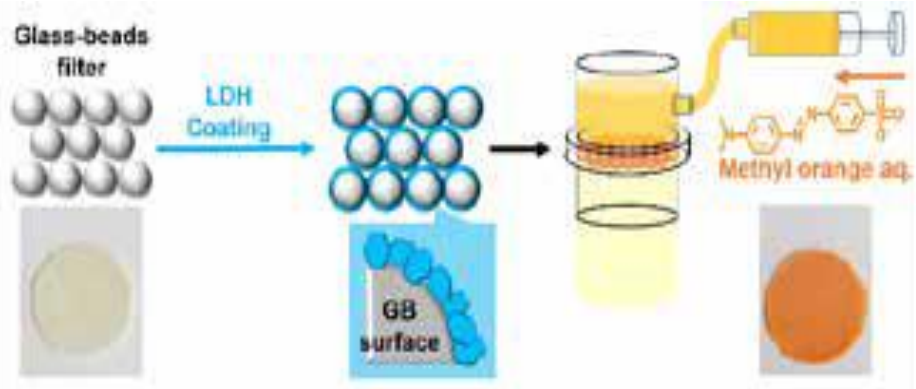


Figure 1

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Formation of mixed Fe-Mn Layered Double Hydroxide using {Fe^{2+},$Fe(OH_2$} and birnessite

Amira Doggaz[1], Romain Coustel[1], Pierrick Durand[2], Damien Cornu[1], François Humbert[1], Christian Ruby[1,*]

[1]Universit de Lorraine, CNRS, LCPME, F-54000 Nancy, France
[2]Universit de Lorraine, CNRS, CRM2, F-54000 Nancy, France

*christian.ruby@univ-lorraine.fr

The chemical interactions between Fe and Mn species could contribute to understanding the interactions between the respective biogeochemical cycles of those two ubiquitous elements in theenvironment. Moreover, ferromanganese solid compounds are potentially interesting materials fordenitrification with an adjustable composition.

The addition of birnessite in a solution containing only $Fe(OH)_2$ did not change much the oxidationpath of the solid with air towards magnetite Fe_3O_4. However, when the molar ratio OH^-/Fe^{II} was reduced to 1.67, a ratio that leads to the formation of Fe-LDH, also called "green rust", the additionof birnessite significantly changed the kinetics of the transformations in the solution as well as theintermediate and final products. Indeed, the oxidation of the {Fe^{2+},$Fe(OH)_2$} mixture into green rust necessitates a time span of more than 300 minutes. The addition of birnessite in the solution reduced this time span by a factor 3. The XPS analysis of the final product containing manganese showed a significant reduction ofmanganese indicating that birnessite was involved in the redox reactions.

Besides, XRD analysis of the oxidation product showed a significant enlargement of the in- tra-lamellar distances for increasing birnessite loading indicating the substitution of Fe^{2+} by thelarge ion Mn^{2+}. The mixed Mn/Fe LDH were also analyzed with Mössbauer spectroscopy and XPSanalysis.

Doggaz A, Coustel R, Durand P, Humbert F, Ruby C (2020), Birnessite: A New Oxidant for Green Rust Formation, *Materials*, 13, 3777.

Tuning the electronic properties of α-Co based Layered Hydroxides as a tool for boosting energy application performance

Youssra Diouane*, **Alvaro Seijas-Da Silva, Víctor Oestreicher, Gonzalo Abelln**

Universitat de Valncia, Instituto de Ciencia Molecular, 46980 Paterna, Spain.

*youssra.diouane@uv.es

As another example of clay materials, layered hydroxides (LHs) are a class of two-dimensional (2D) lamellar structures with versatile chemical tuneability, where layered double hydroxides (LDHs) own the "anionic clays" membership thanks to their anion exchange properties. Nowadays, LDHs are on the spotlight due to their flexible physico-chemical properties, that have positioned them as key materials for energy conversion and storage systems. For instance, LDHs based on earth-abundant elements are good candidates for electrode materials for oxygen evolution reaction (OER) in alkaline condition, as well as for supercapacitors. However, one of the major drawback of these materials is their low electrical conductivity, which represents a limitation in the optimization of the electrochemical performance and the assemble of devices.

Among the different approximation to overcome this issue, we are intensively working on the modulation of the electronic properties of LHs. In this line, Co-based α-layered hydroxides, exhibiting *simonkolleite*-like structure, can be an interesting case of study since the covalent bond between the hydroxylated layer and the anion. Indeed, we have recently demonstrated that the electrical properties can be modulated by halide substitution (Oestreicher 2019), where the band gap can be reduced by ligand to metal charge transfer as demonstrated by DFT+U simulations. Considering these previous results, we decided to analysed the role of these chemical modifications in terms of the electrochemical properties.

Interestingly, our results evidence a better electrochemical activity of Co-based α-LHs in comparison with the typical β-LHs or LDHs analogues, in both OER and specific capacitance performance. Moreover, in the case of α-LHs the values can be further enhanced by tuning the nature of the anion: for instance, structures containing iodide overpass in more than 40% those ones containing chloride, as mentioned by DFT+U simulation.

Hence, this work positions α-Co^{II} hydroxides as key phases among the layered hydroxides family as electrode materials for energy storage and conversion, where the conductivity can be improved by anion substitution.

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Preparation of anisotropic crystals of β-Ni(OH)$_2$ grown along stacking direction using Ni-diamine complexes

Keisuke Muramatsu[1,#,*], Mina Jimba[1], Hiroaki Wada[1,2], Atsushi Shimojima[1,2], Kazuyuki Kuroda[1,2]

[1]Waseda University, Faculty of Science and Engineering, Tokyo 169-8555, Japan
[2]Waseda University, Kagami Memorial Research Institute for Materials Science and Technology, Tokyo 169-0051, Japan
[#](Present address) Shinshu University, Research Initiative for Supra-Materials (RISM), Nagano 386-8567, Japan

*kei_muramatsu@shinshu-u.ac.jp

Brucite-type layered metal hydroxides and layered double hydroxides are structurally analogous and important classes of materials with a wide range of applications. Various attempts have enabled the preparation of layered metal hydroxides with diverse crystal shapes; however, the synthetic chemistry to promote the anisotropic crystal growth along the stacking direction is not mature. Here, we report the preparation of β-Ni(OH)$_2$ anisotropically grown along the stacking direction under the presence of dipodal amine ligands (Scheme 1). We successfully prepared hexagonal prism-like β-Ni(OH)$_2$ crystals with an aspect ratio of the thickness to the lateral size larger than 1. A systematic investigation focusing on the molar ratio of amine ligands to Ni^{2+}, the concentration of Ni-diamine complexes, and stability constants of the complexes revealed that anisotropic growth was promoted when the supersaturation at the growth stage was relatively high and was maintained for a longer time. Amine ligands act as Ni^{2+} reservoirs to control supersaturation through the controlled release of metal ions from stable complexes. This study provides important insights for developing general synthetic chemistry for various layered compounds to control the aspect ratio.

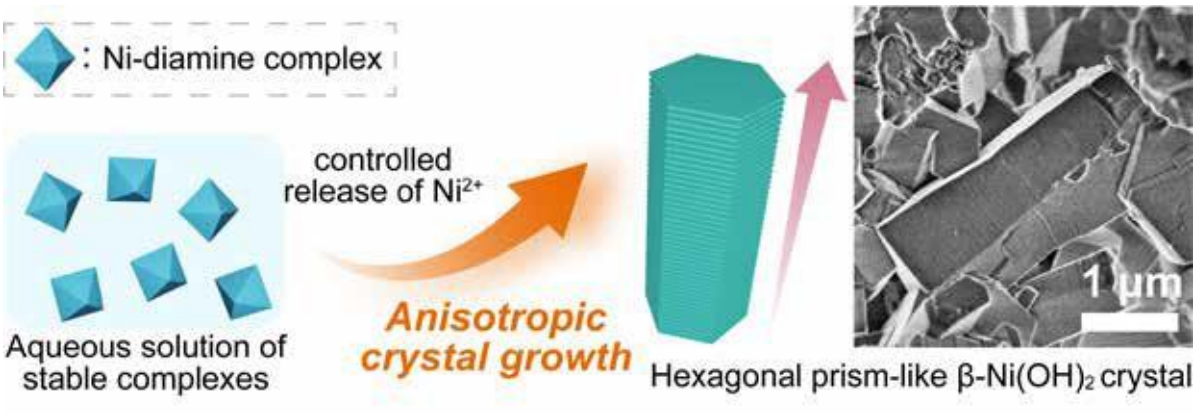


Figure 1. Anisotropic crystal growth of β-Ni(OH)$_2$ using dipodal amine ligands.

TS18 Layered Double Hydroxides

POSTER PRESENTATIONS

The characteristics of V(V and P(V adsorption by LDH derived from magnesite: kinetics, pH influence and competition with common anions

Karolina Rybka[1,*], Jakub Matusik[1], Klaudia Dziewiątka[1], Agnieszka Giera[1], Mateusz Marzec[2]

[1]AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, al. Mickiewicza 30, 30-059 Krakow, Poland

[2]AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, al. Mickiewicza 30, 30-059 Krakow, Poland

*krybka@agh.edu.pl

With a vast amount of research devoted to new adsorbents for wastewater treatment, special attention is given to the development of simple low-cost materials. This study described the adsorption properties of Mg/Al and Mg/Fe LDH derived from magnesite (M) (Rybka et al., 2022). The affinity towards V(V) and P(V) of the studied materials was compared with that of LDH conventionally obtained from chemical reagents.

The structure of LDH is built of brucite-like layers build from divalent (M^{II}) and trivalent (M^{III}) metal octahedra. The positive charge of the layers is balanced by easily exchangeable hydrated anions. This makes LDH a promising material for the removal of anionic pollutants. In this work, the M was used as a M^{II} source substituting the conventionally used chemical reagents. It was dissolved in $AlCl_3$ or HCl to release Mg(II) for the synthesis of Mg/Al and Mg/Fe LDH, respectively. The LDH materials were obtained with a co-precipitation method.

The studied materials were compared to the reference LDH samples obtained exclusively from the chemical reagents. The maximum capacity of the materials was tested in the removal reactions of V(V) and P(V) chosen as toxic and eutrophogenic elements, respectively. The minimal doses of the adsorbents were determined for the effective removal of low initial concentrations (C_{in} = 0.05 mmol/L) of the anions. The kinetics, pH effect (pH = 3 and 5) and co-existing anions (SO_4^{2-}, NO_3^-) influence on adsorption efficiency was described.

The materials showed a high affinity for V(V) and P(V). The Fe-bearing materials were more efficient than their Al-containing analogues. The removal rate of P(V) was lower than that of V(V). The SO_4^{2-} influenced the removal rate of V(V) by Al-bearing LDH. The lower pH increased the removal of P(V) by Fe-bearing materials. In the other cases, the adsorption efficiency of V(V) and P(V) did not decrease, which confirmed the high stability of the materials at pH = 3. In turn, the removal of competitive anions drastically decreased.

Acknowledgement: This project was supported by the National Science Centre Poland, under a research project awarded by Decision No. 2017/27/B/ST10/00898.

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Better insights on layered double hydroxide nanoparticles prepared using epoxide method

Marwa Bouebdellah[1,*], Alexandra Jourdain[1], Gro Nielson Ulla[2], Claude Forano[1], Vanessa Prevot[1]

[1]Clermont Auvergne University, Institute of Chemistry of Clermont-Ferrand, 63000 Clermont-Ferrand, France

[2]University of Southern Denmark, Department of Physics, Chemistry and Pharmacy, 5230 Denmark

*Marwa.bouebdellah@uca.fr

Layered double hydroxides are known as anionic clays, their general formula is [MII 1−xMIIIx (OH)2] x +[An− x/n ·yH2 O]x−,where MII and MIII are divalent and trivalent metal cations, respectively, and An − is an anion. They are particularly interesting materials due to their layered structure allowing the intercalation of different types of anions. These promising materials find their applications in various fields such as catalysis, adsorption, drug delivery and electrochemistry. The synthesis of LDH can be easily done in the laboratory. Interestingly, by modulating the parameters of synthesis pure LDH matrices with different particle sizes and shapes can be obtained displaying in certain cases enhanced surface properties. These characteristics have a strong impact on the reactivity of the phases and on their efficiency in applications.

Various chemical composition of LDH nanoparticles were prepared, in this work, by using a synthesis method that has been recently described for these materials: “the epoxide route” [1]. It corresponds to a simple method based on the use of an epoxide in hydro alcoholic solution which acts as a proton scavenger and induces a spontaneous increase of the pH in the reaction medium leading to the hydrolysis and condensation of metal complexes (aquo-hydroxy) to form hydroxide networks. [1-2]

This poster will bring together the main results concerning the epoxide synthesis of LDH with different chemical compositions mainly Zn-Al, Li-Al, and Zn-Ga. The effect of the synthesis conditions on the purity and properties of these materials was investigated thanks to a multi-technique structural approach (XRD, IR, NMR, microscopy...), in order to better understand the mechanism of LDH formation and to try to establish a relationship between synthetic conditions and morphology of LDH particles. The second step of this work was to study the efficiency of these phases towards the adsorption of pollutants mainly the phosphate ions.

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Porous mineral @ layered double hydroxide composites as encouraging controlled release fertilizers

Alexandra Jourdain[1,*], Sébastien Masclet[2], Claude Forano[1], Vanessa Prévot[1]

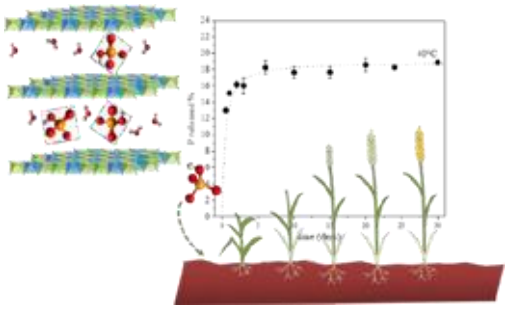
[1]Université Clermont-Auvergne, CNRS, Clermont Auvergne INP, Institutde Chimiede Clermont-Ferrand, ICCF, 63178 Aubière, France
[2]Pouzzolanes des Dômes, LeVauriat, 63230 Saint Oursles Roches, France

*alexandra.jourdain@doctorant.uca.fr

Given the increasing global demography, heighten agriculture production and yield is becoming aneed. This need lead stoan intensive use of input as fertilizers, pesticidesor herbicides which have harmful consequences on health, environment and mineral resource amounts. A real challenge for the next years will be to provide enough food while limiting chemical input and preservingsoilsand- water tanks from pollutions. To reach this aim, research work saref ocusing on developments of sustain- able slow release or controlled fertilizers. Until now, soluble fertilizers coated by polymers (Thompson,1991) or less soluble materials combine with organic (Lu, 2019; de Castro, 2020) or inorganic matrix (Yuan, 2017), do not fulfill the environmental challenges.

Inthiscon tex tLayered Double Hydroxides (LDH), alsocalledanionicclay-likematerialswere described as good candidates for the development of sustainable fertilizers because of their unique anion exchange or sorption properties (Everaert, 2016) and their versatility of compositions, synthe- sis pathways and formulations (Borges, 2019).

The aim of this study is to test composites based on porousrockscoated by LDH for phosphate andni- trate controlled release of wheat growth in realconditions. Porousmineral@LDH_M2Al-



X (M = Mg^{2+}, Zn^{2+}; X = NO^{3-}, $HPO4^{2-}$) composites we reprepared by compacting mechanically copre- cipitated nutrient-loaded LDH at the surface of 0/3 mm size mineral gravels. Formulated materials were- characterized in terms of chemistry, structure and morphologyby respectively ICP-OES, XRD and electron microscopy. Thesenewfertilizersweretested and compared to commercial fertilizer for wheat growth using laboratory soil column experiments. Results of plant growth and soil leaching will be presented.

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Impregnation of smectite with layered double hydroxides of different chemistry for simultaneous removal of Cr(III) and acid blue dye

Anna Jędras*, Jakub Matusik, Karolina Rybka

AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, al. Mickiewicza 30,30-059 Krakow, Poland

*ajedras@student.agh.edu.pl

The deposition of anionic layered double hydroxides (LDH)oncationicsmectites leads to formation of bifunctional adsorbents. This enables a simultaneous removal of contaminants which possess opposite charge from the polluted aqueous solutions. A perfect example of the latter are wastewaters from the tanning industry. These often contain inorganic Cr(III) as cationic pollutant which is used as tanning agent. TheCr(III) maybe accompanied by amixture of variousorganic dyes including an ionic compound. Therefore, the adsorptive remediation of such complex wastewater requires the use of materials showing dual adsorption properties.

Based on the above the aim of this study was to obtain smectites impregnated with LDH of different chemistry and compare their efficiency in simultaneous adsorption of Cr(III) and Acid Blue Dye 129 (AB129). For the experiments 4 materials were obtained by the co-precipitation of LDH (Mg-Fe (S-MF), Mg-Al (S- MA), Ni-Al (S-NA) and Ni-Fe (S-NF)) in the presence of smectite sample from Wyoming (SWy). The mass ratio of smectite/LDH was set to 1:1. The syntheses wereconducted as follows: solutions ofmetal nitrates wereadded to the suspension of smectite in water (pH 4 controlled by the solution of 0.1 M HCl)and left for 24 h with stirring. Then, solution of 2 M NaOH was added to reach the pH range of 9-11. The formed dispersion was aged for 24 h with stirring. Afterwards it was centrifuged, washed with DI water and dried at 60°C for 24 h. For comparison 4 analogous smectite/LDH physical mixtures as well as raw SWy and LDHs were used in the experiments. The Cr(III) and AB129 adsorption was carried out by adding 5 ml of 3 mM $Cr(NO_3)_3$ or 100 mg/LAB129 to 50 mg of adsorbents and shaking for 1 h. The concentration was measured by AAS and UV-Vis, respectively.

The XRD of obtained materials showed a 7.7 Å peak confirming formation of LDH on the smectite surface. Moreover, fortheS-MA and S-NA (Al-containing LDHs) a shift of smectite d_{001}peak was observed to 15.5 Å and 19.0 Å, respectively. This indicated intercalation of Mg and/or Al cationic forms into smectite interlayer space. In turn for the S-MF and S-NF (Fe- containing LDHs) the smectite d_{001}peak disappeared and/or was shifted to ~30.0 Å. This suggests extensive delamination of smectite particles. All 4 materials show similar values of cation exchange capacity (CEC) measured by Co(III)-hexammine approximately 35meq/100 g. This indicates that CEC of starting SWy was lowered from initial value of ~85 meq/100 g. Adsorption of Cr(III) on the mentioned materials differed significantly–the highest efficiency wasfor the S-MF(97%), then for the S-MA(40%) and the S-NF(18%). The adsorption for the S-NAwas negligible. Such differences were due to equilibrium pH values. The pH was highest in the case of S-MF and caused Cr(III)precipitation apart from its removal by ion-exchange. All of the obtained materials have shown high ad- sorption capacity towards AB129 (>75%).

Hydrotalcite-zeolite heterocoagulated materials: towards materials with dual adsorption properties

Klaudia Dziewiątka*, Jakub Matusik, Karolina Rybka

AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, al. Mickiewicza 30,30-059 Krakow, Poland

*dziewiatka@student.agh.edu.pl

With the rapid development of modern industry, an increasing amount of wastewaters is produced. These contain a wide variety of cationic and anionic pollutants, frequently classified as carcinogenic or toxic. Leather manufacturing, especially tanning, is recognized as an enormous source of heavy metals and hazardous dyes. Due to the complexity of their simultaneous removal, the synthesis of materials with dual adsorptionproperties is essential.

In the present study, a one-pot hydrothermal method for combined layered double hydroxide (LDH) and zeolite synthesis was investigated. In total 4 various samples (HM) were obtained containing zeolite synthesized from calcined kaolinite or halloysite and Mg/Al-Cl or Mg/Al- NO_3LDH, respectively. Prior to synthesis all substrates (metakaolinite or metahalloysite with Mg and Al salts) were subjected to aging in 3M NaOH at room temperature. The synthesis was carried out within 24 h in a closed system at 100°C and ~1 bar pressure. For comparison 2 materials (CM) were prepared by coprecipitation of Mg/Al-NO_3LDH in suspension containing earlier synthesized zeolite from metakaolinite or metahalloysite. All synthesized adsorbents were tested for As(V) and cationic safranin O dye (SO) removal.

The XRD patterns of all samples confirmed the presence of hydrotalcite with the basal reflection in the 7.2–8.2 range and sodalite with (110) reflection in the 6.3-6.4 range. The FTIR spectra revealed bands in the 3650-3440cm^{-1} region due to OH stretching vibrations of ads or bed water. In turn the bands in the1420-1370cm^{-1} region confirmed presence of LDH intercalated with nitrates and/or carbonates. The SEMimages of HM samples showed homogenous mixture of LDH and zeolite particles. Whereas clear separa-tion of these phases was observed for the comparative CM samples. This resulted in significant differences of external cation exchange capacity (ECEC). It was in the range of 19.25-6.18 meq/100 g for the HM samples and 0.10-1.33 meq/100 g for the CM materials. This was probably the effect of blocking the surface active sites of zeolite by precipitated hydrotalcite phases. The different synthesis approaches in particular affected the removal efficiency of SO. Regardless of the studied system i.e. single system (SO or As(V))or dual system (SO and As(V)) the removal efficiencies showed same trends. The HM materials adsorbed ~64.6-94.4% of SO (initial concentration: 100 mg/L) while their analogs (CM) removed only ~7.2-11.4%. The anion exchange capacity (AEC) determined by As(V) adsorption provided values in a broad range of ~56.5-120.4 meq/100 g. Despite that the efficiency of As(V) removal for both HM and CM was equal to 20.5- 33.9% (initial concentration: 1000 mg/L). All analyses indicated superior adsorption properties of HM composites in systems containing both As(V) and SO.

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From MOFs to LDHs: application to waste water treatment

Mengwei Li[1,2], Zhixiong You[2], Vanessa Prévot[1], Claude Forano[1]

[1]UniversitéClermont-Auvergne, CNRS, Clermont Auvergne INP, Institutde Chimiede Clermont-Ferrand, ICCF, F-63000 Clermont-Ferrand, France

[2]School of Resource and Environmental Science, Wuhan University, China

*mengwei.li@doctorant.uca.fr

The interes to Layered Double Hydroxides (LDH) for environmental remediation applications has been reported since more than twenty years and is nowadays well established (Zubair, 2016). Adsorption and ion exchange properties of LDHs or modified LDHs (hybrids, nanocomposites, calcined LDHs) allow to efficiently remove a large range of pollutants such as pesticides, phytosanitary molecules, drugs, heavy metals from contaminated waters or wastewaters. Optimization of removal performances has been focused notonlyon chemical composition but also on the tuning of LDH particle and aggregation morphology.Thanks to the recent advances in synthesis methods 3Dhierarchical and porous LDHs can be obtained (Prévot, 2017). Conversion of 3D sacrificial templates based on organic or hybrid structures into LDHs is a soft strategy that preserves the original architecture and leads the formation of nano-structurated mesoporous LDH macrostructure. MOFs are transition metal-based hybrid nano and macrostructures that display various to pology and morphology, with enhanced surface properties and reactivities (Stock,2012). Conversionof MOFs into LDHs offer a very new and interesting strategy route for the preparation of LDH with novel architectures (Zhang, 2020).

In this study, we optimized and compared the preparation of Fe-based MOFs (MIL-88A) by hydrother-mal-assisted and microwave-assisted precipitation in order to tune the size and shape of thehexagonal-rod-like structure of MIL-88A. The pseudomorphic transformation of MIL-88A into MIIFe-LDH was investigated for M_2II:Ni^{2+}, Co^{2+}, Cu^{2+}. Typically, MIL-88A was contacted with an aqueous solution of MII salt under controlled basic conditions and assistance of hydrothermal treatment or microwave. Changes in structure and morphology were monitored by X-ray diffraction, electron microscopy (SEM, TEM), DLS and N2po- rosimetry. The novel LDHs architectures were evaluated for heavymetal (Pb^{2+}, Cd^{2+}, Zn^{2+}) adsorption and adsorption isotherms were fitted using standard models Langmuir, Freundlich).

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TS19 + TS29 High Temperature Bentonite Barriers

ORAL PRESENTATIONS

Stability of smectite at 2°C: How KCl, K-acetate and K-oxalate influences the formation of 10 Å-layers

Julia Schlosser[1], Georg H. Grathoff[1,*], Stephan Kaufhold[2], Jan Dietel[3], Anja Schleicher[4], Laurence N. Warr[1]

[1]Institute of Geography & Geology, Univ. of Greifswald, Greifswald, Germany
[2]BGR, Federal Institute for Geosciences & Natural Ressources, Hannover, Germany
[3]State Laboratory Berlin-Brandenburg, Berlin, Germany
[4]GFZ, German Research Centre for Geosciences, Potsdam, Germany

*grathoff@uni-greifswald.de

The stability of smectite plays a critical role in sealing high radioactive waste repositories. We conducted experiments at high temperatures (200°C) using the <2 µm size separated Milos bentonite and e.g. 0.03 mol/L KCl, 0.06 mol/L K-acetate (KAc) and 0.03 mol/L K-oxalate (KOx) solutions in a rotating oven for 3 months. Known is that the addition of organic anions to smectite in solution can aid the formation of 10 Å-layers. However, the precise nature and mechanism by which they form is a topic of continuing debate, because 10 Å-layers can represent illite, glauconite, celadonite, or K-smectite phases. We present XRD, HRTEM, CEC, and chemistry results, all indicating that the smectite has changed.

To characterize the interstratifications and K-fixation, ethylene-glycol (EG) solvated and Ca re-exchanged reaction products are presented. XRD patterns were modelled using both NEWMOD and Profex. KCl treated samples showed only minor alteration, whereas batches with organic anions produced interstratifications containing 70 to 85 mol-% 10 Å-layers. The neoformation of orthoclase and calcite (with KOx) were also observed. After Ca re-exchange the reaction products still retained10 Å-layer structures. Random powder XRD results also showed an increase in the b-dimension which appears irreversible.

HRTEM study of selected samples showed thin smectite particles of "cornflake" morphology in all samples, however, fringe images revealed variable layer thicknesses for the different samples. The original untreated smectite layers have higher d-spacings with a mean value of ca. 13.3 Å and curved cross-sections. The KCl treated samples show interstratifications of smectite and 10 Å layers with non-uniform packets and also wavy fringes with some lateral transitions of smectite layers (mean value ca. 11.5 Å). KOx treated samples show dominant 10 Å layers before (mean value ca. 10.3 Å, parallel shape) and after Ca saturation (ca. 10.5 Å parallel shape). Based on energy-dispersive X-ray spectroscopy (EDX) analyses, the K^+-content is highest with KOx together with decreasing Si^{4+} and increasing Al^{3+} contents, possibly suggestive of a change in the layer charge. Selected area electron diffraction (SAED) images confirm the smectite-like turbostratic nature of the educts and the KCl treated sample. Diffraction features also confirm 1Md like structures for the KOx samples.

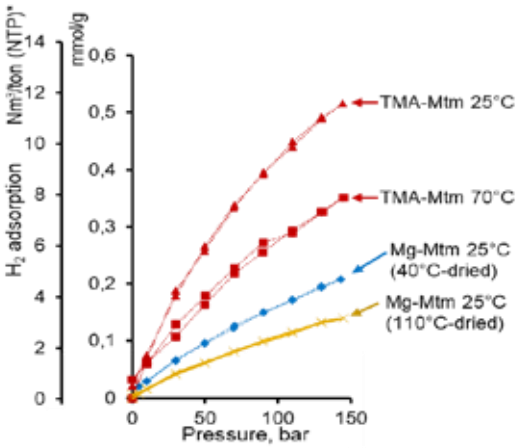
Our results show that the formation of the interstratified10 Å-layers are irreversible and permanent structural changes have occurred. Whether these irreversible changes have any effect on the stability of bentonites in a repository setting needs to be tested further.

Adsorption of hydrogen gas on clay minerals under conditions relevant for underground nuclear waste repositories

Paweł P. Ziemiański*, Arkadiusz Derkowski

Institute of Geological Sciences, Polish Academy of Sciences, Senacka 1, PL-31156 Krakow, Poland

*ndziemia@cyf-kr.edu.pl



In underground nuclear waste repositories after their closure, hydrogen (H_2) will be released into bentonite buffer materials due to anaerobic corrosion of steel containers. Because of the extremely low permeability of bentonite, a smectite-rich rock, up to 100 bar of H_2 pressure will build up and be present there for tens of thousands of years (Xu et al., 2008). These high-pressure conditions will result in a significant portion of H_2 being physisorbed onto smectitic clay minerals.

In this study, we have investigated the high-pressure (0-150 bar) adsorption of H_2 on various cationic forms and hydration states of pure smectites and on illites at ambient and elevated temperatures. The study investigates H_2 intercalation into smectitic interlayers and the influence of sample texture on the adsorption.

The adsorption of H_2 on clay minerals depends on the adsorption temperature, crystallite planar dimensions, and the interlayer hydration state. The results show that the finer the crystallites of illite or smectite, the higher the H_2 adsorption. H_2 intercalates within smectitic interlayers of samples with basal spacing larger than 10.8 Å. Most of H_2 is adsorbed in micropores accessible for carbon dioxide, which can serve as an H_2 adsorption proxy. The measured values of H_2 adsorption on clay minerals under 145 bar are between 0.049 and 0.512 mmol/g. Therefore, H_2 adsorption on smectites and illites under high-pressure at elevated temperatures is significant and will decrease the hydrogen pressure build-up in a bentonite buffer.

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Increased temperature effects on Na Wyoming bentonite: siginificance for deep geological radioactive waste disposal

Gianni F. Vettese*, Noora Pakkanen, Marja Siitari-Kauppi

The University of Helsinki, Radiochemistry Unit, Helsinki, Finland

*Gianni.vettese@helsinki.fi

Generally, international radioactive waste disposal plans use a multi-level engineered and natural barrier system to limit radionuclide mobility in the subsurface. Bentonite barriers are present in multiple disposal planswhere they are often kept in close proximity to the waste cannister itself. Here, it is assumed that the bentonite barrier will be exposed to groundwater ingress and be subjected to heat arising from the decay of spent nuclear fuel. In high heat generating wastes this is expected reach in excess of 100 ºC for extended timescales (Ewing, 2015). Significant savings in space and money can be made by increasing the mass of radioactive components stored in each canister, however, this will increase the heat loading experienced by the external barriers. Here, we aim to understand the changes in thermal, mechanical and sorption properties of Na Wyoming bentonite (BARA-KADE) following increased heat treatment of temperatures up to 150 ºC.

Thermal, hydraulic and mechanical changes to the bentonite were monitored at room temperature, 50 ºC, 100 ºC and 150 ºC. Specifically, we characterized the treated materials using standard analytical techniques: PXRD, SEM, ICP-MS, BET. Moreover, we also measured the potential for colloid formation using Dynamic Light Scattering (DLS) and Zetapotential. Finally, these changes in the material properties of the bentonite were linked to their possible effects as an engineered barrier in nuclear waste disposal. We carried out sorption isotherm experiments on radio-Sr labelled solutions following 18 months of treatment at 150 ºC and compared the results with unheated bentonite.

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Natural evidence for the cementation in bentonite buffer based on transmission electron microscopy observation of bentonite ores

Ryosuke Kikuchi[1,*], Misato Horiuchi[2], Masaki Saito[2], Tobimaru Ishiwata[2], Yuto Nishiki[2], Tsutomu Sato[1], Yusuke Takayama[3], Seiichiro Mitsui[3]

[1]Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8, Sapporo, Hokkaido 060-8628, Japan
[2]Graduate School of Engineering, Hokkaido University, Hokkaido 060-8628, Japan
[3]Japan Atomic Energy Agency, 4-33 Muramatsu, Tokai-mura, Ibaraki, 319-1194, Japan

*rkikuchi@eng.hokudai.ac.jp

In geological disposal of high-level radioactive wastes, the use of swelling clay is intrinsic as a buffer around waste packages. The buffer should keep a sufficient swelling pressure, self-sealing capability and low permeability for a long period, and thus, longevity of montmorillonite, a major constituent of bentonite buffer, under various environmental condition is important. One of the alteration processes of concern is the cementation of clay layers by the precipitation of secondary minerals such as silica [1]. In this study, we examined natural bentonite ores that could serve as natural analogues for bentonite suffered cementation, especially focusing on microstructure of consolidated bentonite.

Bentonite ores were collected from the Tsukinuno Mine in Yamagata Prefecture, North-East Japan. This bentonite deposit is thought to have been formed by the diagenesis of volcanic ash. A completely dry polishing technique was used to form a smooth flat surface that well shows the original microstructure of bentonite ores, allowing petrographic discussion as in the observation of non-clayey rocks. Besides coarse quartz (probably detrital origin), fine silica with grain sizes ranging from a few microns to submicron is widely observed in bentonite ores. The distribution of fine silica is characterized by discrete grains or short chains or small clusters in the fine-grained montmorillonite matrix, suggesting that they formed in closed system diagenesis and a low mobility of silica in clay matrix [2]. Thin foils including fine silica and montmorillonite were extracted from polished sections using a focused ion beam apparatus and observed by transmission electron microscopy (TEM). TEM observations demonstrated a microstructure where montmorillonite edge is directly bonded to the fine silica particles (commonly low-quartz, less commonly amorphous silica). The microstructure as seen in this study, is interpreted to be formed by the authigenic silica precipitation during diagenesis, not by a physical mixture. The silica coating of montmorillonite edge could prevent water access to its interlayer space and free swelling, which leads to a decrease in swelling pressure.

Acknowledgement: A part of this study was supported by the METI Japan (Grant Number: JPJ007597).

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Impact of temperature on mechanical and geochemical behavior of swelling clay minerals

Roy Chaaya[1,2,*], Stéphane Gaboreau[1], Hugues Raimbourg[2], Joachim Tremosa[1]

[1]BRGM,45060 Orléans, France
[2]ISTO, UMR7327–Universitéd'Orléans, CNRS, BRGM, 45071 Orléans, France

*r.chaaya@brgm.fr

The ubiquity of swelling clay minerals in surface and sub-surface geoscience systems, in sedimentary deposits, in fault zones or in their potential application in the context of nuclear waste disposal make the effect of temperature (≥ 60°C) on their hydrological, mineralogical and mechanical behaviour a major scientific issue. Therefore, we aim to assess the swelling behaviour of clays when hydrated at temperature (≥ 60°C) under confined conditions. The swelling results from water-mineral interactions at different scales, from interlayer space within crystallite to pore space between particles, depending on the charge compensating cations. We are tackling these physical and chemical issues using a combined approach of experiments and geochemical modelling in order to apprehend the osmotic and crystalline contributions. Swelling experiments were performed with homoionic clays with different solutes (cations and ionic strength) and at different dry densities from1.4 to1.6 g.cm^{-3}. Preliminary results acquired at temperatures ranging from 25 to 80°C show that swelling pressure of compacted Kunipia-Na form at a density of 1.4g.cm^{-3} decreases by 33% at 80°C (figure 1). This temperature effect seems to become less significant with increasing density (i.e. 24% for d=1.6 g.cm^{-3}). On the contrary, the swelling pressure of Kunipia-Ca remains almost constant showing a very negligible effect of temperature on Ca-form smectites. On the other hand, X-ray diffraction analysis performed on sodium and calcium smectite powders under controlled relative humidity at temperatures of 25°C and 80°C show that the temperature has a very negligible effect on the interlayer water retention capacity and thus on the crystalline component of the swelling pressure (figure 2). Complementary data of water adsorption- gravimetry isotherms, inconfined conditions, were obtained in the same conditions. This set of data will thus allow to assess the temperature effect on both crystalline and osmotic water retention capacity.

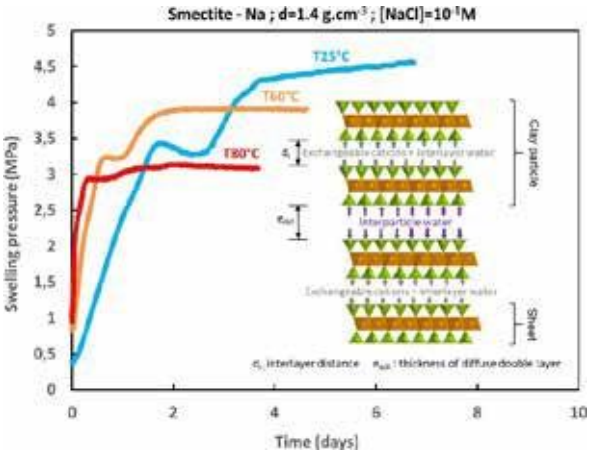


Figure1:The swelling test results of a Kunipia-Na of density1.4g.cm^{-3} hydrated by a NaCl solution of concentration 10^{-1}M at temperatures of 25; 60 and 80°C.

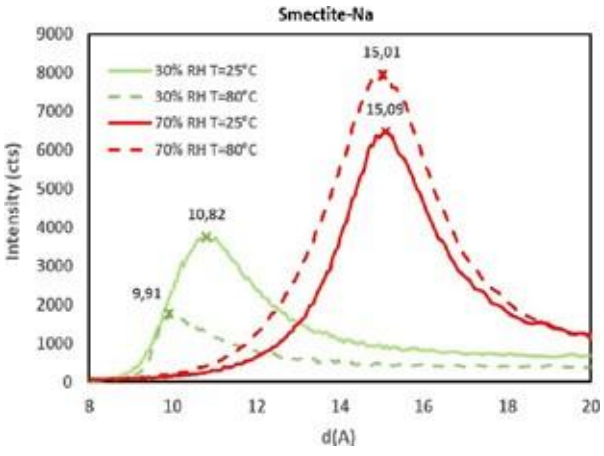


Figure2:Recorded basal distances of Kunipia-Naat temperatures of 25°Cand 80°C for relative humidities of 30% and 80% (XRD).

Mineralogy and geochemistry of a heated bentonite pellets column

M.V. Villar[1*], J. Cuevas[2], A. Ortega[2], A.M. Melón[1], A.B. Zabala[1], R.J. Iglesias[1], C. Gutiérrez-Álvarez[1]

[1]CIEMAT, Avd. Complutense 40, 28040 Madrid, Spain
[2]UAM, Tomás y Valiente 7, 28049 Madrid, Spain

*mv.villar@ciemat.es

To simulate in the laboratory, the conditions of the barrier material used in the HE-E in situ test (Mont Terri, Switzerland), a 50-cm long column of MX-80 bentonite pellets was heated on its base at 140°C while Pearson water was supplied through its upper surface. After a 7-month-long heating phase, heating+hydration went on for nine years. Afterwards the bentonite was sampled for physical, geochemical and mineralogical characterisation.

At the end of the experiment the upper half of the column was virtually saturated, but in the lower half the water content sharply decreased towards the heater, where it was close to 0% and the bentonite was in loose state. The high temperatures (between 60 and 140°C in the 10-cm closest to the heater) resulted in changes in the bentonite microstructure (dense clay packets with carbon and Na-S coated vacuoles at the steel contact), mineralogy and geochemistry, particularly with the increase of salt content, given the high salinity of the hydration solution and the evaporation processes. An indication of this high salinity was the intense corrosion of the bottom sensor. In contrast, the pore water in the upper part of the column, with a diminished density, was significantly dilute. XRD patterns of the samples equilibrated at 50% RH showed sharp 10 Å reflections between two broad ones at 11-12 Å (1-layer hydrate smectite) and 9.6 Å (dehydrated smectite) in the 10 cm closest to the heater. Calcite traces were also present. Illite-like sheets (a more ordered phase) and collapsed dehydrated and monohydrated smectite with disordered stacking seem to have formed at the heater contact. In the upper 40 cm of the column a 1-layer hydrate basal spacing dominates.

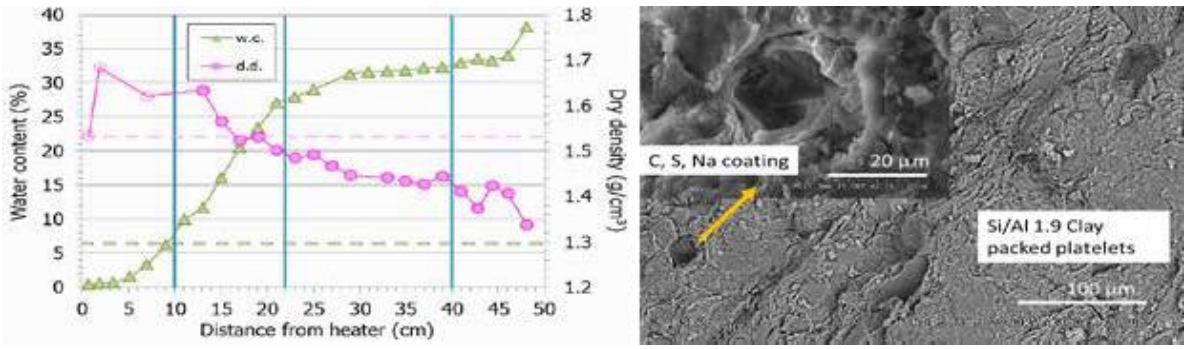


Figure 1. Final distribution of dry density and water content along the column (left) and SEM image of the microstructure of MX-80 bentonite at the heater contact (right).

Cation exchange processes in bentonite buffer material test (ABM-5, after heating to 250 °C

Dohrmann Reiner [1,2,*], **Gröger-Trampe Jens**[1,2], **Kaufhold Stephan**[1]

[1]BGR, Federal Institute for Geosciences and Natural Resources, 30655 Hannover, Germany
[2]LBEG, State Authority of Mining, Energy and Geology, 30655 Hannover, Germany

[*]reiner.dohrmann@bgr.de

Bentonites are candidate materials for High-Level Radioactive Waste (HLRW) repositories and, therefore, investigated with respect to long term stability. In-situ tests are conducted in rock laboratories such as the second phase (2012) of the 'Alternative Buffer Material test' (ABM) in Äspö, Sweden. Here different bentonite buffer materials with various exchangeable cation populations were packed vertically on each other with an iron tube as heater in the centre (SKB, 2018). We report on cation exchange data of the whole package ABM 5 dismantled in 2017. This was the third excavated parcel after ABM-1 and 2 (first phase of the project). The blocks had been heated in three steps starting with 1) a 2.5 years phase at approximately 50 °C, 2) a four months phase of up to 132 °C for, followed by 3) a seven months phase of up to 250 °C. Even in the outer part maximum temperatures of approximately 150 °C were recorded exceeding maximum temperatures observed in most other experiments performed in underground or hard rock laboratories (Table 1).

Table 1: Experimental parameters of important projects for assessment of bentonite buffers in different underground or hard rock laboratories.

Experiment	Lab	Metal (heater)	Host rock	T (max)	Salinity (groundwater)	Scale
LOT	Äspö	copper	crystalline	ca. 140 °C	high (Na-Ca-Cl-SO_4)	intermediate scale
ABM-1	Äspö	iron	crystalline	ca. 140 °C	high (Na-Ca-Cl-SO_4)	intermediate scale
ABM-2	Äspö	iron	crystalline	ca. 140 °C	high (Na-Ca-Cl-SO_4)	intermediate scale
ABM-5	Äspö	iron	crystalline	ca. 250 °C	high (Na-Ca-Cl-SO_4)	intermediate scale
Prototype Repository	Äspö	copper	crystalline	ca. 85 °C	high (Na-Ca-Cl-SO_4)	full scale
FEBEX-DP	Grimsel	iron	crystalline	ca. 100 °C	low (Na-Ca-HCO_3-F)	full scale
Heater B	Mont Terri	iron	clay	ca. 100 °C	Mont Terri pore water	intermediate scale

During heating groundwater entered the blocks for water saturation by diffusion from the rock side to the heater. As expected from former experiments exchangeable cations were redistributed between the different bentonite materials. In contrast to the former experiments ABM-1 and 2, however, the average exchangeable Na^+ occupation of the reacted material (46 %) was much closer to the reference materials (49 %) and average exchangeable Na^+ loss was much lower.

Exchangeable Mg^{2+} occupation of the starting material (20 %) was reduced by half (10 %), whereas exchangeable Ca^{2+} occupation increased accordingly, however the recorded increase exceeded the exchangeable Na^+ and Mg^{2+} loss indicating uptake of saline groundwater. The sum of exchangeable cations was in the range of the total CEC (102 %) in the reference materials and increased to 111 % after retrieval.

SKB (2018). ABM45 experiment at Äspö Hard Rock Laboratory. Installation report ABM45. SKB P-18-20. ISSN 1651-4416 https://www.skb.se/publikation/2491709/P-18-20.pdf

Characterization of bentonites from the in situ ABM5 heater experiment at Äspö hard rock laboratory, Sweden

Ana María Fernández[1,*], José F. Marco[2], Paula Nieto[1], Fco. Javier León[1], Luz María Robredo[1], M.Angeles Clavero[1], Ana Cardona[1], Sergio Fernández[1], Daniel Svensson[3], Patrik Sellin[3]

[1]CIEMAT, Departamento de Medio Ambiente, Madrid, Spain
[2]CSIC, Instituto de Qumica Fsica "Rocasolano", Madrid, Spain
[3]Department of Research and Safety Assessment, SKB, Stockholm, Sweden

*anamaria.fernandez@ciemat.es

The Alternative Buffer Material ABM5 experiment is an *in situ* medium-scale experiment performed at sp Hard Rock Laboratory (HRL) conducted by SKB in Sweden with the aim of analysing the long-term stability of bentonites used as engineering barrier for a high-level radioactive waste repository (Kaufhold et al., 2021).

In this work, four different ring-shaped Ca- and Na-bentonite blocks (Asha 505, FEBEX, Rokle, IBECO and MX-80), which were pilled around a carbon steel cylindrical heater, subjected to a maximum temperature of 250°C and hydrated with saline sp groundwater (0.91 M ionic strength), were characterized after dismantling by using different techniques (XRD, FTIR, XRF, Mssbauer, squeezing, etc.). This work allowed to identify the main geochemical processes involved in this system, as well as the modifications in physico-chemical properties and pore water chemistry after 4.4 years of treatment.

No significant modifications in mineralogy were observed in samples close to heater contact, except an increase in Fe content due to C-steel corrosion, carbonate dissolution/precipitation (mainly calcite and siderite) and Mg increase. No magnetite and low amount of Fe(II) inside the clay mineral structure were detected, indicating prevalence of oxidizing conditions. No modifications were observed in smectite structure, except a slight increase in total and tetrahedral charge. A decrease in external surface area and CEC was detected in all samples, lower values being more stressed at the heater contact. It seems that temperature and water vapor fluxes have affected to CEC parameter, due to the differences observed from top to bottom of the bentonite column. As consequence of the advective-diffusion infiltration of the saline Na-Ca-Cl Äspö groundwater, a modification of the composition at clay mineral exchange sites occurred with a tendency to achieve equilibrium in all types of bentonites. Ca-bentonites increased their Na content at exchange sites whereas Na-bentonite increased their Ca content. Exchangeable Mg content decreased in all bentonites, except in MX-80 located at the bottom part of the package. The initial bentonite pore water was modified after their interaction with the saline groundwater. A salinity gradient is observed through the bentonite blocks from the granite to heater contact, lower ionic strengths being detected at the bottom part of the bentonite column. Thus, no geochemical equilibrium conditions were achieved after 4.4 years of experiment.

Kaufhold, S., Dohrmann, R., Ufer, K., Svensson, D. & Sellin, P. (2021). Mineralogical Analysis of Bentonite from the ABM5 Heater Experiment at Äspö Hard Rock Laboratory, Sweden. *Minerals,* 11, 669.

Microwave leaching of aluminum from kaolin by HCl

Mohammad Al-Harahsheh[1*], Naser Abo Olaem[2], Omar Tahat[3]

[1]Department of Chemical Engineering, Jordan University of Science and Technology, Irbid 22110, Jordan
[2]Jordan Phosphate mining company, Amman Jordan
[3]Ministry of Energy and natural resources, Amman, Jordan

*msalharahsheh@just.edu.jo

Kaolin is an important industrial mineral which has many industrial applications. It is also considered as an important source of aluminum, however, great technical challenges are required to be overcome to extract Al from kaolin. In this work the extraction of aluminum from kaolin using HCl, as leaching agent, was studied. Kaolin samples were collected from Wadi Al-Hafira, south of Jordan; these were crushed and ground to a particle size of 100% less 75 µm. The ground samples were characterized in term of chemical and mineral composition using X-ray fluorescence (XRF) and X-ray diffraction analysis (XRD) techniques. Kaolin was found to contain kaolinite, muscovite, and quartz as main mineral phases, while the chemical analysis revealed that kaolin contains about 36.1% Al_2O_3, 54% SiO_2, 2.5% CaO, 1.96% Fe_2O_3 and 1.2% TiO_2 as major oxides. The minor oxides were K_2O, Na_2O, and SO_3. Microwave digestion vessel was used to provide suitable environment for high pressure and temperature leaching. Several leaching parameters were studied in this work including, leaching time (30 to 120 min), leaching temperature (90 to 200 °C), and molarity of leaching reagent (1, 2, 3 and 4 M). Additionally, several sources of HCl were used include analytical grade HCl, HCl collected from potassium sulphate industry and HCl prepared from waste H_2SiF_6 of phosphoric acid industry. The extraction of four main elements were monitored during the leaching process employing ICP-OES multi element analysis technique, namely, aluminum, iron, titanium and silicon. The findings of this work suggests that the recovery of these elements increases of temperature and leaching time. The recovery of silicon dropped with the increase of acid molarity. Complete extraction of Al from kaolinite was obtained at temperatures above 180 °C and leaching time of 120 min, while Al present in muscovite was not amenable to leaching except when HCl, as leaching agent, was obtained from waste H_2SiF_6; such acid contained traces of fluoride which provided complete destruction of muscovite as evident from the XRD analysis of leaching residues. Solvent extraction was applied to separate iron from the leaching solution achieving 100% iron removal while leaving Al in the solution. Additionally, $Al(OH)_3$ was obtained after pH adjustment followed by CO2 injection. The obtained precipitate was low in iron and suitable as feed material for aluminum fluoride industry

Impact of temperature on mechanical and geochemical behaviour of swelling clay minerals.

Roy Chaaya[1,2,*], Stéphane Gaboreau[1], Hugues Raimbourg[2], Joachim Tremosa[1]

[1]BRGM, 45060 Orléans, France
[2]ISTO, UMR 7327 – Université d'Orléans, CNRS, BRGM, 45071 Orléans, France

*r.chaaya@brgm.fr

The ubiquity of swelling clay minerals in surface and sub-surface geoscience systems, in sedimentary deposits, in fault zones or in their potential application in the context of nuclear waste disposal make the effect of temperature (≥ 60°C) on their hydrological, mineralogical and mechanical behaviour a major scientific issue. Therefore, we aim to assess the swelling behaviour of clays when hydrated at temperature (≥ 60°C) under confined conditions. The swelling results from water-mineral interactions at different scales, from interlayer space within crystallite to pore space between particles, depending on the charge compensating cations. We are tackling these physical and chemical issues using a combined approach of experiments and geochemical modelling in order to apprehend the osmotic and crystalline contributions. Swelling experiments were performed with homo-ionic clays with different solutes (cations and ionic strength) and at different dry densities from 1.4 to 1.6 g.cm^{-3}. Preliminary results acquired at temperatures ranging from 25 to 80°C show that swelling pressure of compacted Kunipia- Na form at a density of 1.4 g. cm^{-3} decreases by 33% at 80°C (figure 1). This temperature effect seems to become less significant with increasing density (i.e. 24% for d=1.6 g.cm^{-3}). On the contrary, the swelling pressure of Kunipia-Ca remains almost constant showing a very negligible effect of temperature on Ca-form smectites. On the other hand, X-ray diffraction analysis performed on sodium and calcium smectite powders under controlled relative humidity at temperatures of 25°C and 80°C show that the temperature has a very negligible effect on the interlayer water retention capacity and thus on the crystalline component of the swelling pressure (figure 2). Complementary data of water adsorption gravimetry isotherms, in confined conditions, were obtained in the same conditions. This set of data will thus allow to assess the temperature effect on both crystalline and osmotic water retention capacity.

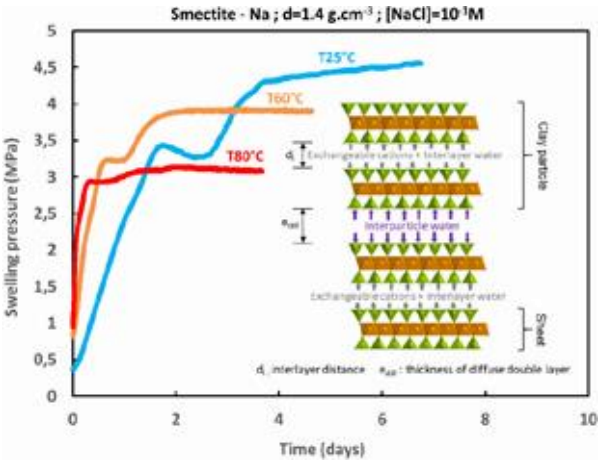


Figure 1: The swelling test results of a Kunipia-Na of density 1.4 g.cm^{-3} hydrated by a NaCl solution of concentration 10^{-1}M at temperatures of 25; 60 and 80°C.

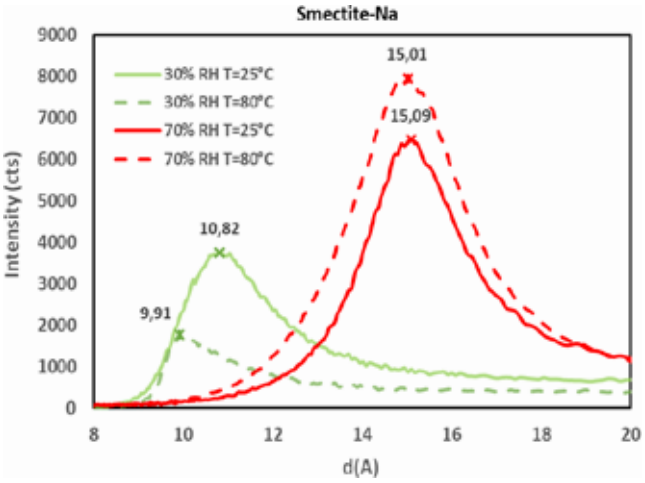


Figure 2: Recorded basal distances of Kunipia-Na at temperatures of 25°C and 80°C for relative humidities of 30% and 80% (XRD).

TS19 + TS29 High Temperature Bentonite Barriers

POSTER PRESENTATIONS

Smectite alteration in the presence of accessory minerals (+/- K-oxalate: Experimental constraints from 180°C batch reactor experiments

Ritwick Sudheer Kumar[1*], Laurence N. Warr[1], Georg H. Grathoff[1], Stephan Kaufhold[2], Artur Meleshyn[3]

[1]Institute of Geography and Geology, University of Greifswald, 17489 Greifswald, Germany
[2]Department of Technical Mineralogy and Clay Mineralogy, BGR–Bundesanstalt für Geowissenschaften und Rohstoffe, Stilleweg 2, D-30655 Hannover, Germany
[3]Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) gGmbH, 38122 Braunschweig, Germany

[*]sudheerkur@uni-greifswald.de

Knowledge of the thermal and chemical stability of smectites under enhanced high-level radioactive waste repository conditions is currently of importance as bentonites are currently being considered as suitable buffer materials. Within the framework of a BMBF financed project (UMB2), we have conduced batch reactor experiments focused on the alteration of smectites under varying temperatures, solution chemistry and the addition of accessory minerals over fixed periods. The smectite used for the studies was extracted from Moosburg bentonite (TS-1057) using Stokes law.

Currently, our study focuses on experiments conducted at 180°C using purified smectite with 10% accessory minerals in solutions with and without organic acids (Table 1). The mixtures along with solutions were kept in a rotary oven at 20 rpm and 180°C for a period of one month. The reaction products are studied using XRD, TEM, MPAES and EDS-SEM to study potential alterations. The expected results will provide new insight into the alteration of smectites, neoformation of minerals as well as mineral dissolution-precipitation mechanisms.

Table 1. Experimental mixtures and solutions.

Sample Nr	Smectite	Accessory minerals (10 %)	Solution (40 ml)
1	✓	-	0.1M NaCl
2	✓	Calcite	0.1M NaCl
3	✓	Gypsum	0.1M NaCl
4	✓	Pyrite	0.1M NaCl
5	✓	-	0.1M NaCl + 0.3M $K_2C_2O_4$
6	✓	Calcite	0.1M NaCl + 0.3M $K_2C_2O_4$
7	✓	Gypsum	0.1M NaCl + 0.3M $K_2C_2O_4$
8	✓	Pyrite	0.1M NaCl + 0.3M $K_2C_2O_4$

Effect of long-term thermal loading on Ca-bentonites (Ünye, northeast Turkey)

Oğuzhan Çamcı[1,*], Ceren Kücüküysal[1], Cansu Güngör[2], Hamit Tecer[2]

[1]Muğla Sıtkı Koçman University, Department of Geological Engineering, Muğla 48000, Turkey
[2] Ünye Mining Industry Trade Limited Corporation, Ordu, Turkey

*camcioguzhan93@gmail.com

Bentonite is the most preferred clay as a buffer material for natural or engineered clay barriers for nuclear waste storage. In this study, the effect of long-term (20, 30, and 40 days) thermal loadings at 100, 150, and 200 °C on Ca-bentonites from nye (NE Turkey) was monitored in terms of physicochemical and mineralogical properties. The dehydration behavior of the Ca-bentonite samples (CaB) was characterized by the cation exchange capacity (CEC), specific surface area (SSA), pH, swelling index (SI), crystal structure, and molecular fingerprints.

CEC of Ca-bentonites (52.3–62.7 meq/100 g) remarkably decrease at 40 days of thermal loading experiments to 29.9–37.3 meq/100 g at 100 °C, to 19.4–25.4 meq/100 g at 150 °C and to 20.9–23.9 meq/100 g at 200 °C. SSA shows a very similar pattern to CEC by long-term thermal loading in that the SSA of raw Ca-bentonites (42.8–51.4 m^2g^{-1}) decrease to 19.6–30.6 m^2g^{-1} at 100 °C, to 15.9–20.8 m^2g^{-1} at 150 °C, and to 17.1–19.6 m^2g^{-1} at 200 °C. The pH of Ca-bentonite samples (9.3-9.7) lowers from strong alkalinity to slight to moderate alkalinity (7.7–8.6) at 200 °C. A remarkable decrease in the SI value of Ca-bentonite samples occurs at 200°C at 40 days (from 4.4–7.5 mL/2 g to 3.7–5.8 mL/2 g). Long-term heating also causes the loss of condensed and adsorbed water vibrations (~ 3388 cm^{-1}). This study reveals that the long-term thermal loading of Ca-bentonite samples at 100 and 150°C influences the dehydration kinetics; on the other hand, that of CaB at 200°C at 40 days lead to the formation of ~1 nm reflection, suggested to be the beginning of illitization (Çamcı et al., 2022).

Çamcı, O., Küçükuysal, C., Güngör, C., Tecer, H. (2022). Long-term thermal loading study on the dehydration behavior of Ca-bentonites of nye (Ordu, NE Turkey). *J Therm Anal Calorim* 147, 2073–2082. https://doi.org/10.1007/s10973-021-10647-z

Response of Ca-bentonites (Ünye, northeast Turkey) to short-term high-temperature calcinations

Öykü Ataytür[1,*], Ceren Kücüküysal[2], Cansu Güngr[3], HamitTecer[4]

[1]Muğla Sıtkı Koçman University, Department of Geological Engineering, Muğla 48000, Turkey
[2]Sorbonne University, IMPMC, Paris75000, France
[3]ÜnyeMiningIndustry Trade Limited Corporation, Ordu, Turkey

*oyku.ataytur@sorbonne-universite.fr

Bentonite is one of the most important geo-materials revaluated as a source for many applications by its various physicochemical properties (e.g. high thermal resistance, high swelling capacity, low hydraulic conductivity). The northeastern region of Turkey is one of the most important bentonite-producing districts for various industrial applications (e.g cat litter, ceramic, medical, pharmaceutical, cosmetics). In this work, short-term high- temperature calcinations up to 1000 °C with 200 °C increments at 25 min were applied to modify three Ca-bentonite samples (CaB1,CaB2,CaB3) that were supplied from Ünye Mining Industry Trade Limited Corporation, Ordu, NE Turkey.In this respect, physicochemical and mineralogical changes upon high-temperature loading assessed by X-ray diffraction (XRD), Fourier- Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Brunauer–Emmett– Teller (BET), and Loss on Ignition (LOI) analysis.

The main component of all Ca-bentonite samples is dioctahedral type Ca-smectite. The experimental results show that calcination at 400 °C dominated by the dehydration effect is not enough to alter the Ca-bentonite structure. On the other hand, heating the Ca-bentonite samples between 400-800°C leads to the dehydroxylation process which causes the gradual disappearance of structural hydroxyl groups and is revealed by intense collapse on the basal reflection from 1.4 to 1.0 nm. The BET analysis shows the decrease in specific surface area at higher temperatures and the closure of micropores. The specific surface area reaches the minima of 1.33–2.05 m2g−1by calcination at 1000 °C. The structures of CaB2 and CaB3 are completely decomposed and mullite formation is enhanced. However, incomplete dehydroxylation for CaB1 causes partial decomposition. The mineralogical transformations are further identified by the formation of amorphous silica phases at 1000°C for all samples. Micromorphological results of calcinated samples at 1000°C reveal much larger aggregates with more rounded morphologies due to sintering. It is also concluded that the mesoporous characteristics of Ca-bentonite samples do not show significant changes up to 1000 °C (Ataytür et al., 2022).

Ataytür, Ö., Küçükuysal, C., Güngör, C., Tecer, H. (2022). Effects of short-term high-temperature calcinations on the physicochemical and mineralogical properties of Ca- bentonites from Ünye (Ordu, NE Turkey). *J Therm Anal Calorim* 147, 2091–2099(2022). https://doi.org/10.1007/s10973-021-10626-4.

Dehydroxylation effect of smectite and kaolinite during alkaline attack

Noel N'Guessan Essey[1], Emmanuel Joussein[1,*], Alexandra Courtin[2], Erwan Paineau[3], Marilyne Soubrand[1], Delphine Vantelon[4], Cristina Coelho[5]

[1]Universitéde Limoges, FST, E2Lim,123avenue Albert Thomas, 87060 Limoges, France
[2]Université Paris Saclay, Géosciences Paris Sud GEOPSUMRCNRS-UPS 8148, 91400 Orsay,France
[3]Laboratoire de Physiquedes Solides, CNRS, Université Paris-Saclay, 91405 Orsay, France
[4]Synchrotron Soleil, Lucia Beamline, L'Ormedes Merisiers, 91190 Saint-Aubin, France
[5]Institutdes Matériaux de Paris Centre Sorbonne Université, Facultédes Scienceset Ingénierie, 4place Jussieu 75005 Paris, France

*emmanuel.joussein@unilim.fr

Alkali-activated materials ar etypically prepared from the activation of an aluminosilicate source (typically metakaolin) by an alkaline solution. Nevertheless, it is possible to use other mineral sources as substitutes for value-added purposes. For example, smectitic minerals can either be used as such or after heat treatment (metasmectite). It is therefore important to determine their activity of metakaolins, but more particuraly to compare them with smectites or metasmectites. In order to determine the most important parameters controlling the reactivity in a basic medium for geomaterial formulation issues. The objective of this study is to investigate their activity in alkaline medium of metakaolins and metasmectites obtained after dehydroxylation at different temperatures. For this purpose, reference kaolinites and smectites samples have undergone a dihydroxylation step from 450 to 850°C and from 600 to1000°C to form either metakaolinites or metasmectite, respectively. The samples are then alkaline treated at 80°C at different times (5, 10, 15, 20 & 30 min) in 2M KOH, NaOH or KOH+NaOH solution. The concentration of Al and Si in the liquid phase has been determined by MP-AES, while the resulting solid phase has been characterized by coupling XRD, FTIR, solid state NMR, TEM and XAS (Si and Al K-edge on Lucia beamline, soleil synchrotron) experiments.

The results high light the effect of temperature on their activity of metaphases in alkaline medium. The crystal chemistry of the initial kaolinites and smectites plays an important role as well as the type of alkaline at- tack and the charge/substitution of the smectites. NaOH is the most efficient (followed by mixed solutionand KOH). All the results will be discussed by considering the solid phase.

TS21 Clays in Petroleum, Oil, and Gas

ORAL PRESENTATIONS

Effect of different types of smectites on nonaqueous bitumenextraction from Alberta oil sands

Yuqing Bai*, Marek Osacký, Peter Uhlík

Comenius University in Bratislava, Department of Mineralogy, Petrology and EconomicGeology, Bratislava 84215, Slovakia

*bai2@uniba.sk

Smectite was reported as the common clay minerals in Alberta oil sands and have a detrimental effect on bitumen recovery because of its fine particle size and swelling characteristics. Two trioctahedral smectites and seven dioctahedral smectites were mixed with bitumen and reacted for 8 days. Before the experiment, Na-saturated clays were equilibrated at 0% and 90% relative humidity for 24 hours. The clay-bitumen mixtures were then washed three times each with cyclohexane to extract bitumen fromthe clays. The re-action products were examined by X-ray powder diffraction (XRD), Infrared spectroscopy (IR), Scanning electron microscopy (SEM), element analysis (CHNS), and UV–Vis spectroscopy. The aim was to better understand the role of various smectites on nonaqueous solvent bitumen extraction. More specifically, we would like to better understand the impact of smectite crystal-chemistry (di- vs tri-octahedral smectites), layer charge density (high vs low charged smectites) and particlesize (02−2 um vs <0.2 um) on the bitumen extraction. The preliminary results showedthat the cation exchange capacity (CEC) for all samples was reduced by the reaction with bitumen due to organic coatings on the clay mineral surfaces and/or due to gluingof clay particles to aggregates. In the case of SHCa-1 (<0.2 μm), SWy-3 (<0.2 μm and0.2−2 μm) SCa-3 (0.2−2 μm) and SWa-1 (<0.2 μm), the CEC after nonaqueous solventbitumen extraction was heavily affected by different relative humidity (RH) conditions. Overall, this new and original knowledge makes a value for oil sands producing areas in different parts of the world to solve the influence of smectites or mixed-layered clayminerals with smectite layer type in bitumen extraction.

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The importance of authigenic clays in petroleum exploration

Rona J. Donahoe

University of Alabama, Department of Geological Sciences, Tuscaloosa, AL 35487-0338

rdonahoe@ua.edu

Petroleum reservoirs typically contain both allogenic and authigenic clay minerals. Allogenic clays form elsewhere and are transported to the point of deposition, whereas authigenic clays are formed in place during diagenesis, catagenesis and metagenesis. Wilson and Pittman (1977) examined thousands of sandstone samples and concluded that authigenic clays are much more common in petroleum reservoirs than had been previously recognized. They also provided textural, structural, morphological and compositional criteria by which authigenic clays can be distinguished from allogenic clays.

Authigenic clays can concentrate organic matter through adsorption and possess catalytic properties that may significantly influence the formation of kerogen as well as the maturation and production of petroleum. Wu et al. (2012) provided a review of previous studies showing that the amount and type of clay present in reservoir rocks influence petroleum composition through complex chemical and cracking reactions that are not fully understood. The diagenetic transformation of smectite to illite is known to accompany petroleum formation. In addition, clay exchangeable cation and interlayer water contents determine the catalytic activity of Bronsted acid sites that drive the conversion of kerogen to hydrocarbons and the migration of petroleum from source rocks, respectively.

The distribution and type of authigenic clay minerals play critical roles in the production potential of a petroleum reservoir (Sarkisyan, 1972). Authigenic clays may significantly impact reservoir quality by their influence on rock permeability and porosity. Authigenic clays can occur as pore-filling, fracture-filling, pore-bridging, pore-lining and pseudomorphous replacement materials in sandstone reservoirs. The formation of authigenic clays can therefore significantly affect pore architecture, dramatically decreasing reservoir permeability and primary petroleum production. In addition, the type and amount of clays present in the reservoir must be considered in the proper selection of stimulation fluids to avoid reservoir damage.

Papers presented in this session will cover all aspects of the importance of authigenic clays for petroleum exploration.

Sarkisyan, S.G. (1972). Origin of authigenic clay minerals and their significance in petroleum geology. *Sedimentary Geology*, 7: 1-22.

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Wu, L.M., Chun, H.Z., Keeling, J., Tong, D.S., Yu, W.H. (2012). Towards an understanding of the role of clay minerals in crude oil formation, migration and accumulation. *Earth Science Reviews*, 113(2012): 373-386.

Origin of authigenic chlorite in deep marine siliciclastic turbidites and their implication on reservoir quality

Fares Azzam[1,*], Thomas Blaise[1], Patricia Patrier[2], Daniel Beaufort[2], Ahmed Abd Elmola[2], Eric Portier[3], Benjamin Brigaud[1], Jocelyn Barbarand[1], Sylvain Clerc[4]

[1]Paris-Saclay university, CNRS, GEOPS, France
[2]Poitiers university, IC2MP, CNRS, France
[3]CV Associes Engineering, France
[4]Neptune Energy, Norway

Authigenic chlorite grain-coatings are very common in siliciclastic rocks. Their presence can either improve or reduce the reservoir properties of sandstones. To date, only a few studies have focused on their origin and formation mechanisms in turbidite sandstones. Here, we discuss the origin and distribution of chlorite coatings in the turbiditic sandstones of the Agat Formation (Aptian/Albian) in the northern North Sea.

Chlorite coats exert a major control on the reservoir quality in the Agat Formation. In the lower part of the reservoir, chlorite forms a thick coat (15-30 µm) around detrital grains that strongly reduce permeability. Conversely, in the upper part of the reservoir, chlorite coats are thinner (4-10 µm), favoring porosity preservation by inhibiting the development of quartz overgrowth. X-ray diffraction and electron microscope observations indicate Fe-rich chlorite of Ib (β = 90°) polytype suggesting a transformation from a 7 berthierine precursor. Transmission electron microscopy revealed the presence of 7 iron-rich phases disseminated in the chlorite coat, supporting a transformation from berthierine. Chlorite/Berthierine formation was favored by the presence of abundant Al and Fe-rich detrital grains (glauconite, ooids, and mudclast). The dissolution of these grains at low temperature under reducing conditions created a suitable environment for the growth of berthierine. This step was followed by the transformation of berthierine into chlorite at higher temperatures (>50 °C) through a solid-state transformation. The development of thick chlorite coatings in the lower part of the reservoir was mainly related to highly abundant Fe-grains, providing a significant amount of iron upon dissolution.

This study shows the important role of chlorite coatings in controlling the reservoir quality in turbidite sandstones. It also highlights the role of inherited sediment composition in controlling the abundance and thickness of the chlorite coats. The Spiro Sandstone is encountered within the horse structures in a duplex structure at a depth ranging from 15,000 to 18000 feet (~5.0 to 5.6 km) in the footwall of the Choctaw fault zone. It contains Chamos- ite-rich facies clay minerals, which exhibit highly distinctive diageneticpatterns. Preservation of primary porosity occurs in all chamositic sandstones because Chamositeprovides a clay coating around the quartzgrains and prevents quartz overgrowth to preserve primary porosity.

When we plotted different sandstone sedimentary facies of the Spiro Sandstone on the cross-sections to locate the extent of the porous zones likely to have hydrocarbon reservoirs, we foundout that a successfulgas well in the Arkoma Basin was almost always drilled into the footwall ofthe folded sandstone reser- voirs in the duplex structure where porosity is preserved by chamositic sandstone facies. The duplex is floored by the Woodford Detachment and roofed by the Lower Atakon Detachment. Backthrusts in the horses within the duplex structure may cause structural thickening and enhance reservoir thickness.

Adsorption properties of natural gas molecules on the surface of calcium carbonate under different conditions: a first-principles study

E. Elbashier[1], I. Hussein[1], G. Carchini[1], A. Kasha[2], G. R. Berdiyorov[3,*]

[1]Gas Processing Center, College of Engineering, Qatar University, P.O. Box 2713, Doha, Qatar
[2]Petroleum Engineering Department, University of Houston, TX, USA
[3]Qatar Environment and Energy Research Institute, Hamad Bin Khalifa University, Doha, Qatar

*gberdiyorov@hbku.edu.qa

Carbonate rocks, which are the main component of the natural gas reservoirs, are characterized by a large diversity of depositional faces and complex porosity system. Therefore, understanding the structural effects on the adsorption properties of natural gas components can be of practical importance. In this work, we use density functional theory calculations to study the adsorption behavior of natural gas molecules on the surface of $CaCO_3$ with a particular focus on:

- *Effect of surface morphology on methane interaction with calcite* [1]. The simulation results show that the adsorption capacity of the materials can be more than an order of magnitude larger for a certain surface orientation.
- *Effect of vacancy defects on the adsorption of methane on different surfaces of calcite* [2]. The simulations results show that both types of vacancy defect results in strong adsorption of the gas molecules as compared to defect-free sample due to the orbital-overlap/hybridization between the organic molecules and the substrate.
- *Effect of strain on gas adsorption (CH_4, CO_2, C_2H_6 and N_2) in tight gas carbonates*, which can occur due to natural thermodynamics or environmental changes [3]. We found that depending on the type of the molecule the adsorption capacity of the materials can be increased by more than 25% by changing the strain.
- *Effect of the size of the calcite nanopores on the adsorption properties of CH4 and CO2 gas molecules* [4]. The simulation results show that as the nanopore diameter decreases, the adsorption energy increases exponentially due to the geometry of the smallest pore that increases the affinity of the molecules to the surface.

These findings can be useful for determining the estimated ultimate recovery in carbonaceous tight gas reservoirs by quantifying the geomechanical effects on the adsorbed gas and accounting for heterogeneous porosity and permeability of the carbonate reservoirs.

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TS23 Rare-Earth Elements and Clays

ORAL PRESENTATIONS

Rare-earth heavy-minerals in kaolin ore, mine tailings, and associated heavy-mineral sands of the central Georgia Coastal Plain

Anthony Boxleiter*, **W. Crawford Elliott**

Department of Geosciences, Georgia State University, Atlanta, GA 30302-3965, USA

*aboxleiter1@student.gsu.edu

World-class kaolin deposits are presently being mined in the Georgia Coastal Plain. Geologic studies of these kaolin deposits have focused on their mineralogy and on the genesisof kaolinite in these de- posits. Only a few number of these studies have considered the occurrences of the rare-earth elements (REE) in these kaolin ore deposits. REE-bearing heavy- minerals (monazite and xenotime) have been found as detrital minerals within sand units, mined kaolin ore, and tailings (mine waste) associated with the kaolin deposits. Both light (LREE) and heavy (HREE) contents of the sands and mine tailings are strongly correlated with the amounts of monazite and xenotime. Localized concentrations of monazite and xenotime in the Paleocene sands contain 4.6 wt.% total REE (TREE). The tailings derived from min- ing the Cretaceous kaolins contained high concentrations of monazite + xenotime (0.9 to 3.2 wt.%.). The TREE contents of these tailings ranged from 0.7 to 1.9 wt.%. The mine tailings derived from Eocene kaolins contained only ~0.1 wt.% monazite + xenotime. TREE content of thesetailings was ~300 ppm.

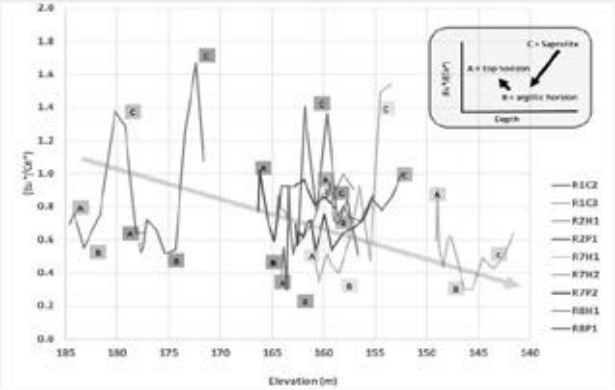
Heavy-mineral content of the mined Cretaceous kaolin is enriched in the HREE (La/Lu <1.0, UCC norm.) with a monazite:xenotime ratio of 1:3.4. The mine tailings derived frommined Cretaceous kaolin contained a monazite:xenotime ratio of 2.7:1 and were enriched inthe HREE (La/Lu <1.0, UCC norm.). The heavy-mineral sands present overlying theCretaceous kaolins is enriched in the LREE (La/Lu >1.0, UCC norm.) with a monazite:xenotime ratio of 13.3:1. The heavy-mineral content from the mined Cretaceous kaolin was determined to contribute 81 wt.% of the observed heavy-mineral content in the mine tailings. The heavy-mineral sands contributed the remaining 19 wt.%, representing incorporation during the mining of the kaolin.

Rare Earth element trends in regolith on historically managed sites in the southeastern United States Piedmont

Paul A. Schroeder[1,*], Jason C. Austin[1,2], Aaron Thompson[3], Daniel D. Richter[2]

[1]University of Georgia, Department of Geology, Athens, GA 30602-2501 USA
[2]Duke University, Earth and Climate Sciences Division, Durham, NC 27708-0328 USA
[3]University of Georgia, Department of Crop and Soil Sciences, Athens, GA 30602 USA

*schroe@uga.edu



Deeply weathered regolith in the southeastern United States has undergone rapid erosion in the last century from intensive agricultural practices, which has altered the landscape and its inherentfertility. Parent material, landscape position, and land use are important factors controlling the mineral and elemental composition of soil profiles. Clay mineral assemblages are dominated by kaolinite, but profiles differ by the amount of interstratified clay minerals, halloysite, hematite, goethite, and gibbsite. Rare earth element totals vary between 30 and 1048 ppm and are generallypositively correlated with clay mineral content. Ce [Ce*= 3xCe/(2xLa+Nd)] and Eu [Eu* = 2xEu/(Sm+Gd)] anomalies reflect parent rocks and subsequent hydrolysis and redox history, withtrends depending upon landscape position and location in the weathering profile. A key repeatingfeature of the REE+Y data in our datasets is the variable Ce* anomalies and low Y/Ho ratios (below unity) coinciding with the argillic horizons. A plot of (Eu*/Ce*) versus elevation shows consistent trends within each profile where the (Eu*/Ce*) ratio is lowest in the argillic horizon (Figure below). Ce^{4+} and Eu^{3+} adsorption is associated with Fe-oxyhydroxide, kaolinite, and interstratified clay surfaces. (Eu*/Ce*) increases in the saprolite because Eu^{2+} and Ce^{3+} are likelycontained in primary minerals or adsorbed on to halloysite and/or smectite at depth. The A-horizon (Eu*/Ce*) ratios trend to a slightly larger value above the argillic horizons, which we attribute tolower pH and organic acid rich conditions that would preferentially reduce, chelate, and mobilizeEu, while not affecting Ce^{3+}. Secondly, there is an overall trend of decreasing (Eu*/Ce*) values with decreasing hillshed orders, which suggest there is a broad geomorphic effect on the degree of redox weathering. This hints that the landscape REE's are recording a long-term signal that is, in part, related to interfluve order. There is no consistent trend in the land cover type (i.e., hardwood versus pine) in the (Eu*/Ce*) values.

Yttrium and rare earth modes of occurrence in manganese crusts from bentonite deposits of the Texas coastal plains

Debora Berti[1,*], Niall C. Slowey[1], Youjun Deng[2], Thomas E. Yancey[3], Ana L. Barrientos Velazquez[3]

[1]Department of Oceanography, Texas A&M University, College Station, TX 77843 USA
[2]Department of Soil & Crop Sciences, Texas A&M University, College Station, TX 77843 USA
[3]Department of Geology & Geophysics, Texas A&M University, College Station, TX 77843 USA

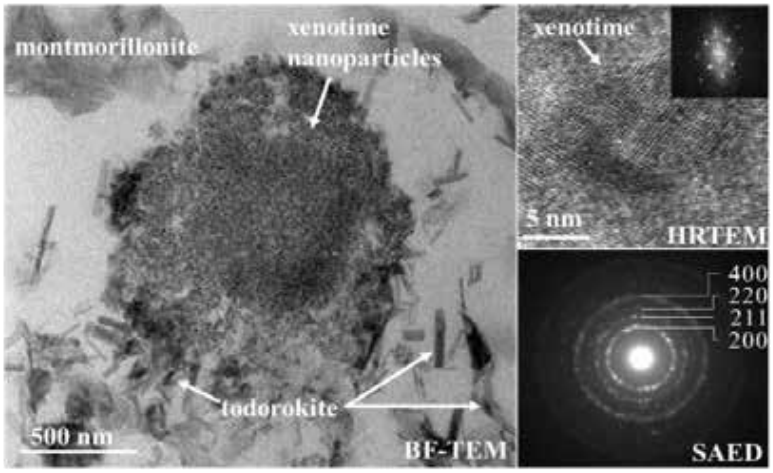
*debora-berti@tamu.edu

Bentonite deposits formed by alteration of Eocene-aged volcanic ash in the Texas coastal plain show varying degrees of enrichment in rare earth elements and yttrium (REE). Remarkably, concentrations of yttrium reach levels of 2000 ppm in manganese oxide crusts occurring at bentonite layer boundaries and in fractures.

This study investigated the modes of occurrence of yttrium and other REEs that occur in association with manganese oxide crusts to shed light on the processes that led to their accumulation as well as the economic potential of these deposits.

Samples of manganese oxide crust with a positive yttrium anomaly were embedded in epoxy, polished, and analyzed by SEM-EDS. Ultramicrotome sections and FIB-liftout sections extracted from sites identified by SEM were examined by TEM-EDS.

The SEM and TEM results revealed the presence of abundant yttrium phosphate nanoparticles identified as xenotime, arranged in large globular aggregates that reach several microns in diameter. These xenotime aggregates also host trace concentrations of Zr, Dy, Er, Yb and Ce. Variable amounts of other REEs were also identified in smaller aggregates of phosphate nanoparticles with Ce occurring separately from La and Nd. The association of yttrium and REE phosphates with the manganese oxide crusts indicates their precipitation was driven by redox gradients at bentonite layer boundaries and fractures.



Uniquely high rare earth element enrichment in regolith from Mount Weld REE deposit, Western Australia

Irina A Zhukova[1,*], Aleksandr S Stepanov[2], Shao-Yong Jiang[2], David Murphy[3]

[1]State Key Laboratory of Geological Processes and Mineral Resources, Collaborative Innovation Center for Exploration of Strategic Mineral Resources, School of Earth Resources, China University of Geosciences, Wuhan 430074, PR China

[2]Collaborative Innovation Center for Exploration of Strategic Mineral Resources, School of Earth Resources, China University of Geosciences, Wuhan 430074, PR China

[3]Queensland University of Technology, 2 George St, QLD 4000 Brisbane, Australia

*irina@cug.edu.cn

Mount Weld in Western Australia is one of the world's richest rare-earth element (REE) deposits and a major REE source outside of China. REE ores occur within a laterite cup of carbonatite and the highest concentrations of REE (up to 51.8 wt% $\sum REE_2O_3$) are observed in regolith. We performed a detailed geochemical and mineralogical study of Mount Weld regolith in order to improve the understanding of the processes that resulted in the extreme REE concentrations.

The high-REE regolith is light-colored crumbly material compo sed of large euhedral monazite, rhabdophane-(Nd) [$(LREE)PO_4*nH_2O$)], florencite-(Ce) [$(LREE)Al_3(PO_4)_2(OH)_6$] and cerianite (Zhukova et al., 2021). Unique geochemical characteristics include: significant negative Ce anomaly and positive Eu anomaly of the whole rock REE patterns, variable Ce anomaly in lithogenic monazite, and presence of tubular object about 2 mm in diameter composed of radially oriented fibers of rhabdophane-(Nd) and interpreted as remains of paleo-plants. The textures record evolution from magmatic monazite without Ce and Eu anomalies to corroded lithogenic monazite with Ce depleted domains and to late supergene minerals such as rhabdophane-(Nd) and florencite-(Ce) with pronounced Ce and Eu anomalies.

The super enrichment of REE at Mount Weld is the result of a multistage process, including an initial magmatic stage that generated carbonatites with exceptionally high REE content, followed by the bio-assisted weathering, resulting in the loss of Ca, Mg and CO_2, fractionation of Ce and enrichment of REE.

Zhukova I., Stepanov A.S., Jiang S.Y., Murphy D., Mavrogenes J., Allen C., Chen W., Bottrill R. (2021) Complex REE systematics of carbonatites and weathering products from uniquely rich Mount Weld REE deposit, West Australia. *Ore Geology Reviews* 139 Part B: 104539.

Effective visible/near infrared reflectance spectroscopic proxies for exploration of regolith-hosted rare earth element resources

Wei Tan*, **Xiaorong Qin**, **Hongping He**

Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

*tanwei@gig.ac.cn

Regolith-hosted rare earth element (REE) deposits predominate global resources of heavy REEs. Regoliths underlain by various types of igneous rocks and do not always host economically valuable deposits. The lack of studies on spectral features of ion-exchangeable REEs and REE mineralization in a particular regolith limit the application of visible/near infrared reflectance (VNIR, 350-2500 nm) spectroscopy to provide diagnostic parameters for targeting REE orebodies in regoliths. This study presents a systematic study on VNIR spectral features of ion-exchangeable REEs hosted by a series of synthetic REE-adsorbed clay minerals and some effective proxies to evaluate weathering intensities and chemical/mineralogical composition in natural regolith samples.

The obtained results show that ion-exchangeable Nd^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+} and Tm^{3+} display diagnostic absorption features at the bands of 730-870, 805, 641, 652, and 684 nm. Specifically, the Nd^{3+} related absorption bands of regolith samples at ~800 nm show a shoulder at ~802 nm that are distinguishable from unweathered primary REE(-bearing) minerals. The maxima of second derivative curves derived from the Nd^{3+} absorption at ~802 nm, M802_2^{nd}, can be used to quantify variations of ion-exchangeable REEs in regoliths. Moreover, the spectral parameters, M1396_2^{nd}/M1910_2^{nd} ratios can serve as proxies to evaluate weathering intensities in a regolith. Abrupt changes of specific spectral features related to mineral abundances, chemical compositions and weathering intensities can be correlated with variations of protolith that formed a regolith. These VNIR proxies are robust and can be used for exploration of regolith-hosted REE deposits. This study demonstrates that field-based VNIR spectroscopy can be deployed as a powerful tool for regional and deposit-scale exploration of regolith-hosted ion-exchangeable REE resources.

Tan, W., Qin, X.R., Liu, J.C., Michalski, J., He, H.P., Yao, Y.Z., Yang, M.J., Huang, J., Lin, X.J., Zhang, C.Q., & Liang, X.L. (2021). Visible/near infrared reflectance (VNIR) spectral features of ion-exchangeable Rare earth elements hosted by clay minerals: Potential use for exploration of regolith-hosted REE deposits. *Applied Clay Science,* 215, 106320.
Tan, W., Qin, X.R., Liu, J.C., Zhou, M-F., He, H.P., Wang, C.Y., Huang, J., Zhu, J.X., Yao, Y.Z., & Cudahy, T. (2022). Feasibility of Visible Short-Wave Infrared Reflectance Spectroscopy to Characterize Regolith-hosted Rare Earth Element Mineralization. *Econom- ic Geology,* 117, 495-508.

Geochemical and mineralogical evolution of cerium during the chemical weathering for ion-adsorption type rare-earth element deposits in Southern China

Mei Lu*, **Hongping He**, **Wei Tan**, **Xiaoliang Liang**

Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

*lumei@gig.ac.cn

The ion-adsorption type rare-earth element (iREE) deposit in Southern China is of great importance for the global supply of REEs. Among the chemically coherent series of REEs, thecerium (Ce) exhibits distinctive geochemical behavior due to its unique environmental oxidizability, leading to the excursion of Ce from the REEs, defined as the Ce anomaly. However, the geochemical mobility of Ce during the weathering process and the implication ofCe anomaly are poorly constrained and yet essential to understanding the formation of iREE deposits.

To investigate the geochemical and mineralogical evolution of Ce, we have conducted an analysis of SEM/TEM observation, EPMA, and selective extraction on an approximately 90- m-long mature weathered profile in Southern China. The strong hydrothermal alteration contributes to the primary enrichment of the Ce minerals in the bedrock, such as bastnasite, parisite, and monazite. Subsequent weathering substantially changes the mineralogical characteristics through supergene water-rock reactions. The released Ce ions from the breakdown of Ce minerals are predominantly scavenged by Fe-Mn oxides and a few forms secondary Ce phosphates and Ce-bearing clay minerals. Further weathering makes the ferrihydrite transform to the goethite and hematite, and these transformations between Fe oxides plus the crystallinity upgrade pose a significant influence on the mobility of Ce, from the first Fe-Mn-Ce mixture to the ultimate separated well-crystallized hematite and cerianite (CeO_2) nanoparticle aggregations. We argue that even though a small amount of Mn oxides is present in the whole profile, as adsorbed by Fe oxides, they signifi- cantly control the geochemistry of Ce through oxidative scavenging as demonstrated by previous studies (Ohta and Kawabe, 2001). Above the water table, Ce is survived from being entrained by the downward groundwater due to the stabilization by Fe-Mn oxides. Inversely, other REEs are abundantly transported to the accumulation position, just beneath the water table, where there is a spatial association between the total REEs contents and negative Ce anomalies. The discussions on the Ce mobility constraint by the groundwater and Fe-Mn oxides make it reasonable for using surficial Ce enrichment and lower negative Ce anomaly as an indicator for iREE deposits.

Ohta, A., and Kawabe, I. (2001). REE(III) adsorption onto Mn dioxide (delta-MnO2) and Fe oxyhydroxide: Ce (III) oxidation by delta-MnO2: *Geochimica Et Cosmochimica Acta,* 65(5), 695-703.

TS26 Clays Geotherms Fluid Migrations in Sedimentary Basins

ORAL PRESENTATIONS

Diagenesis of the sedimentary Fe-Ni deposits of Euboea: Evidence based on phyllosilicate mineralogy and geochemistry.

Spyros Cheliotis-Chatzidimitriou[1], Georgios E. Christidis[1,*], Ioannis Marantos[2]

[1]School of Mineral Resources Engineering, Technical University of Crete, 73100, Chania, Greece
[2]Hellenic Survey of Geology and Mineral Exploration (H.S.G.M.E), Greece

*christid@mred.tuc.gr

The sedimentary Fe-Ni deposits of Central Euboea were formed from lateritic weathering of Jurassic ophiolites, followed by erosion, transportation and deposition of the lateritic mantles in shallow marine/ lagoonal environment in the Upper Cretaceous, over Triassic limestones or ophiolites or rarely, chert-schist stones. The main hosts of Ni are phyllosilicates, mainly chlorite, serpentine and talc, whereas Fe-oxides and Fe-oxyhydroxides are of minor importance. The role of smectite is not known with certainty. In this study we report on the phyllosilicate mineralogy of the deposits of Katsikiza, Pagondas, Koutos, Platani, Vrysakia, Rekavetsi and Zygos, and examine its significance on the evolution of the deposits during diagenesis.

The deposits consist of peloids, scarce pisoids and individual grains of hematite with variable sphericity, as basic components. They also contain angular to rounded quartz, calcite and accessory chromite fragments, as well as, pyrite in certain sectors. The grain shape and texture designate limited transportation from the source rocks. The bulk and clay mineralogy were determined by XRD. Mineral texture characterization and semi-quantitative analysis were conducted with SEM-EDS. Complex peaks from diffraction patterns were deconvolved into individual mineral phases with Fityk software. The main phases of the phyllosilicate mineralogy are R0 mixed layered chlorite-smectite (Chl/Sme) with 10-20% smectite layers and discrete chlorite (Chl). Talc (kerolite-pimelite) is minor phase in all deposits, being a main phase locally in the Vrysakia deposit, while minor serpentine is present in most of the samples. Corrensite (Crr) is present in Vrysakia and Platani deposits. Discrete smectite (Sme) is present as a major phase in sectors of the Vrysakia deposit, and discrete illite in Katzikiza and Rekavetsi deposits. Finally, the presence of a LREE-rich phosphate, monazite-like phase in Vrysakia deposit, suggests a rather diverse origin of the ore.

The coexistence of R0 Chl/Sme, Crr, discrete Sme and discrete Chl, as well as, the limited abundance or lack of serpentine suggest a) a Sme to chlorite conversion during diagenesis, b) lack of equilibrium in the Sme-to-Chl transformation and c) dissolution of serpentine during diagenesis. The occurrence of talc layers might be attributed to the transformation of stevensite, that probably existed in the primary lateritic mantle during diagenesis. Hence, Chl, R0 Chl/Sme and Crr are considered diagenetic. The Sme to Chl transformation, dissolution of serpentine and transformation of stevensite to talc are related to the mobilization of Ni and Co. The reaction paths suggest a burial temperature of 70-100°C.

The influence of clay-fluid interactions on sealing properties of cap rocks revealed by high-resolution imaging: an example of chalky marls from the Outer Carpathians (Węglówka Marls, Upper Cretaceous, Poland)

Katarzyna Górniak[1,*], Mariusz Młynarczuk[1], Aneta Zięba[2], Grzegorz Machowski[1], Tadeusz Szydłak[1], Adam Gaweł[1], Anna Tomczyk-Chmiel[1], Monika Wójcik-Bania[1]

[1]AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, 30-059 Kraków, Poland

[2]Nanores Sp. Z o.o.Sp. k, 51-317 Wrocław, Poland

*gorniak@agh.edu.pl

Sealing rocks are important elements of both petroleum systems and aquifers. Currently, deeply understanding how sealing rocks work has become particularly worthy of interest, as e.g., the sequestration of CO^2 in hydrocarbon depleted formations is considered one solutionto mediate climate change.

The Węglówka Marls are sealing rocks in the oldest oil field in the Carpathian region, which was discovered in 1888 and is currently at the end of its production. Grain assemblages and the pore network of this rock were examined using integrated petrographical andpetrophysical methods: XRD, thermal analysis, grain size distribution, FEG-SEM, FIB-SEM, Mercury intrusion, Nitrogen Gas Absorption, and Helium picnometry. Outcrop samples from the Węglowka Oil Field (19 samples) have been analyzed to understand the relationship between clay minerals with formation fluids during deposition of hydrocarbon, and to reveal which processes produced chalks with fairly good porosity (15.12 to 26.78%) and very low permeability (800 – 3000nD).

The rocks studied: (1) are classified as chalky marls having about 50% clay minerals, 30% carbonates (coccolith debris), 15% nanquartz and 5% quartz and feldspar grains; (2) clay minerals are dominated by illite-smectite comprising 60% swelling layers; (3) according to the classification by sealing capacity the rocks studied represent Seal Type A (hydrocarbon column > 300m), i.e., they provide a very effective seal; (4) their average pore diameter ranges from 19.8 to 24.4 nm; (5) the pore network imaged in 3D mode by FIB-SEM revealed leakage pathways and their occlusion by clay; (6) clay minerals, both migrated and neoformed, are identified as self-sealing agents of inter- and intragranular pore space in chalky marls studied.

K-white mica b cell dimension: a complementary clay minerals tool to decipher polyphasic basin evolution

Potel Sébastien[1,*], Ferreiro Mählmann Rafael[2]

[1]B2R, Institut Polytechnique UniLaSalle Beauvais, Geosciences Department, F 60026 Beauvais, France
[2]Technische Universität Darmstadt, Institut für Angewandte Geowissenschaften, D-64287 Darmstadt, Germany

*sebastien.potel@unilasalle.fr

Since the pioneer work of Sassi (1972) on the K-white mica b cell dimension BCD), the method has been used to characterize the factor pressure in meta-pelitic rocks. This method is used as an estimate of different pressure facies. Studies in the last two decades reached in low-grade metapelitic rocks. Studies in the last two decades have been carried out in different basins and meta-sedimentary rocks with poly-phase evolutions. It could be demonstrated that this method is less prone to resetting than the Kübler-Index (KI) or organic matter (OM) indices. Also, in supposed mono-phase metamorphic settings, the *b* cell method detected earlier higher-pressure events. A poly-phase history that KI values, the clay mineral reactions progress or OM evolution did not indicate.

Case studies conducted in New Caledonia in the SW Pacific (Potel et al., 2006), in the Vosges in the NE of France (Potel et al., 2016) and in the Montagne Noire in the S of France, using K-white micas BCD, have allowed to outlined poly-metamorphic evolution hitherto unknown. In New Caledonia an early K-white mica neoformation at high-pressure conditions after a pluri-facies metamorphic evolution (late prograde temperature overprints) is preserved by K-white micas BCD. In the Vosges, The K-white mica BCD indicates the limit of the contact metamorphism halo of intrusion in contrast to exclusively burial and orogenic thermal patterns shown by e.g. index minerals like biotite or actinolite. To substantiate these findings, results concerning the evolution of the eastern part of the Montagne Noire will be presented. The Montagne Noire is a gneiss dome flanked by Paleozoic sediments. The K-white mica BCD was used to decipher the burial effect compared to the contact metamorphism on the Paleozoic sediments.

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Sassi, F.P. (1972). The tetrological and geological significance of the b0 values of potassic white micas in low-grade metamorphic rocks. An application to the Eastern Alps. *Tschermaks Mineralogische Petrographische Mitteilungen* 18, 105–113.

TS26 Clays Geotherms Fluid Migrations in Sedimentary Basins

POSTER PRESENTATIONS

Sedimentology and origin of Karabk-Safranbolu Paleogene Basin evaporites (West Black Sea Region, Turkey)

Burak Demiral[1,*], Erdoğan Tekin[2], Muhammed Sami Us[3]

[1]Eskişehir Osmangazi University, Department o f Geological Engineering, Eskişehir, Turkey
[2]Ankara University, Department of Geological Engineering, Ankara, Turkey
[3]Munzur University, Faculty of Literature, Departmant of Geography Tunceli, Turkey

*jeoburakdemiral@gmail.com

Pürçükören Formations which is located in the Inner Pontide Suture Belt in the Western Black Sea Region, aged Paleogene, between İğdir, Yukarıgüney, Terke, Gergen, Karcılar Göde villages in the Southeast of the Karabük-Safranbolu Basin, were evaporitic (gypsum-anhydrite) character. Sedimentological, petrographical thin section, SEM-EDS, mineralogical XRD and geochemistry (main oxide-trace element and isotope) studies had been carried out for occured that origin, age, depositions conditions, paleotemperature/paleosalinitiy values of these evaporites. Stratigraphic columnar sections were taken from eligibles areas with sedimentological studies and different evaporitic litofacies were defined within this section. These are; massive gypsum facies (F1), banded-laminated gypsum facies (F2), nodular gypsum facies (F3), twinned selenitic gypsum facies (F4), and fibrous satin-spar gypsum facies (F5). Samples of these lithofacies these were detected to generally alabastrin and porphyroblastic texture late diagenetic secondary gypsum were at petrographical thin section studies. Moreover, celestine, calcite, dolomite and detrital quartz and clay mineral deposits some of F2 facies samples had been observed at SEM-EDS studies were made for determine the detail properties of evaporite thin sections that cannot be detected in polarizing microscope examinations. The clay and clastic material shown indirectly that the evaporite deposition is not uniform, clastic material inflows into the basin during the deposition so partly tectonism is active. It has been determined that these clays were illite-chlorite group clays, which are indicate that arid climate conditions at mineralogical XRD studies. When main oxide-trace element values measured in ICP-MS the evaporites of Pürçükören Formations correlated with the detail oxide-trace element values of Paleogene evaporites in the world and in Turkey, it was concluded that this evaporites were deposited in a shallow marine environment. On the other hand, $\delta^{18}O$, $\delta^{34}S$ ve $\delta^{86/87}Sr$ isotope values evaporites of Pürçükören indicated they were formed under marine environmental conditions evaporation and shown that sedimentation age was Late Eocene.

Consequently, determined that regional compressional tectonics, Late Eocene regression, MECO (Middle Eocene Climatic Optimum) global warming processes were effective in the deposition of Pürçükören Formation evaporites in the study area, the evaporites in the region are of marine origin and the age is Middle? - Late Eocene (Bartonian-? Priabonian).

TS27 Clays - Burial Diagenesis - Low Temperature Metamorphism

ORAL PRESENTATIONS

Chlorite REE geochemistry to unveil hydrothermal processes at the incipient stage of oceanization of Mid-Triassic Dinaridic Tethys

Branimir Šegvić[1,*], Luka Badurina[1], Bethany Morgan[1], Damir Slovenec[2]

[1]Texas Tech University, Department of Geosciences, Lubbock TX 79401, U.S.A.
[2]Croatian Geological Survey, Department for Geology, 10000 Zagreb, Croatia

*branimir.segvic@ttu.edu

The hydrothermal metamorphism that takes place in the oceanic lithosphere facilitates our understanding of crustal evolution and offers deep insights into the processes characteristic for hydrothermal systems. Mafic extrusive and intrusive rocks of the oceanic crust react with circulating and percolating hydrothermal fluids resulting with transformation of primary magmatic minerals into new deuteric assemblages. This process commonly results with partial recrystallization and prevalent formation of clay phyllosilicates which are essentially out of thermodynamic equilibrium and hence adumbrate broad compositional ranges. These hydrothermal processes are metasomatic and allochemical, prone to a selective addition and removal of chemical components.

This research pays attention to REE mobility during ocean metasomatism which had long beena matter of concern because of its bearing on a life cycle of the oceanic crust. Chlorite is omnipresent in the studied crustal rocks being either a clay-size replacement of a pyroclastic/effusive matrix and/or a coarse vein or vesicules infill. As such chlorite serves as anexcellent polygon to investigate the mobility of REE in hydrothermal media controlled by temperature, redox potential, acidity and ionic complexation of pervasive fluids. The purpose of this research is therefore to report on the REE distribution in hydrothermal, texturally diverse, chlorite and to test a possible relation between its REE geochemistry and prevailing hydrothermal conditions.

Our preliminary results have shown that clay-matrix and columnar topotactic chlorite is Fe-richwith REE content similar to those of black smokers albeit enriched for several orders of magnitude. Conversely, the coarse amygdaloidal Mg-rich chlorite outlines REE levels on par with those of seawater. An inference can be made that in Fe-chlorite virtually all of the REE stem from the host rock while for Mg-rich chlorite amygdules this is not necessary the case. This means that chlorite from basaltic amygdules originated from the cold seawater that penetrated down in the recharge zone of the hydrothermal system but did not reach the hot reaction zone, or alternatively, the hydrothermal system was temporarily inactive or cooled down. In such solutions REE are mostly complexed; LREE are however less complexed than HREE with the former displaying a considerable complexing by Cl^-, SO_4^{2-} and CO_3^{2-}, while the latter is commonly complexed by CO_3^{2-}, which explains our experimental normalization curves. On the other hand, matrix and replacive Fe-rich chlorite is the product of fluid-facilitatedfast chemical degradation of primary miner- als, notably plagioclase, which takes place far fromequilibrium. Plagioclase REE budget thus effectively controlled the REE content of deep- seated, high-temperature hydrothermal fluids parental to the second geochemical type ofinvestigated chlorite.

Origin of trioctahedral clay minerals in the Padul-Nigelas fault rocks (Betic Cordillera, Spain)

Isabel Abad[1,*], Fernando Nieto[2], Matías Reolid[1], Juan Jiménez-Millán[1]

[1]Departamento de Geología y CEACTEMA, Unidad Asociada IACT (CSIC-UGR, Universidad de Jaén, 23071, Spain
[2]Departamento de Mineralogía y Petrología e IACT (CSIC-UGR, Universidad de Granada, 18002, Spain

miabad@ujaen.es

The recent tectonic activity in the south eastern Iberian Margin (Trans-Alboran Shear Zone is a consequence of the convergence of the Eurasian and the African plates and includes normal faults. One of them is the Padul-Nigüelas fault, which is located in the Internal Zone of the Betic Cordillera that separates the highest reliefs of Sierra Nevada (footwall block from the Padul graben (hanging wall. The fault offers evidence of recent activity with a continuous scarp developed in the contact with the footwall basement being the most remarkable normal fault from the geomorphic point of view of this area. The rocks affected by this fault are mainly low-grade metamorphic Triassic dolostones. The fault rocks studied include ultracataclasites and cataclasites. This research is focused on the clay minerals of the fault rocks with special emphasis in the authigenic trioctahedral phyllosilicates.

Although the studied rocks are mainly composed by dolomite as the major mineral phase, the presence of subordinated micas (muscovite and phlogopite) and quartz grains in the protolith was also described. In addition to phlogopite, fault rocks contain also another two trioctahedral clays: Mg- chlorite and sporadically, talc. Other clays are kaolinite, illite-white mica and smectites, which were detected in the transmission electron microscopy (TEM). The presence of calcite is common in the fault rocks but much more significantly in the ultracataclasites, sealing veins or as cement. The chemical analyses of chlorites have shown that there are differences among chlorites from the fault rocks and those located directly on the fault plane. Despite all chlorites are Mg-rich, the first ones usually host Zn whereas chlorites from the fault plane have no Zn and are chemically more homogeneous. As well, they show textural differences. The chlorites from the fault plane are preferential oriented and bigger than the others described in the fault breccia. In fact, the TEM characterization of the fault breccia chlorites has shown that their origin is related with a layer-by-layer transformation from phlogopites. However, in the chlorites from the fault plane, the data point to a dissolution-precipitation process. The application of chlorite thermometry (Bourdelle et al., 2013; Inoue et al., 2018) to both populations show a predominance of higher temperatures for the fault plane chlorites (around 200 ºC), than for the chlorites of the cataclasites (100–120 ºC). The talc grains observed at nanoscale (< 0.5 µm) and always located in voids among carbonates (dolomite and calcite) suggest a genesis from dolomite promoted by the activity of silica-rich hydrothermal fluids in a low- temperature environment (<200 ºC) which is coherent with the chlorite thermometry data and the textures observed in the fault rocks.

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Clay Mineralogy of the Tomanova Formation – inland fresh water sediments of upper Triassic age

Michał Skiba*, Marta Kisiel, Piotr Jaglarz, Katarzyna Maj-Szeliga, Dorota Salata, Beata Żymełka, Magdalena Makiel

Institute of Geological Sciences, Jagiellonian University, 30-387 Kraków, Gronostajowa 3a, Poland

*michal.skiba@uj.edu.pl

The aim of the present work was to study clay mineralogy of Tomanova Formation a ~65m thick complex of deposits of periodic swamps and lakes developed on river flood plains during Upper Triassic. The Tomanova Formation is a part of a Mezosoic sedimentary cover deposited on the Variscian crystalline basement rocks of the Tatra Mountains. Despite the fact that in general the sedimentary cover underwent high-grade diagenesis, as indicated by a commonly observed lack of smectite and presence of illite and chlorite, the Tomanova formation was expected to serve as a kind of time capsule preserving the primary clay mineralogy. This was expected because the formation was composed mainly of fine grained sediments containing only up to 2% of K.

Samples used in the present study were collected from outcrop located within Czerwone Żlebki in the Tomanova Valley in the Polish part of the Tatra Mountains. Seven horizons rich in clays were selected for detailed mineralogical study. Both bulk samples and the clay fractions were analyzed using XRD, FTIR, and ICP OES methods. Layer charges of swelling clays separated from the samples were measured using O-D method.

All studied samples contained dioctahedral vermiculite with some admixtures of kaolinite, berthierine, and quartz. Measured mean layer charge values for the vermiculites were in the range of 0.64-0.76/ $O_{10}(OH)_2$.

Obtained results indicated that the Tomanova Formation indeed served as a kind of sealed time-capsule which protected primary dioctahedral vermiculite from diagenetic changes despite the high-grade diagenesis within the entire Mezosoic sedimentary cover of the Tatra crystalline basement. This finding is of great importance because in general dioctahedral vermiculite is regarded to be a meta-stable and a very reactive phase limited to soils and young fresh water sediments. According to our knowledge this is the first report of dioctahedral vermiculite occurring in high-grade diagenetic sedimentary rocks. This is of exploration importance because dioctahedral vermiculite has a potential to serve as a molecular sieve for radiocesium immobilization.

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Diagenesis of magnesian clay minerals in Santos Basin (Aptian)

Camila W. Ramnani[1,*], Julice F. Santos[1], Yaro Parizek-Silva[1], Vanessa Madrucci[2], Maria Rosilene F.M. Santos[1], Carlos C. Araújo[2]

[1]PETROBRAS - Research and Development Center, Rio de Janeiro, Brazil
[2]PETROBRAS – Exploration, Rio de Janeiro, Brazil

*camila.wense@petrobras.com.br

The pre-salt province is located on the southeastern coast of Brazil and covers approximately 150,000 km^2. It is known for the occurrence of supergiant oil accumulations in lacustrine carbonate reservoirs. The paleogeography of the Lower Cretaceous lake system of the Santos basin favored the formation of Mg- clay minerals in depositional environments with specific physico-chemical conditions. This work focuses on the characterization of the early and burial diagenesis of the Mg-clay minerals, extensively sampled in drilled wells in this basin. The Mg-clay minerals were studied by means of petrography; XRD, SEM/ EDS; EMPA and TEM.

Mineralogical data show that the intervals with Mg-clay have an average of 15% clay content, and rarely exceed 50% of the total rock mineralogy. Calcite and dolomite are the main minerals in these intervals. The authigenic Mg-clay minerals identified were kerolite, stevensite, saponite, mixed-layer kerolite-stevensite and sepiolite. Talc and lizardite occur in metamorphosed host rocks in contact with diabase sills. Illite, montmorillonite, kaolinite, chlorite, and mixed-layer illite-smectite and chlorite-smectite occur in trace amounts, mainly as detrital and more rarely as digenetic components. The Mg-clay minerals are between and inside carbonate components, such as shrubs, spherulites and crusts. The clay texture reveals syngenetic (depositional) phases (massive, laminated, peloidal, granular, intraclastic and ooid), early diagenetic phases (coating) and mesodiagenetic phases (fringe). The syngenetic clay were deposited in low energy environments (claystone, spherulitite, laminite and stromatolite with clay). With a small increase in energy, Mg-clay sediment was fragmented and clasts were re-sedimented (packstone and grainstone with intraclasts of carbonate and Mg-clay).

The early diagenetic features observed in clays are saponite forming by transformation of a precursor mineral, sepiolite coating and dissolution of syngenetic Mg-clay minerals. The sepiolite coating forms around *in situ* components, such as stromatolite, and around intraclasts of packstone and grainstone. It is noted that packets of sepiolite fibre mats mimic stevensite and kerolite sheets, showing that sepiolite formation is related to partial dissolution of previous Mg-clay minerals. The dissolution of syngenetic clay minerals is followed by precipitation of quartz, magnesite, and dolomite, and also can form secondary porosity.

During mesodiagenesis, the Mg-clay minerals begin the transformation under the new conditions of burial pressure and temperature. The mixed-layer kerolite-stevensite shows an increase in the percentage of kerolite layers. The crystallinity of kerolite is increased. The effects of compaction are observed in both clay layers and clay intraclasts. In grainstones that occur in areas with deeper burial, the deformation of clay intraclasts forms a pseudomatrix, which is squeezed into the pore space, clogging the throat of pores and reducing the primary porosity. The solution formed due to the partial dissolution of clay intraclasts and pseudomatrix leads to the formation of a microporous fringe around the grains, with composition of mixed-layer kerolite-stevensite rich in kerolite.

Illitization of smectite in ammonium solutions under hydrothermal conditions

F.J. Huertas[1,*], M.J. Bentabol[2], A.E.S. Van Driessche[1]

[1]Instituto Andaluz de Ciencias de la Tierra (CSIC-University of Granada), 18100 Armilla, Granada, Spain
[2]Departamento de Química Inorgánica, Cristalografía y Mineralogía. University of Málaga.Campus de Teatinos. 29071 Málaga (Spain)

*javier.huertas@csic.es

Ammonium in diagenetic solutions may be adsorbed on smectites as exchangeable cation, and fixed in the interlayer space of illites and white micas. A series of hydrothermal experiments were carried out at 100-200ºC, for 15 to 90 reaction days and NH_4^+ solutions (0.1 and 0.2 M) to study the influence of NH_4^+ on the smectite-to-illite transformation. Solids were characterized by XRD, FT-IR and TEM/AEM. The XRD results show that smectite incorporates NH_4^+ in the structure, forming non-swelling layers, and partially transforms into illite to produce disordered I/S. In addition, a small reflection at ~10 Å suggested the formation of illite domains. FT-IR spectra show a NH_4^+ deformation bands at 1400 and 1430 cm^{-1}, corresponding to exchangeable NH_4^+ in smectite and fixed NH_4^+ in non-swelling layers, respectively. TEM images showed smectite crystals contains abundant defects such as stacking, wedge and layer terminations, with variable basal spacing (12-15 Å and inclusionof illite layers, as well as illite single crystals (10-10.5 Å). AEM results were consistent with formation of irregular I/S and illite crystals.

Smectite transformed into illite under experimental conditions that corresponds to slightly alkaline hydrothermal solutions enriched in ammonium. The reaction is triggered by ammonium adsorption at the interlayer space in smectite crystals. Simultaneously, smectite dissolved and released Si and Al to the solution. At the nanometric scale smectite dissolution and ammonium fixation produced a layer-by-layer transformation of smectite into illite, with an increase of tetrahedral Al in the illitic layers, and formation of disordered I/S poor in illite layers. Moreover, single illite crystals were formed by precipitation from solution, favored at 150 and 200°C, which incorporated interlayered ammonium. Our experimental results show that at moderate temperature conditions, ammonium ions contribute to stabilize the forming illite layers and favor the smectite-to-illite reaction. This process is favored at increased temperature and ammonium concentration.

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Clay mineral formation in Permian rocks of a geothermal borehole at Northern Upper Rhine Graben, Germany

Lan Nguyen Thanh[1,*], Rafael Ferreiro Mählmann[1], Thao Hoang Minh[2], Rainer Petschick[3], Thomas Reischmann[4], Heinz Dieter Nesbor[4], Myriam Ruttmann[4], Johann Gerhard Fritsche[4]

[1]Technische Universität Darmstadt, 64287 Darmstadt, Germany
[2]University of Science, Vietnam National University, Hanoi, Hanoi 10000, Vietnam
[3] Department of Geosciences, Goethe University, 60438 Frankfurt am Main, Germany
[4]Hessian Agency for Nature Conservation, Environment and Geology, 65203 Wiesbaden, Germany

*nguyen@geo.tu-darmstadt.de

Hydrothermally altered rhyolite rocks in the Permian Donnersberg Formation of a geothermal borehole in the Northern Upper Rhine Graben (Germany) were investigated to find out answers for the low hydraulic conductivity of the rocks. The composition of clay minerals and the temperature of smectite–illite transformation were carried out using X-ray difraction, X-ray fuorescence, transmission electron microscopy, Fourier transform infrared spectroscopy, and polarized-light microscopy analyses. Clay mineral (CM) composition includes illite/muscovite (1*M* and 2M_1 polytypes), illite–smectite interstratifications (IS-ml), smectite, and chlorite; and non-clay minerals such as quartz, feldspars, epidote, calcite, dolomite, and hematite were detected. The 2M_1-polytype mica might be the only primary sheet silicates from the parent rocks, while the others occur as authigenic neo-formed CMs under decreasing heat flow, geothermal gradients and hydrothermal events. The development of CMs indicates different mechanisms of illitization and smectitization. Based on the texture, morphology, structure/polytype, and chemistry of rocks and minerals, in particular CMs, the study grouped the CM formation into three transformation processes: smectitization during magma cooling and possible contact metamorphisms with decreasing and low temperature, smectite illitization controlled by burial diagenesis and hydrothermal alteration, and illite smectitization followed exhumation and Cenozoic subsidence with decreasing temperature. The rhyolites were altered to all of the orders IS-R0, IS-R1, and IS-R3 by the dissolution-precipitation and layer-to-layer mechanisms. The first one supported small xenomorphic plates and fakes of 1M_d, elongated particles of 1*M*, and pseudo-hexagonal forms of 2M_1. The second one could lead to the platy particles of 1M_d and 2M_1 polytypes. The dominant temperature range for the transformation in the area has been 140 –170 °C – ~230 °C

Multi stage illitization of K-bentonites from diagenesis to very low-grade metamorphism: An example from Early Carboniferous of southern Turkey

Ömer Bozkaya[1,*], Asuman Günal Türkmenoğlu[2], Mehmet Cemal Göncüoğlu[2], Jan Środoń[3], Marek Szczerba[3], I. Tonguç Uysal[4]

[1]Pamukkale University, Department of Geological Engineering, 26040 Denizli, Turkey
[2]Middle East Technical University, Dept. of Geological Engineering, 06531 Ankara, Turkey
[3]Institute of Geological Sciences, Polish Acad. Sci., Senacka 1, 31002 Krakow, Poland
[4]İstanbul University-Cerrahpaşa, Dept. of Geological Engineering, 34320 İstanbul, Turkey

*obozkaya@pau.edu.tr

The yellowish green tephra (K-bentonite) layers are exposed along two sections in the South of Akşehir (Konya, southern Turkey) within the Early Carboniferous (Mississippian) red dolomite-dolomitic limestone succession of the Sultandağ Unit in the central Tauride Belt (Bozkaya et al., 2021). K-bentonites display typical porphyritic texture with euhedral plagioclase phenocrysts which completely replaced by white K-micas and dolomites within the fine-grained sericitized volcanic matrix has vitrophyric texture. Bulk mineral composition of K-bentonites is clay minerals, dolomite and calcite, indicating the absence of detrital components. Illite is the only clay mineral in all K-bentonite samples. Illite polytypes are characterized by the association of 2M1, 1M and 1Md. Illit e Kübler index values (KI, Dº2θ) reflect high- grade diagenetic to anchizone conditions. The polytype quantifications obtained from several methods (WILDFIRE, BGMN, QMIN etc.) indicate the 2M1 content increase with increasing grain size and therefore with diagenetic/metamorphic grade. The wide range of K/Ar age data, ~ 90 to 50 Ma, were obtained from different grain sizes of illlites (<0.2 µm, 0.2-0.5 µm, 0.5-1.0 µm, 1.5-2.0 µm). The extrapolations of ages and polytype ratios give different estimated ages for different polytypes, i.e., ~ 50 Ma for 100% 2M1, ~ 80 Ma for 100% 1Md, ~ 78 Ma 0% 2M1, 50 Ma for 0%1Md and 77 Ma for 0%1M. The negative ages for 100% 1M mean that 1M never reaches 100% because of recrystallization into 2M1. These data suggest that 2M1 crystallization is the youngest phenomenon, 1M intermediate, and 1Md oldest. The illitization ages correspond to ophiolite emplacements (Late Cretaceous) and the imbrication of the Tauride nappes (Early-Middle Eocene) during geodynamic evolution of the Taurus belt. The obtained results showed that the evaluation of age and polytype data of illites in K-bentonites can be very important tool in determining subsequent geological events.

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TS27 Clays - Burial Diagenesis - Low Temperature Metamorphism

POSTER PRESENTATIONS

Clay minerals as indicators of thermal alterations in rocks from the western part of the Papuk Mt. (Slavonian Mts., NE Croatia): preliminary results

Darko Tibljaš[1,*], Bruno Tomljenović[2], Matija Vukovski[3]

[1]University of Zagreb, Faculty of Science, 10000 Zagreb, Croatia
[2]University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, 10000 Zagreb, Croatia
[3]Croatian Geological Survey, 10000 Zagreb, Croatia

[*]dtibljas@geol.pmf.hr

Mount Papuk is located in the north-eastern Croatia within the Pannonian Basin (PB), the Neogene back- arc basin formed within the Alpine-Carpathian-Dinaric orogenic system. Pre-Neogene basement of the PB is divided into two major tectonic units. The eastern one, the Tisia unit, consists of Variscan crystalline complexes and post-Variscan Alpine (PV overstep sequences both exposed on the Papuk). For a long time, Papuk PV rocks were considered unmetamorphosed. However, Biševac et al. (2010) studied Late Permian and Triassic clastic-carbonate sedimentary succession in the eastern part of the Papuk Mountain and revealed the existence of Eoalpine (Cretaceous metamorphism). The observed Kübler (KI and rkai (I indices indicated that these rocks passed through a high-anchizonal to epizonal thermal alteration. This is consistent with previous observations (rkai, 2001 and references therein that large areas of pre-Neogene PB basement were metamorphosed during the Alpine event).

In order to better constrain the metamorphic conditions that prevailed in this area, new samples of PV rocks (Permo-Triassic, Triassic, and Jurassic from the western part of Papuk Mt. were investigated in this study using X-ray methods. KI and I were measured simultaneously on air-dried samples according to the recommendations of Kisch (1991).

The majority of KI (values ranging from 0.25 to 0.40 and I values measured on PV rocks (previously classified mainly as siltstones, sandstones, conglomerates, shales and a limestone from the western part of the Papuk showed that the majority of the rocks studied were thermally altered by anchizonal metamorphism. The measured KI and I are mostly in good correlation, deviations were only observed in samples with lower chlorite content. Only one sample, from a layer of shale occurring in dolomites, was according to KI (0.61 altered in the diagenetic zone. Thus, this preliminary investigation indicate that rocks sampled from the western Papuk Mt. were also affected by a PV metamorphic event most probably corresponding to the one described in the eastern part of the mountain.

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On the occurrence and significance of biopyribole from maficsub volcanic rocks from the External Dinarides

Luka Badurina[1,*], Mirko Belak[2], Damir Slovenec[2], Branimir Šegvić[1]

[1]TexasTech University, Department of Geosciences, Lubbock TX7 9401, USA
[2]Croatian Geological Survey, Department for Geology, 10000 Zagreb, Croatia

*luka.badurina@ttu.edu

Triassic magmatism in the Dinarides has been related to the formation of the Tethyan Mesozoic Adriatic-Dinaridic carbonate platform(s) and its (their subsequent disintegration. Sporadically occurring subvolcanic rocks emerge along the major fault zones found at the rims of the platform(s). One of such occurrences has been reported in north Dalmatia (Konj Hill), Croatia representing a hypabyssal dyke made of basaltic dolerite in its corewhich laterallyevolves into the medium-grained diabase. Rocks' mineral paragenesis include altered plagioclase and K- feldspar, clinopyroxene, tschermakite and pargasite amphibole, Fe-Tioxide and apatite. Deuteric phases encompass tremolite/actinolite, fine-grained muscovite, chlorite, prehnite, and pumpellyite.

Of particular importance is a complete topotactic replacement of primary amphibole by micaceous phases. The amphibole to mica mechanism is complex and leads to theformation of biopyribolic structures. These are defined by restructuration of amphibole double-chain I-beams to form alternating double and triple chains, pure triple chains, and lastly continuous sheets of silicate tetrahedra (i.e., phyllosilicate structure). Our preliminary data shows that such formed mica is phengitic muscovite which is defined by the in- creased Mg and Fe contents along the Tschermak substitution vector. This Mg-Fe muscovite is characterized by a reduced dimensional difference between the larger *trans*-oriented *M1*site and smaller *cis*-oriented *M2* octahedral site. Diagnostic peaks related to the *2M2* polytype may be explained by such space reduction.

Formation of Fe-Mg muscovite which is essentially controlled by the Tschermak exchange reaction which requires lower values of a$K^+$and/or neutral pH. Such conditions were likely buffered by igneous hostrocks where by liberated Na^+ likely vacated the system. All this suggests high fluid activity and element diffusion during alteration event. The crystallization of phengitic mica required at least low-temperature hydrothermal conditions (200-300°C. This further implies that the studied rocks were impacted by a large-scale hydrothermal volcanism characteristic for the ocean-floor setting.

Characterization of hydrothermal circulations in faultzones by phyllosilicates mineralogical analysis (Argentera-Mercantour massif)

Gaétan Milesi[1], Henri Leclère[1], Delphine Charpentier[1,*], Pierre Trap[1], Léo Lacker[1], Martine Buatier[1], Marguerite Perrey[1], Pierre Lanari[2], Yann Rolland[3]

[1]UMR Chrono-Environnement, Universitéde Bourgogne Francheomté, Besançon, 25030, France
[2]Institute of Geological Sciences, University of Bern, Bern, CH-3012, Switzerland
[3]EDYTEM, Université Savoie Mont Blanc, CNRS, UMR5204,73370 LeBourgetdu-Lac, France

delphine.charpentier@univ-fcomte.fr

Hydrothermal fluid-flow in orogenic belt is currently of great interest for the development of geothermal energy. Crustal-scale fluid-flow is related to deep fault-zones that localize deformation and fluid/rock interactions including mineralogical transformations and precipitations. Phyllosilicates are common minerals found in hydrothermal systems and their study is particularly important because (i their large friction range has direct impact on fault reactivation (Behnsen & Faulkner, 2012), ii) synkinematic phyllosilicate can register the X-T-t conditions of fault-zone activity.

The present study focusses on the Valetta fault-zone (VFZ, located in Argentera-Mercantour massif (French-Italian Alps which is marked by natural hotsprings. The VFZ is a major plurikilometric NW-SE fault-zone with a km-scale offset that was reactivated during Alpine tectonics (Bogdanoff et al., 2000). The VFZ has an anastomosed structure and is composed of fault gauge strands surrounded by phyllonite. Here, sampling was conducted along a transect normal to the fault-zone to determine i) the mineralogical andgeochemical changes and ii) the conditions of fault activity.

The well-defined foliation in the fault-zone is overlined by preferentially oriented inherited and newly formed mica and chlorite. Fault gouge is the onlyzone also composed of low-temperature smectite. The mixture of low and high temperature phyllosilicates in the fault core-zone suggests a polyphase fault activity with newly formed mica and chlorite related to deep fault activity (T>150°C) while newly formed smectite particles is likely related to shallow fault activity with meteoric fluid-flow. Moreover, the transition from white mica to smectite can reduce fault friction leading to fault weakening during the exhumation of the Argentera massif.

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TEM study of the illitization of smectite in ammonium solutions under hydrothermal conditions

M.J. Bentabol[1,*], F.J. Huertas[2], A.E.S. Van Driessche[2]

[1]Departamento de Química Inorgánica, Cristalografíay Mineralogía.University of Málaga. Campus de Teatinos, 29071 Málaga, Spain
[2]Instituto Andaluzde Cienciasdela Tierra(CSIC-UniversityofGranada),18100Armilla, Granada, Spain

*bentabol@csic.es

Smectite was transformed into illite under experimental conditions that correspond to slightly alkaline hydrothermal solutions (100, 150, 200 °C, pH~10.5 enriched in ammonium (0.1 M. The reaction is triggered by ammonium adsorption at the interlayer space in smectite crystals. The smectite-to-illite transformation was characterized by HRTEM and AEM in samples prepared as ultrathin sections and as dried drops of ethanol suspension on Cu grids.

Samples consisted of subparallel crystals with low angle contacts, with thickness in the order of tens to hundred nm that increased with temperature. At 100 °C smectite particles showed lattice fringes of 12.5, 13.5 and 15.0 . Single layers with 10.0 spacing (illite were frequently identified within the smectite domains, and occasionally stacks of regular 10.0 spacing. Disordered illite-smectite (I/S mixed-layers were also observed, as well as small domains of ordered I/S sequences of up to 6 layers. At 150 °C most of the crystals showed regular spacing of 12.2-12.5 , although values of 13.0-15.0 were also common. Illite layers at 10.0 or 10.3 usually appeared intercalated in the smectite crystals as single layers or forming stacks of a few layers (2-4, occasionally associated to along-layer terminations. Domains of I/S were also observed, for example with 10.0-12.5 spacing. Crystalscomposed exclusively of illite layers were rarely observed. The samples obtained at 200 °C contained particles thicker than those produced at lower temperature, reaching more than 100 nm, frequently composed of planar crystals with 20-40 smectite layers exhibiting regular spacing, usually 12.0-12.5 . Occasionally 10.0 layers were included within the smectite crystals. Illite was more common at 200 °C than at lower temperatures, exhibiting planar morphology and lattice fringes at 10.0-10.5 . Reaction fronts of smectite-to-illite were identified in some crystals as along-layer transformation from ~12.5 to 10.0 .

The chemical composition of stacks of curved particles was similar to that of natural smectite (montmorillonite, with Si contents in the range 3.78 to 3.96 apfu, being the main difference the presence of NH_4^+. The analyses of thin particles showed lower Si (3.50-3.70 apfu and higher Al^{IV}(>0.30 contents, as well as a higher number of interlayer cations, consistent with illitic layers.

NH_4^+adsorption on smectite induced layer by layer transformation into illite. Simultaneously smectite dissolution released Si and Al, allowing precipitation of single illite crystals.

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TS28 Computational Modeling of Clays and Fluid Interfaces

ORAL PRESENTATIONS

From coupling second-order stresses to understanding and predicting the structural response of a dioctahedral smectite

Chadha Mejri*, Walid Oueslati, Abdsslem Ben Haj Amara

University of Carthage, Faculty of Sciences of Bizerte, LR19ES20: Resources, Materials and Ecosystems (RME), 7021 Bizerte, Tunisia

*chadha.mejri@fsb.ucar.tn

The use of nonporous clay media in the in water, nutrient, and contaminant storage and transport depends on several parameters such as ion exchange efficiency, ion exchange reversibility, hydration behaviour, permeability and more... The decoding of the structural response, of the dioctahedral smectites (Wyoming montmorillonite, SWy-2) used in this context, to the applying external constraints is poorly developed (Oueslati et al., 2012; Chalghaf et al., 2013). The swelling and collapse of clay particles process, the water retention mechanism, the hydration heterogeneities created within crystallite and the Interlamellar space organization remains weakly understood through applying external stress. This work aims at characterizing the link between geochemical, thermal, and kinetic constraints (created at the laboratory scale) and intrinsic properties of Na-rich montmorillonite (Na-SWy-2), exchanged respectively with Ni^{2+}, Mg^{2+} and Zn^{2+} cation. To assess the clay mineral structural response, quantitative XRD analysis and porosity measurements are used. The quantitative XRD analysis, which consists of comparing the experimental 00ℓ reflections with the calculated reflections deduced from the structural models, makes it possible to rebuild theoretical model describing the layer stacking mode and to describe interlayer space IS configuration along the c* axis. The XRD modeling shows, regardless the exchangeable cation nature, that all samples have a heterogeneous hydration behaviour within the crystallite size, indicating probably an incomplete or partial saturation of the IS. Theoretically, this result is traduced by the coexistence of four hydration states (0W, 1W, 2W and 3W), unrelatedly to the strain strength which means an increase in the structure heterogeneities degree. The theoretical decomposition of the experimental XRD profiles allowed us to identify all the different existing layers populations and their stacking mode. Also, an obvious dominance for the segregated and the random stacking modes as a function of stress strength is detected.

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Molecular dynamics simulations of the interaction of model petroleum compounds with clay mineral surfaces

Stanislav R. Stoyanov*, Jonathan Y. Manne

Natural Resources Canada, CanmetENERGY Devon, 1 Oil Patch Drive, Devon, Alberta T9G 1A8 Canada

*stanislav.stoyanov@nrcan-rncan.gc.ca

Petroleum recovery from oil sands and shale rock deposits, and challenges posed to oil spill responders by the increased transportation of heavy petroleum involve complex petroleum-sediments interactions. Starting with model compounds and a clay mineral surface helps address this complexity. We employ molecular dynamics (MD) simulations to study i) the interactions of model asphaltene molecules with kaolinite in the conditions of oil spills on water and ii) the behaviour of octane in rock nanopores under tight oil recovery conditions.

In the first study, MD and umbrella sampling simulations have been employed to explore the adhesion of interfacially active and non-interfacially active asphaltenes on kaolinite surfaces and self-assembly in water, toluene and water-toluene mixtures. The study examines the effects of asphaltene model compounds and their interfacial properties on intermolecular and molecule-surface interactions. The free energies of intermolecular and molecule-surface interactions are calculated from the potentials of mean force. The computational results highlight the competitive interfacial interactions in a scenario representative of asphaltene-rich diluted bitumen spills in the presence of water and clay minerals (Mane & Stoyanov, 2022).

In the second study, the MD simulations of nanopores of kaolinite, illite and quartz (representing shale rock), containing *n*-octane (a representative hydrocarbon) are conducted at 20-120°C and 1-300 bar. The MD trajectories provide insights into the interactions occurring in bulk hydrocarbons and with nanopore walls at conditions representative of tight oil recovery. The density profiles within the nanopores show the temperature and pressure (T&P) effects on hydrocarbon organization. The hydrocarbon-rock interaction parameters calculated for several thermo-dynamic conditions can be used to address broad T&P ranges (Zeng et al., 2019).

The MD simulations enable the calculation of important thermodynamic and structural properties of model petroleum compounds near clay interfaces in aqueous and hydrocarbon solutions. These findings contribute to the development of mechanistic insights into the behavior of petroleum and its components that are key not only to improving hydrocarbon recovery from tight formations but also to evaluating the environmental impact of oil spills.

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Determination of layer charge density by alkylammonium ions: A combined experimental and theoretical assessment of the method

Bruno Lanson[1,*], Pierre Mignon[2], Mélusine Velde[1,3,4], Andreas Bauer[3], Martine Lanson[1], Nathaniel Findling[1], Carlos Perez del Valle[5]

[1]Univ. Grenoble Alpes, CNRS, ISTerre, F-38000, Grenoble, France
[2]Univ. Lyon, CNRS, Institut Lumire Matire, F-69622, Villeurbanne, France
[3]Friedrich-Schiller-Univ., Institute of Geosciences, D-07749, Jena, Germany
[4]Department of Biological Sciences, University of Chicago, USA
[5]Univ. Grenoble Alpes, CNRS, DCM, F-38000 Grenoble, France

*bruno.lanson@univ-grenoble-alpes.fr

Layer charge deficit is a key crystal-chemical parameter for the classification and nomenclature of 2:1 phyllosilicates that also controls some of their fundamental properties such as cation exchange capacity, expandability, water content, or rheology. Significant efforts were thus devoted to determine this parameter either from smectite/vermiculite chemical composition (the structural formula method) or experimentally using the alkylammonium method, that theoretically allows the determination of the mean layer charge density and of its distribution. Comparison of atomistic simulations with X-ray diffraction data supported the robustness of the experimental approach, allowed describing the organization of interlayer alkylammonium cations, and provided insights into the molecular-level interactions responsible for the changes in layer-to-layer distances as a function of interlayer alkyl chain length.

In the present study density functional theory (DFT) and classical molecular dynamics (MD) simulations are compared to experimental X-ray diffraction data for a series of synthetic saponites with layer charge ranging from medium-charge smectite to medium-charge vermiculite. Consistency of computed and measured layer-to-layer distances confirms the ability of computational approaches to accurately predict the organization of alkylammonium cations in smectite interlayers. Thermalization of DFT-optimized structure models through MD simulations allows probing possible alternative interlayer configurations allowed by thermal expansion, such as the electrostatically-favored location of ammonium heads above/below Al-substituted tetrahedra. X-ray diffraction results showed that layer-to-layer distances intermediate between those corresponding to the stable interlayer configurations described initially (h1, h2, etc) result from the interstratification of these stable configurations although similar distances may be computed for a single interlayer configuration.

The overall consistency of computational and experimental results confirms further the ability of the alkylammonium method to accurately determine a mean value of layer charge density consistent with smectite structural formula when using the revised equations proposed by Laird et al. (1989). The validity of the method appears however limited to smectite-group minerals [layer charge density ranging from ~0.5 to ≤1.2 per $O_{20}(OH)_4$] most likely owing to the coexistence of both stable "layered" and paraffin-like interlayer configurations for higher values of layer charge. In addition, this consistency challenges the ability of the method to quantitatively describe distributions of layer charge in expandable phyllosilicates even when using the complete series of alkylammonium cations thus promoting the use of a reduced number of alkyl chain lengths.

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Pore size effects on noble gas uptake in naturally occurring zeolites

Jeffery A. Greathouse*, Matthew Paul, Guangping Xu, Todd R. Zeitler

Sandia National Laboratories, Albuquerque NM 87123, USA

*jagreat@sandia.gov

Hindered transport of weakly interacting gases through geomaterials with nanosized pores and cages such as zeolites is controlled primarily by size effects. Gas adsorption and diffusion can be significantly hindered or blocked when the pores and interpore cages of zeolites are similar in size to the gas diameter. Anomalous trends in reported field studies of gas migration in zeolite-bearing rock could be a result of gas-rock interactions. Fundamental studies of these size-based interactions will inform experimental and field results on mixed rock phases, particularly when anomalous gas transport behavior is seen.

Results will be presented from molecular dynamics simulations of noble gas uptake in two naturally occurring zeolites (clinoptilolite and mordenite) representative of a variety of geologic environments. The simulation model consists of a gas phase in contact with a nanosized zeolite slab with exposed faces corresponding to the primary diffusion path for each zeolite. The different zeolite cage sizes and noble gas diameters, along with varying water content, allow size effects to be systematically investigated. A fully flexible zeolite model is applied, which is critical to accurately model gas transport through cages and windows of similar size. Characteristic loading times and gas diffusion coefficients are obtained by applying a kinetic model to the simulations results with varying temperature and slab thickness. Accompanying experiments measure the time evolution of gas uptake in the same zeolites. Laboratory results confirm that the kinetics of gas uptake shows a critical dependence on zeolite morphology.

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Stabilization and organization of water in clay nanotubes

Arianna D'Angelo[1,2,*], Stéphane Rols[2], Erwan Paineau[1], Stéphan Rouzière[1], Viviana Cristiglio[2], Pascale Launois[1]

[1]Laboratoire de Physique des Solides, CNRS-Université Paris Saclay, Orsay, France
[2]Institut Laue-Langevin,Grenoble, France

*arianna.dangelo@universite-paris-saclay.fr

Imogolite nanotubes (INT) with stoichiometry $(OH)_3Al_2O_3Si(OH)$ are peculiar clay nanomaterials formed o-farolled gibbsite sheet with isolated $SiO_3(OH)$ units inside (Paineau, 2019). They can be synthesized by soft chemistry and Si atoms (Si-INT) can be replaced by Ge ones (Ge-INTs). The inner diameters of these hydrophilic nanotubes are trulynanometric (1.5 nm for Si-INT, 3 nm for Ge-INT). Surface properties t-hus prevail and INTs are model systems to study the role of interfaces on water properties. Recent investigations on Ge-INTs (Monet,2020) highlighted the stabilization of an original wetting-layer with local triangular symmetry, solid-like up to 300K.

Here, we investigate water under increased confinement within the smaller diameter Si-INTs. Our study is based on synchrotron and in-situ X-rayscattering (XRS) and on neutron diffraction experiments, combined with- Molecular Dynamics (MD) simulations using an interaction potential proposed recently (Scalfi, 2018). The complementarity between the experimental approaches and the decisive contribution of MD simulations will be underlined. A 1D periodic structuration of nanoconfined water is evidenced by MD (Fig. (a)) and XRS (Fig. (b)). Molecules in the wetting layer are the most ordered but interestingly, periodicity remains towards the center of the tube. Finally, detailed comparison between MD results and X-rayandneutron- datapoints toward astonishingly long equilibration times for nanotube filling by water as well as for waterordering inside.

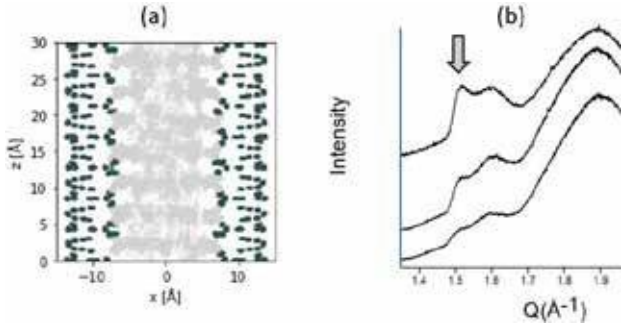


Figure. (a) Slice of a Si-INT full of water, from MD simulations; z axis: nanotube long axis, back dots: nanotube atoms, grey ones: water inside; (b) Wide angle XRS diagrams of INTs (synchrotron SOLEIL) for increasing amount of water inside (dry nanotube: upper curve, most hydrated one: lower curve). The arrow points toward the 002 peak and its intensity variation highlights the periodic arrangement of water molecules along the nanotube axis.

Monet, G., Paineau, E., Chai, Z., Amara, M., Orecchini, A., Jimenéz-Ruiz, M., Ruiz-Caridad, A., Fine, L., Rouzière, S., Liu, L., Teobaldi, G., Rols, S., Launois, P. (2020), Solid wetting layer in inorganicnanoreactors: thewaterin imogolite nanotube case, *Nanoscale Advances,* 2, 1869-1877.

Paineauand P. Launois (2019) Nanomaterials from Imogolite: Structure, Propertiesand Functional Applications, Elsevier; pp 257-284.

Scalfi, L., Faux, G., Boutin, A., Coudert, F. (2018), Structure and dynamics of water confined in imogolite nanotubes, *Langmuir,* 34, 6748−6756.

Classical atomistic simulations of the 10Å phase at high temperatures and pressures

Evgeny Tararushkin[1], Andrey G. Kalinichev[1,2,*]

[1]HSE University, International laboratory for supercomputer atomistic modelling and multi-scaleanalysis, Moscow 123458, Russia

[2]Laboratoire SUBATECH (UMR 6457 - IMT-Atlantique, Universit de Nantes, CNRS), 44307 Nantes,France

*kalinich@subatech.in2p3.fr

The 10Å phase, $Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O$, is an important member of the family of dense hydrous magnesian silicates playing a major role in the transport and balance of water in the Earth's upper mantle. A ideal model of the 10Å phase has already been successfully investigated by classical atomistic simulations (Wang, 2004). However, more recent experiments show that tetrahedral silicate layers of the real 10Å phase may contain a certain amount of hydrogarnet-type structural defects (Welch, 2006), which would affect its properties, especially at high temperatures and pressures. Here we are using the most recent modification of the ClayFF force field (Cygan, 2021), which can now more accurately account for the bending of Mg-O-H angles in the mineral layers and Si-O-H angles of the hydrogarnet-type defects in atomistic simulations. The pressure and temperature dependencies of the 10Å phase properties are calculated in a series of molecular dynamics simulations and compared with experimental data.

Acknowledgement: The research was conducted within the framework of the HSE University Basic Research Program.

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Interactions between hydrophobic organic compounds and clay minerals - effect of clay surface charge

Peter Grančič[1,*], Leonard Böhm[2], Martin H. Gerzabek[1], Daniel Tunega[1]

[1]University of Natural Resources and Life Sciences, Institute of Soil Research, Vienna, Austria
[2]Justus Liebig University Giessen, Institute of Soil Science and Soil Conservation, Giessen, Germany

peter.grancic@boku.ac.at

Risk assessment and management of soils and sediments is inevitably connected to the biological availability and accessibility of contained pollutants. Particularly, our understanding of the sorption and desorption processes of hydrophobic organic compounds (HOCs) in the environment is of vital importance. However, mechanisms of sorption and desorption processes of hydrophobic organic compounds (HOCs) at reactive mineral surfaces are still not very well understood. In the present work, interactions between HOCs (represented by hexachlorobenzene) and smectite clay minerals (represented by set of models of montmorillonite clay with varying number of isomorphic substitutions and, thus, varying excess layer charge) are investigated by series of density functional theory calculations including both explicit and implicit solvent models. Based on the calculated electron densities, conclusions are drawn revealing the nature of their mutual interactions, the related stability of such complexes, as well as possible molecular arrangements. A number of the calculated properties are correlated with experimental findings from adsorption experiments. These systematic studies aim to contribute to a better mechanistic understanding of the interactions of hydrophobic organic compounds and clay surfaces. The combination of molecular modeling methods and laboratory adsorption experiments are conducted within the framework of the bilateral project “ClayHOC”.

Stabilization and organization of water in clay nanotubes

Arianna D'Angelo[1,2,*], Stéphane Rols[2], Erwan Paineau[1], Stéphan Rouzière[1], Viviana Cristiglio[2], Pascale Launois[1]

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[2]Institut Laue-Langevin, Grenoble, France

*arianna.dangelo@universite-paris-saclay.fr

Imogolite nanotubes (INT) with stoichiometry $(OH)_3Al_2O_3Si(OH)$ are peculiar clay nanomaterials formed of a rolled gibbsite sheet with isolated $SiO_3(OH)$ units inside (Paineau, 2019). They can be synthesized by soft chemistry and Si atoms (Si-INT) can be replaced by Ge ones (Ge-INTs). The inner diameters of these hydrophilic nanotubes are truly nanometric (1.5 nm for Si-INT, 3 nm for Ge-INT). Surface properties thus prevail and INTs are model systems to study the role of interfaces on water properties. Recent investigations on Ge-INTs (Monet, 2020) highlighted the stabilization of an original wetting-layer with local triangular symmetry, solid-like up to 300K.

Here, we investigate water under increased confinement within the smaller diameter Si-INTs. Our study is based on synchrotron and in-situ X-ray scattering (XRS) and on neutron diffraction experiments, combined with Molecular Dynamics (MD) simulations using an interaction potential proposed recently (Scalfi, 2018). The complementarity between the experimental approaches and the decisive contribution of MD simulations will be underlined. A 1D periodic structuration of nanoconfined water is evidenced by MD (Fig. (a)) and XRS (Fig. (b)). Molecules in the wetting layer are the most ordered but interestingly, periodicity remains towards the center of the tube. Finally, detailed comparison between MD results and X-ray and neutron data points toward astonishingly long equilibration times for nanotube filling by water as well as for water ordering inside.

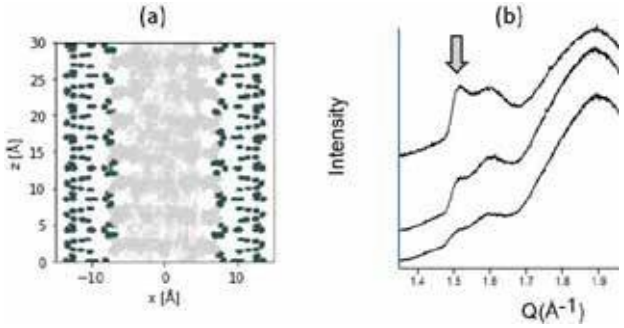


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Scalfi, L., Faux, G., Boutin, A., Coudert, F. (2018), Structure and dynamics of water confined in imogolite nanotubes, *Langmuir,* 34, 6748−6756.

TS28 Computational Modeling of Clays and Fluid Interfaces

POSTER PRESENTATIONS

Simple lattice model of alkali cation adsorption from an aqueous solution on the basal surface of muscovite

Olga Solovyeva*, Vitaly Gorbunov, Alexander Myshlyavtsev

Omsk State Technical University, Department of Chemistry and Chemical Engineering, 644050 RussianFederation

*iolgasergeevna@yandex.ru

Adsorption of metal cations on clays and clay minerals plays a central role in the radioactive waste disposal and removal of heavy metals, wastewater treatment, agriculture, and others. Adsorption capacity of the adsorbents for metal cations is determined by its structure and chemical composition, as well as the composition of the solvent. Muscovite is a typical aluminosilicate mineral consisting of alternating tetrahedral and octahedral layers. On the basal (001) surface of muscovite, some silicon atoms are replaced by aluminum atoms in tetrahedral layers. This induces hydrophilic properties of the surface and makes the material interesting as natural adsorbent for different substances.

In this work, we study alkali cations adsorption from an aqueous solution on the muscovite (001) surface with a regular arrangement of tetrahedral aluminum atoms. A simple lattice model was created based on literature data. To simplify the model, we assumed that metal cations are usually in a hydrated state. Therefore, the model does not explicitly account for the «water-cation» interactions GROMACS (Van Der Spoel, 2005) software package was used for the parametrization of our model. Using umbrella sampling technique, we have calculated the PMF for the «cation-cation» () interaction in aqueous solution and interaction between the adsorbing cation and two types of adsorption sites on the basal plane of muscovite. Relying on the principle of a minimum of the grand thermodynamic potential in the equilibrium state of an open system we analyze the ground state (T= 0K) of the system. Phase behavior at non-zero temperatures was studied with the Grand Canonical Monte Carlo simulation as implemented in the SuSMoST toolkit (Akimenko, 2020). It reveals a rich phase behavior of the adsorption monolayer of alkali cations on the (001) muscovite surface when is weaker than. In this case, we have observed 7 ordered phases at the temperatures RT/|| below 2.07. If these interactions are commensurate or is stronger, the phase diversity is lost.

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Molecular dynamics simulations of hydrogen gas adsorption and transport in hydrated montmorillonite

Sylvia M. Mutisya, Pinar Citli*, Andrey G. Kalinichev

Laboratoire SUBATECH (UMR 6457 - IMT-Atlantique, Universit de Nantes, CNRS), 44307 Nantes, France

*pinar.citli@imt-atlantique.fr

Callovo-Oxfordian (COx) clay formation was selected as the host rock for the radioactive waste repository facility in France. It contains 25-55% of clay minerals (illite, smectite, interstratified illite/ smectite, chlorite, and kaolinite). Fundamental understanding of fluid transport processes in clayey materials on many different time- and length- scales are crucial for ensuring the safety geological disposal and storage of radioactive waste. There are several physical and chemical mechanisms leading to H_2 gas formation during the storage of high-level radioactive waste: due to the anoxic corrosion of steel waste containers ($3Fe+4H_2O=Fe_3O_4+4H_2(g)$) or H_2O radiolysis reactions caused by alpha decay. Hydrogen gas accumulation in the repository may cause pressure build-up, resulting in a risk of overpressure and fracture of the surrounding host rocks unless it diffuses, reacts, or gets absorbed by constituent clay materials, which have high sorption capacities due to their high surface areas.

Here we present first results of molecular dynamics computer simulations of such systems by means of classical molecular dynamics and Monte Carlo simulations in order to improve fundamental molecular scale understanding of the physical and chemical processes controlling the interactions between H_2 gas, aqueous solutions, and clay minerals. Montmorillonite was selected as a model smectite clay. The molecular mechanisms of H_2 gas adsorption, retention, and diffusional transport in porous clay media are evaluated with a special focus on the effects of local compositional and structural heterogeneity of montmorillonite. The qualitatively and quantitatively different contributions to the entire picture of the basal and edge surfaces of individual clay nanoparticles are also taken into account.

ClayCode: A tool for automating the setup of atomistic clay models for molecular dynamics simulations with GROMACS

Hannah Pollak*, Valentina Erastova

University of Edinburgh, School of Chemistry, EH9 3JF UK

*h.pollak@sms.ed.ac.uk

Clays minerals are characterised by a great diversity of their properties and applications. Clay-based materials have found applications as barriers for waste disposal, pollution sequestration agents, pharmaceutical excipients; while their presence in the environment determines soil properties, fertility and accumulation of contaminants. The slightest perturbations in the clay structure may lead to large-scale effects on their performance.

Molecular modelling is a powerful technique that allows one to examine with an atomic-level resolution the effect of structures on physicochemical properties. However, models used in molecular dynamics sim- ulations often oversimplify the clay structure, sacrificing the accuracy and representability of computa- tional predictions. The bottleneck is not in the limitations of the computational resources or methodology itself, but rather in the lack of user-friendly tools to prepare representative clay model systems. We present ClayCode, a tool for the generation of clay systems according to user-defined clay stoichiome- try, hydration and ionic composition. ClayCode holds a library of unit-cell building blocks, assigned with ClayFF force filed (Cygan et al., 2004). As an output of ClayCode, a user obtains simulation input files ready to run with the GROMACS engine (Berendsen et al., 1995).

ClayCode is written in Python, and its modularity allows for the ease of its development by the computational community. Through our work, we hope to facilitate the uptake of molecular modelling routines, and the exciting future of clay research.

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Protolysis reaction on surfaces of phyllosilicates: a density functional theory study

M. J. Bentabol[1,*], C. Pérezdel Valle[2], A. E. Svan Driessche[3], A. Hernández-Laguna[3], F.J. Huertas[3]

[1]Universidadde Mlaga, Departamentode Qumica Inorgnica, Cristalografay Mineraloga, 29071 Mlaga, Spain.
[2]Universit of Grenoble Alpes, DCM, F-38058 Grenoble, France
[3]Instituto Andaluzde Cienciasdela Tierra (CSIC-University of Granada),18100 Armilla, Granada, Spain

*bentabol@uma.es

Phyllosilicates are one of the most abundant minerals of the Earth's crust. These minerals interact with interstitial fluids, experiencing adsorption, dissolution, and precipitation reactions at the mineral/ solution interface. Therefore, a detailed comprehension of the hydrolysis mechanisms of phyllosilicates is of upmost importance.

The aim of this study is to further our understanding of the hydrolysis reaction of (010) surfaces of phyllosilicates using density functional theory (DFT) calculations. The hydrolysis mechanism was studied in two different structures, pyrophillite-type and palygorskite-type, using a similar cluster model formed by two tetrahedral cavities with a hexagonal crown of SiO4 units with one octahedral sheet. Gaussian16 was used to perform the calculations. Critical Points of Potential Energy Surface of the hydrolysis reaction models were calculated at the B3LYP/lanl2dz level.

The results of this study showed no hydrolysis mechanism but instead a protolysis mechanism was observed in the (010) surface model. In the pyrophyllite case, the H_3O^+ cation attacked one of the bridging Al- O-Si sites. Two stable protonated structures were found. A second H_3O^+ attacked another bridging site and disrupted it. On these attacks, when the H_3O^+ is in the surrounding of the (010) surface, no transition state (TS) was found for leading to stable structures. For the palygorskite-type cluster model similar results were obtained, but a TS was found in this procedure. In addition, the (010) surface appeared to be more reactive than the (001) surface, which was studied in our previous works.

Acknowledgement. Research supported by Grant PID2020-114355GB-I00 funded by MCIN/AEI/ 10.13039/501100011033 and by "ERDF A way of making Europe".

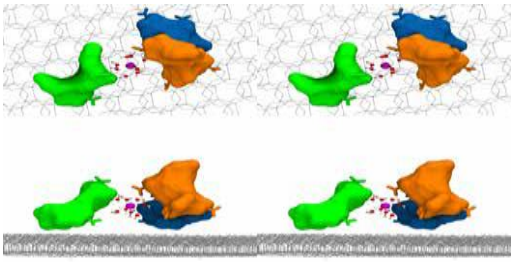
Molecular view at organo-clay interfaces of soil microaggregates

Edgar Galicia-Andrés[1,2,*], Chris Oostenbrink[1], Martin H. Gerzabek[2], Daniel Tunega[2]

[1]University of Natural Resources and Life Sciences, Muthgasse 18, A-1190 Vienna, Austria
[2]University of Natural Resources and Life Sciences, Department of Forest and Soil Sciences, 82, A-1190 Vienna, Austria

*edgar.galicia@boku.ac.at

Soil components are bound by physicochemical and biological processes forming microaggregates. These microaggregates are described as organo-mineral aggregates formed mainly by typical soil minerals such as clays and soil organic matter (SOM). The structure and compositional complexity of such aggregates is linked to soil properties and functions. The use of molecular modeling (MM) is key to understand the protection and resilience mechanisms of SOM against degrading processes at microscopic level.
With the development of the CLAYFF force field (Cygan et al., 2004), the description of structural and physicochemical properties of clay minerals and their interfaces is possible (Vasconcelos et al., 2007; Galicia-Andrs et al., 2019). Moreover, coupling the CLAYFF with the recently developed Vienna soil-organic-matter modeler (VSOMM) to create humic substances (HSs) models (Sndermann et al., 2015; Escalona et al., 2021) information on the chemical structure and three-dimensional conformation is scarce. Here we describe the Vienna Soil-Organic-Matter Modeler, which is an online tool to generate condensed phase computer models of humic substances (http://somm.boku.ac.at promises to generate representativemodels of soil microaggregates (Galicia-Andrs et al., 2021a). Our MM results show that HSs adsorb strongly to clay minerals surfaces. The adsorption is driven by the polar environment stabilizing organic matter at surfaces mainly by electrostatic interactions and hydrogen bonds. Furthermore, adsorption leads to HSs dispersion over the surface forming the so-called electric double layer (EDL). In the non-dispersed form, patches of HSs are held together through cation-bridges (CaBs) (Galicia-Andrs et al., 2021b). Therefore, the amount of HSs adsorbed depends on the competition between the EDL and CaBs. These new findings promise to explain phenomena of interest such as carbon sequestration as well as the fate of pollutants and nutrients in soils.



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Molecular modelling of interactions of beryllium hydroxide species with calcium-silicate-hydrate phases

Iuliia Androniuk*, **Nese Çevirim-Papaioannou, Xavier Gaona, Marcus Altmaier**

Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

*iuliia.androniuk@kit.edu

Beryllium is a unique metal with effective neutron mediation and reflection properties. It is used in the design of technologies to be applied under challenging conditions, including nuclear fission and fusion reactors (Beeston, 1970). The beryllium-containing components require to be regularly replaced and disposed of (Longhurst et al., 2011) and, therefore, Be is expected to occur in specific nuclear waste streams which have to be disposed in repositories. In this work, interaction of beryllium with cementitious materials is addressed, as cement is one of the important materials used in the design and construction of waste repositories, especially for low and intermediate level wastes (L/ILW). Calcium silicate hydrate phases are one of the main binding phases of the cement responsible for the sorption of both cationic and anionic species, and they are in the focus of this study. We used classical molecular dynamics (MD) simulations and the potential of mean force (PMF) calculations to obtain mechanistic understanding of the uptake process for Be species. The simulations were performed on systems constituted of (001), (004), and (100) C-S-H surfaces, and the C-S-H interlayer in contact with aqueous solutions containing the ions of interest. Calculations were conducted using ClayFF force field parameters (Cygan et al., 2004) for C-S-H, and the SPC water model and parameters for Ca^{2+} and Be^{2+} as proposed in Li et al. (2020). Beryllium speciation in alkaline solutions as reported in Çevirim-Papaioannou et al. (2020) was considered in the calculations, which are complementary to the sorption experiments performed in Çevirim-Papaioannou et al. (2021). The common sorption sites and surface complexes were identified. The results indicate that Be(II) mainly sorbs on C-S-H through binding via hydroxo groups to surface Ca^{2+}, while the PMF calculations revealed the most favorable binding with multiple Ca^{2+} sites at the surface. Be(II) immobilization in the C-S-H interlayer has been additionally assessed in this work.

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TS30 Clays for Ceramics

ORAL PRESENTATIONS

Deposits of kaolinitic clays in Europe and the Mediterranean: situation and outlook

Michele Dondi[1,*], **Gian Paolo Bertolotti**[2]

[1]CNR-ISTEC, Faenza, Italy
[2]Ceramin Consulting, Italy

*michele.dondi@istec.cnr.it

The strategies that are being developed to face the social, environmental, and economic challenges of sustainable industrial production are based on some pillars. In the sectors of cementitious binders, concrete and ceramics, they are mainly represented by circular economy and resource efficiency, along with the decarbonization of manufacturing and the supply chain. These strategies – such as waste recycling and the use of local raw materials – leverage the availability of strategic resources that act as enablers, because they allow the introduction of new technologies and the use of waste and raw materials with unsatisfactory technological properties. Kaolinitic clays represent an emblematic case of strategic raw materials: they are indispensable for ceramics and cementitious binders but cannot be replaced by waste or synthetic analogues. It is therefore essential to know the available resources and prospect of kaolinitic clays, taking into account the transformations taking place in the production of building materials. This is to direct both the exploration of new clay deposits and the search for technological solutions that take into due account the characteristics of the available raw materials. For this purpose, a survey of the main kaolinitic clay deposits in European and Mediterranean countries was carried out. The type of deposits, the situation of the mining activity, and the amount of reserves are presented and discussed. On the other hand, the demand in the next years is estimated by considering various applications, in particular the ceramic and cement sectors. There is a need to relaunch mineral prospecting for new clay deposits and direct R&D activities to improve resource efficiency. A pathway towards the full exploitation of clay deposits, seeking new technological solutions to overcome existing problems (e.g., coarse grain size, excessive alumina and iron oxide content) is envisaged.

Utilisation of industrial/constructional waste materials for fired clay brick production: A step towards sustainable economy

Sen Wang[1, 2, 5,*], Lloyd Gainey[3], Ziyang Wu[6], Ian D. R. Mackinnon[2, 4], Yunfei Xi[1, 2, 5]

[1]Central Analytical Research Facility (CARF), Queensland University of Technology (QUT), Brisbane, Queensland 4001, Australia

[2]Centre for Clean Energy Technologies and Practices & Centre for Materials Science, Queensland University of Technology (QUT), Brisbane, Queensland 4001, Australia

[3]Austral Bricks, Rochedale, Queensland 4123, Australia

[4]School of Earth and Atmospheric Sciences, Faculty of Science, Queensland University of Technology (QUT), Brisbane, Queensland 4001, Australia

[5]School of Chemistry and Physics, Faculty of Science, Queensland University of Technology (QUT), Brisbane, Queensland 4001, Australia

[6]School of Mechanical, Medical and Process Engineering, Queensland University of Technology (QUT), Brisbane, Queensland 4001, Australia

*s211.wang@hdr.qut.edu.au

The production of ceramic clay bricks from industrial, agricultural or constructional wastes, either as raw materials or additives, has received increased interest in the last few decades. A wide variety of waste materials has been studied, including wood sawdust, fly ash, volcanic ash, mine tailings, wastewater sludge, construction and demolition (C&D) waste *etc.* (Al-Fakih et al., 2019). Sustainable substitutions of clay matrix with waste materials can benefit the 3R (reuse, reduce and recycling) system and lead to the enhanced technical performance of finished brick products (Cultrone *et al.*, 2020). More importantly, cultivated land and our environment can be effectively protected by minimising overuse of soil clays.

In this work, two typical industrial/constructional wastes – residual glaze slurry from brick production and plasterboard sheet waste, were evaluated as potential additives for fired clay brick manufacturing. The effects of waste additions on thermal behaviours of clay matrix during the drying and firing processes have been analysed through integrated *in-situ* techniques, and correlations between thermal behaviours and microstructures, phase compositions, physical, mechanical and thermal properties of obtained bricks. Furthermore, an environmental assessment was conducted using toxicity characteristics leaching procedure (TCLP) to predict the leaching behaviour of fired bricks with different waste materials. This study shows the feasibility of incorporating residual glaze slurry and plasterboard sheet in fired clay brick production, which can help to reduce topsoil exploitation while achieving a circular economy by bringing wastes back into the anthropogenic material cycle.

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Firing behaviour of Westerwald ball clay mixed with α-alumina filler and K_2CO_3 flux

Aydın Aras

Van Yuzuncu Yil University, Engineering Faculty, Geological Engineering Department65080 Van / Turkey

aras5549@yahoo.com

The effect of K_2CO_3 on mullite-cristobalite formation and physical properties of ceramic bodies derived from Westerwald ball clay (WBC) and α-alumina mixtures activated by high energy ball milling (HEB) has been investigated. Additionally, the elastic modulus (E) of the ceramic bodies was evaluated by the resonance frequency method using a Grindosonic instrument. The α alumina was added with regular increment in the range 20-40-60 % while 5 % K_2CO_3 stay constant to non-activated and activated bodies by high energy ball (HEB) milling. From the X ray intensities and SEM data, the amount of mullite, cristobalite and α alumina at 1200°C and 1400°C could be evaluated. It was found that the effect 5 % K_2CO_3 on mullite-cristobalite formations and dissolution α-alumina depends on concentration degree of and its diffusion rate of soluble K_2CO_3, which themselves are largely determined by the wet mixing or 0.5h, 4h and 8h HEB milling time. The introduction of 20 % alumina together with 5 % K_2CO_3 to HB ball clay caused maximum secondary mullite formation in 0.5h activated bodies. A further increase in the amount of alumina from 20 % to 40 and 60 and milling time from 0.5h to 4h and 8h was accompanied by decreasing of the amount of mullite and disappearing mullite respectively. The X-ray powder diffraction analysis (XRD) together with scanning electron microscopy (SEM-EDS) revealed the microstructure consist of two types of secondary mullite; one variety with very high aspect ratio (3–5 µm /1 µm) and the second one of with lower aspect ratio (1-2 µm/100-200 nm). They all derived from polymorphic transformation of spinel in the presence of Al-Si rich aluminosilicate glass at 1200-1400°C. According to their E-modulus measurements, it was possible to divide the bodies into 3 groups; the highest E (125 GPa) was measured from a wet-mixed 60 % α-alumina and 5 % K_2CO_3 body. On the other hand, the most abundant mullite formation is observed in the K_2CO_3-free and 0.5, 4, 8h ground bodies. Although in grounded and K_2CO_3 added bodies, the formation of mullite and cristobalite was decreased and totally inhibited in clay and alumina rich bodies respectively and HEB milling has strong effect in producing agglomeration of the used alumina powders and increased closed porosities and caused to E to fall in these bodies.

Sintering behaviour of α-alumina containing low amounts of kaolinite andauxiliary molecules

Rana Al-Tahan[1*], Cécile Pagnoux[1], Nicolas Tessier-Doyen[1], Gilles Gasgnier[2]

[1]IRCER, European Ceramics Center, University of Limoges, 12 Rue Atlantis 87068 Limoges, France
[2]Imerys Tableware France, 1 rue Jeanne d'Albret, 87700 Aixe-sur-Vienne

*rana.al-tahan@unilim.fr

Within the framework of the development of ceramic materials based on mixed alumina/mullitecompositions, kaolinite appears to be a suitable raw material to consider in the formulation to supply silicon. Natural kaolinite generally crystallizes in the form of pseudo-hexagonal plateletsexhibiting a slight thickness (from 1 µm to 100 nm). They are composed of both stacked layers of SiO_2 tetrahedral sheets and $AlO_2(OH)_4$ octahedral sheets. After a heating treatment up to 950°C, mullite phase occurs.

This research work consists in the elaboration of multilayer materials by alternating pure alumina and mullite-alumina layers shaped by uni-axial pressing. At high temperatures, the competing mechanisms of sintering and mullite growth control the densification of the aluminamatrix. The presence of acicular mullite crystals in the densified matrix and interfaces betweenthe layers contributes to improve the mechanical properties particularly fracture toughness. Forthis purpose, different compositions of a mixed system based on alumina and kaolinite were prepared varying from 0 to 10%vol the kaolinite content. Two kaolin powders exhibiting a different state of crystallinity were added so as specific molecules (Tiron/Citrate) required to properly disperse both Alumina and kaolinite.

The effect of kaolinite proportion, crystallinity, and the nature of dispersant was then studied on the sintering behaviour of alumina through extensive dilatometric and DTA/GTA analyses (differential and thermogravimetric thermal analysis). It has been highlighted that Kaolinite andspecific molecule addition leads to a significant modification of the sintering kinetic of the alumina matrix. Secondly, mechanical properties were studied as a function of kaolinite additions and mullite crystallization.

Composition and ceramic properties of Santa Maria clays (Azores, Portugal)

Fernando Rocha[1,*], **Cristiana Costa**[2]

[1]GeoBioTec, Department of Geosciences, Aveiro University, 3810-193 Aveiro, Portugal
[2]Technological Center for Ceramics and Glass, 3025-307 Coimbra, Portugal

*tavares.rocha@ua.pt

There are evidences and records concerning clay exploitation for pottery in the island of Santa Maria (Azores, Portugal) in the past. Nowadays this activity is almost extinct, but this is the only island in the archipelago with abundant residual and sedimentary clay deposits. To evaluate the applicability of clays from this island for modern ceramics, a campaign made in May 2017 allowed collecting twenty samples in several outcrops all over the island. All samples were subsequently analyzed in terms of granulometry, mineralogy, chemical composition and ceramic properties.

First studies (Cerqueira et al., 2019), focused on mineralogy (XRD), chemistry (XRF), granulometry, plasticity and viscosity, gave very positive results since most part of samples are rich on phyllosilicates (69% to 98%, being kaolinite the most common), being fine-grained, and showing adequate plasticity and viscosity. Geological formations showing good potentialities for ceramics outcrops on a large part of the island, therefore assuring the existence of good reserves.

For the present work three samples were selected, taking into account they present the best characteristics in terms of mineralogical composition, Al_2O_3/SiO_2 ratio, Fe_2O_3 content and LOI. They were blended into 2 formulations for red ceramics, with different proportions of quartz, phyllosilicates, feldspars and Fe-oxides and hydroxides. EUROATOM blend was used as standard. Specific Surface Area, Apparent density and Plastic Index were assessed. Low grade / low cost Portuguese Kaolin and Ball Clay were incorporated, on different amounts (0 to 20 %), on studied blends, as additives.

Ceramic properties such as Linear shrinkage and Water absorption were assessed and Dilatometry was also performed to compute Expansion coefficient. SEM micrographs were useful to analyse the increment of vitreous phase with Temperature.

Santa Maria clays show good clay minerals composition but lacking quartz and feldspars. Mixed alone they show some improvements but still not accomplish some specifications, with high water absorption and Linear shrinkage (14% and 9%, respectively). Additives solved main deficiencies on quartz and feldspars, also improving plasticity and thermic properties; addition of Kaolin (refractory, improving Linear Shrinkage) and Feldspar (fluxing agent, favouring lower porosity) to the blends improved gresification. Expansion coefficient is practically similar to EUROATOM. Compared to commercial EUROATOM, the tested floor red body showed optimum results in terms of Water absorption, Density and Linear shrinkage.

Cerqueira, A., Sequeira, C., Terroso, D., Moutinho, S., Costa, C., & Rocha F. (2019) Santa Maria clays as ceramic raw materials. In S. Glagolev (Ed.), ICAM 2019 (pp. 311–312). SPEES. https://doi.org/10.1007/978-3-030-22974-0_74

Mineralogical and technological properties of the Eskişehir dolomite-bearing sepiolite (Turkey), and its usage possibilities ceramic tile manufacturing

Kağan Kayacı[1,*], Ş. Can Genç[1,2], Yıldız Yıldırım[1]

[1]Kaleseramik Research & Development Center, Çanakkale, Turkey
[2]İstanbul Technical University, Dept. of Geological Engineering, Maslak-İstanbul, Turkey

*kagankayaci@kale.com.tr

The Eskişehir sepiolite deposited in the Oligo-Miocene lacustrine basin which is constructed on a composite basement consisting of the ultramafic (ophiolitic) rocks, recrystallized limestone/dolomite and alkaline magmatic rocks. X-ray diffraction (XRD) studies revealed the main mineralogical composition is as follows; *sepiolite* ± *palygorskite* ± *dolomite* ± *calcite* ± *montmorillonite* ± *organic materials*. In the sedimentary succession there are different compositionally zones vary from nearly pure sepiolite to the dolomite-bearing sepiolite, sepiolite-bearing dolomite and pure dolomite. Two open pits were systematically sampled and then mineralogical and chemically characterized by XRD and XRF. XRF results indicated that the MgO, SiO_2 and the LOI are the dominant constituents additionally Al_2O_3, Na_2O and K_2O are the subordinates. In order to understand the behaviour and usability of the Eskişehir sepiolitic clays in ceramic tile production new recipes, containing the variable amount of the Eskişehir sepiolite instead of the common ball clays have been formulized. These new body recipes were fired at 1150°C and 60 min in the industrial roller kiln, and then studied in terms of phase analysis. XRD studies showed that the major phases of fired bodies are enstatite (pyroxene), anorthite (Ca-Plagioclase) and ± amorphous (glassy) components. In the light of data obtained from this study we concluded the Eskişehir dolomite-bearing sepiolitic clays have the potential to be used instead of common ball clays in wall tile compositions at a maximum rate of 10%.

Effect of Şile region clay addition on sintering and mechanical behaviour of traditional ceramic bodies

Nermin Demirkol

Kocaeli University, Faculty of Fine Arts, Department of Ceramics, 41300 Turkey

nermin.demirkol@kocaeli.edu.tr

The Şile region is part of the Şile Neogene Basin as described in the geological literature of Turkey. It is a very important plays for sources of clays and quartz used for various industrial fields [1]. In this study, Şile clay was used as a binding material to produce traditional ceramic bodies. Two traditional ceramic recipes (S1 and S2) containing different amount of Şile clay were prepared. They were mixed for 3 hours. Slip casted samples were prepared and they sintered at 900, 950 and 1000ºC.

Green and sintered density, water absorption, firing shrinkage of samples were determined. The present crystalline phases in the sintered samples were identified by XRD. Bending strength and microhardness tests were carried out to determine mechanical properties.

S2 sample sintered at 1000ºC showed the best mechanical and technological properties. Also, glaze studies were carried for S2 sample sintered at 1000 ºC. As a result, the developed S2 traditional ceramic body, which is sintered at 1000°C, besides its mechanical and technological properties, the compatibility of the glaze and body is also very good.

[1] https://icc.aipea.org/wp-content/uploads/sites/3/2021/02/ICC2022-Field-Trip-1-SILE-CLAY-DEPOSITS.pdf. Accessed March 03, 2022.

TS30 Clays for Ceramics

POSTER PRESENTATIONS

Ceramic properties of the argillaceous sediments in the Miocene volcano-sedimentary units of the Cappadocia region, central Anatolia, Turkey

Tacit Külah[1,*], Gürsel Yanık[1], Rasim Ceylantekin[2], Selahattin Kadir[3]

[1]Kütahya Dumlupınar University, Department of Geological Engineering, TR-43100 Turkey
[2]Kütahya Dumlupınar University, Metallurgy and Materials Engineering, TR-43100 Turkey
[3]Eskişehir Osmangazi University, Department of Geological Engineering, TR-26040 Turkey

* tacitkulah@gmail.com

The argillaceous sediments of the Miocene Mustafapaşa member of the Ürgüp Formation have economical clay reserves for ceramic production. The potential use of six representative clayey sediment samples, from different stratigraphic levels, were determined using mineralogical [X-ray diffraction (XRD), Scanning electron microscopy–energy dispersive X-ray analysis (SEM-EDX), differential thermal analysis (DTA-TG), and Fourier transform infrared spectroscopy (FT-IR)], geochemical [X-ray fluorescence spectrometry (XRF)] methods. The thermal and physical tests were also applied. The plasticity, particle- size distributions firing properties (water absorption, apparent porosity, linear shrinkage, fired bending strength), and color parameters of the fired samples were determined. According to the mineralogical and geochemical analyses the samples are composed of mainly smectite associated with kaolinite, minor amounts of illite and chlorite, and non-clay type quartz, feldspar, opal-CT, pyroxene, gypsum, calcite, and goethite/hematite. Smectite and kaolinite were identified by sharp reflections at 14.12–14.90 and 7.14–7.17 Å, 3.57–3.58 Å, respectively. Particle-size analysis of the samples showed that the samples are dominated by the silt fraction. The positive correlation of SiO_2 vs. Na_2O, LOI vs. Al_2O_3, and SiO_2/Al_2O_3 ratio (2.48–3.74) of the samples correspond to the presence of quartz, feldspar, and mica. The negative correlation of Al_2O_3 vs. Fe_2O_3 reflects the presence of iron oxide minerals, which is responsible for the red coloration of the fired pieces. The increasing amount of the high-temperature minerals such as mullite, cristobalite, spinel, and hematite and amorphous phases were identified after firing at 1000, 1100, and 1200°C. The increase of firing temperatures of the samples resulted in a decrease in the porosity and an increase in the fired bending strength values. Micromorphologically, the development of acicular mullite on the amorphous materials and pore-filling of spinel aggregates are indicating the increase of the strength of the fired materials. Mineralogical, chemical analysis, and technological tests show that argillaceous sediments of the Mustafapaşa member of the Ürgüp Formation are suitable for use as additives in brick and tile production.

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Producing glazed porcelain tiles with local clay

Şule Kanca Eryılmaz, Gülay Sarıkaya, Batuhan Cem Makkak*

Yurtbay Seramik, R&D Deparment, 26670 Eskisehir, Turkey

*batuhan.makkak@yurtbay.com

Porcelain tiles are the most common products in ceramic tile industry because of excellent mechanical properties, low water absorption and also superior aesthetic properties. The main raw materials for ceramic tile production are clay, kaolin and feldspar. In ceramic body composition Ukrainian clay mostly preffered raw material due to its low iron content, strong plasticity and also it's whiteness property.

Although, Ukrainian clay provides various technical qualification to the tile body, the transportation procedure is the negative effect on the cost margin. Both variable parity and current conjucture that occurs between Russian and Ukraine government push the industries tocreate new raw material sides.

In this study, Ukrainian clay is replaced with local area clays in ceramic body composition andanalyzed the effects on technical properties. Ceramic bodies without Ukrainian clay are fired ina SACMI industrial roller kilns between 1185-1195^{0}C for 66 minutes. All technical propertiesof the developed bodies were tested. Thermal expansion coefficient is examined by dilatometer, phases and microstructre were examined by X-Ray Diffraction and scanning electron microscopy.

In this search, the main focus area is both efficiency and cost analysis. As a result, the capacityof the mill almost increase %15, the body cost is nearly reduce %15.5.

TS31 Clays and the Molecules of Life

ORAL PRESENTATIONS

The role of iron-rich minerals in the emergence of proto-biomolecules and preservation of biomarkers

Hannah Pollak[1,*], Valentina Erastova[1,2]

[1]University of Edinburgh, School of Chemistry, EH9 3JF UK
[2]University of Edinburgh, UK Centre for Astrobiology, EH9 3FD UK

*h.pollak@sms.ed.ac.uk

Origin of life remains as one of the biggest unresolved puzzles of science, and can be seen as a transition from a geochemistry to a biochemistry. Life as-we-know-it is driven by polymeric molecules (proteins and RNA), able to encode the information and transfer it further with small number of inheritable mutations. Nearly a century ago, Oparin (1938) and Bernal (1949) suggested the role of minerals in enabling the emergence of life. While minerals can concentrate and catalyse formation of proto-biomolecules, they can also protect them from degradation. Indeed, minerals are common throughout the Universe and meteorites have been found to host peptidic sequences (Lange et al., 2021). But how to identify the molecules as biomarkers, and by such evidence of an ancient extraterrestrial life, remains an open question.

Focusing on iron-rich layered minerals, such as nontronite and fougerite, we attempt to rationalise the key properties determining the role these minerals on the formation or preservation of biomolecules. To this end, we use molecular modelling which gives us access to hypothetical Martian and early Earth minerals. Inspired by our previous findings (Erastova et al., 2017), we test a potential for the emergence of prebiotic molecular sequences, driven by the mineral surfaces. We believe that the formation and evolution of life's building blocks requires a very dynamic, energetic environment, e.g. hydrothermal vents (Martin et al., 2008). Such environments may not be ideal for the preservation of potential biosignatures (McMahon et al., 2018). Therefore, we also investigate potential neighbouring environments for their ability to trap formed proto-biomolecules, preserving them as a fossil of very first steps of life.

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Connecting organics to minerals and vice-versa: a key step on the route of the origins of life

Maguy Jaber[1], Jean-François Lambert[2]

[1]Sorbonne Université, UMR 8220, Laboratoire d'Archéologie Moléculaire et Structurale, Tour 23-33, 3ème étage – BP225, 4, Place Jussieu, F-75252 Paris CEDEX 05, France

[2]Sorbonne Université, UMR 7197, Laboratoire de Réactivité de Surface, 4, Place Jussieu, F-75252 Paris CEDEX 05, France

To unravel the interactions of biomolecules with clays, which is important in understanding the first steps of life on earth, two different approaches can be followed:

(1) The "bottom up" approach where the complexity of the organization of matter is gradually increased. For instance, one can study the adsorption of several aminoacids in expanding and non-expanding clays and then the peptide condensation by thermal activation to yield precursors of protein, or the formation of nucleotides from their precursors. A multi-technique approach was used to this purpose, including macroscopic measurements of the adsorption process (adsorption isotherms, pH-metry), and in situ molecular-level characterization of the solids obtained before and after activation (X-ray diffraction, thermogravimetric analysis and infrared spectroscopy) (Akouche et al., 2017, Jaber et al. 2014).

(2) The "top down" approach where accelerated ageing is applied to polymeric biomolecules in presence of minerals leading to the transformation of both components. A series of experiments in hydrothermal conditions at 180°C with crystalline and amorphous phyllosilicates were carried out. Microscopic and spectroscopic techniques clearly reveal the influence of the mineral matrix on the kinetic of degradation processes. In parallel, these experiments show that the presence of organic matter during hydrothermal treatment modifies the crystallization of mineral phases and leads to formation of new phases, including nano-minerals (Viennet et al., 2019).

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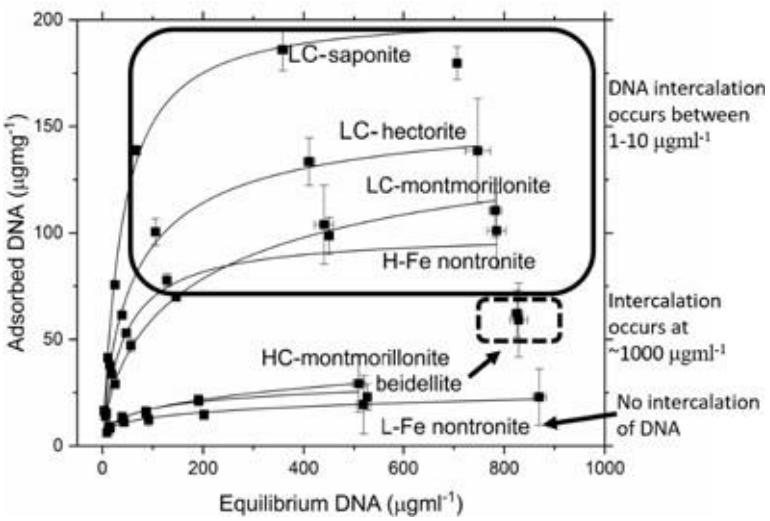
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DNA intercalation in smectites at neutral pH

S. Jelavić*, N. Findling, M. Lanson, B. Lanson

Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, Univ. Gustave Eiffel, ISTerre, F-38000 Grenoble, France

*stanislav.jelavic@univ-grenoble-alpes.fr



DNA found in sediments (sedDNA) represents valuable information for detection of past and present organisms (Taberlet *et al.*, 2012). Since DNA degrades in matter of days in solution (Lindahl, 1993), interca- lation in smectite can stabilize DNA by disrupting the enzymatic molecular recognition and by physically shielding DNA from environmental hazards such as heat, humidity and UV light. At neutral pH, DNA intercalation in smectite is unlikely because of electrostatic repulsion between negatively charged layers and DNA's phosphate backbone (Greaves & Wilson, 1969), limiting smectite's suitability as a DNA sta bilizer. However, there are a few reports of successful DNA intercalation in smectite but systematic study has never been conducted. Through batch adsorption and X-ray diffraction of smectite films, we showed that at pH 7 (1 mM $CaCl_2$) double-stranded DNA intercalates in a variety of smectites of contrasting compositions but the capacity for intercalation depends strongly on the smectite species (Figure 1). This result suggests that most smectites can successfully stabilize DNA and that smectite-intercalated DNA is a likely, but overlooked, source of environmental genetic information pending its efficient recovery.

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TS31 Clays and the Molecules of Life

POSTER PRESENTATIONS

Experimental crystallization of trioctahedral smectites under hydrothermal conditions: Implication for alkaline hydrothermal vents

F.J. Huertas[1,*], M.J. Bentabol[2], A.E.S. Van Driesche[1]

[1]Instituto Andaluz de Ciencias de la Tierra (CSIC-University of Granada), 18100 Armilla, Granada, Spain
[2]Departamento de Química Inorgánica, Cristalografía y Mineralogía. University of Málaga.Campus deTeatinos. 29071 Málaga (Spain)

*javier.huertas@csic.es

Present day hydrothermal vents are considered as plausible analogues of sites where livecould have emerged on primitive earth. Strtan (Iceland) is a shallow hydrothermal system composed mainly of vertical silico-magnesium structures, whose mineral association corresponds to a low crystallinity silica, trioctahedral smectites and smaller amounts ofcarbonates. To better understand mineral formation in such vent systems we have synthesized trioctahedral smectites in the kerolite-stevensite-saponite series using hydrothermal conditions in slightly alkaline solutions from amorphous hydrous Mg-Al silicates. The starting material consisted of coprecipitated gels with the following chemical composition (Si/Mg/Al/Na atomic ratios): Gel 1: 4.0/2.97/0/0.48, Gel 2: 4.0/2.69/0.17/0.63, Gel 3: 4.0/2.43/0.34/0.69. Gels (250 mg) were aged with 30 mL of water for 60 days at 150, 175,200 and 225 °C in Teflon lined reactors. The formed solid was repeatedly washed with distilled water by centrifugation, saturated overnight in $CaCl_2$ (1 M) and washed again with distilled water. The solid samples were characterized by XRD, DTA-TG, FTIR and TEM.

XRD revealed the formation of low crystallinity phyllosilicates. The 001 reflection (absent in most of the samples) evolved with increasing temperature and Al from 9.7, to 12 and 14.5 . The patterns contained peaks corresponding to kerolite (Krl) and stevensite/saponite (Stv/Sap). In oriented mounts, solvation with ethylene glycol shifted the 001 peak to 17.4 in gels 2 and 3, whereas in Gel 1 it remained at 9.7 with a shoulder at 17.2 . FTIR bands were also associated to trioctahedral phyllosilicates, talc-Krl and Stv-Sap. TEM images of samples obtained at 225°C from Gel 1 showed unresolved aggregates of tiny crystals of tens of nanometer, with turbostratic structures. Gel 3 produced layered crystals containing numerous defects and with spacings of 10-11 , typical of trioctahedral smectite.

Thus, aging treatment transformed Si/Mg/Al/Na gels into Krl-Sme interstratified minerals andtrioctahedral smectites. Temperature increased the conversion rate from 40 to 75% at 150 to 225 °C, respectively. Magnesium silicate (Gel 1) produced a 20-80% Stv-Krl interstratified mineral, composed of tiny crystals. Increasing Al content improved the crystallinity and the proportion of the smectite. Gel 2 consisted of a Sme-Krl interstratified mineral richer in smectite, while Gel 3 is fully transformed into smectite. The smectite synthesized in gels 2and 3 is likely Saponite with Al in the tetrahedral positions.

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TS32 Clay Geotechnical Applications

ORAL PRESENTATIONS

Swelling behavior of clays for tunneling relevant boundary conditions

Florian Christ*, **Arash L. Lavasan, Torsten Wichtmann**

Ruhr-University Bochum, Chair of Foundation Engineering, Soil and Rock Mechanics, 44780Bochum, Germany

*florian.christ@rub.de

Mechanized tunneling in swellable soils is a challenging procedure that involves a high potential of damage to the tunnel in the long term. The conventional solution to minimize the risk of damage to the tunnel lining, is the construction of a thick lining structure to counteract the swelling pressure. However, a more sustainable and environmentally friendly solution would be the installation of a tunnel support system, tolerating deformations such as the one developed in the framework of collaborative research center 837 'Interaction modelling in mechanized tunneling' at Ruhr-University Bochum.

In order to predict the swelling process of swellable clay shales induced by mechanized tunneling, it is necessary to consider various relevant boundary conditions. In this study, the focus is set on significant saturation modes (water and vapor saturation) and volumetric boundary conditions.

Stress redistribution and dilation results in the development of a so-called Excavation Damaged Zone (EDZ) around the tunnel in the clay shale (aquitard). Shear strain evolutions within the EDZ create preferential flow paths along the tunnel, transporting water from the aquifer (advective flux) and trigger the swelling process. Additionally, dilation in the EDZ leads to an increase of void ratio, decrease of degree of saturation and therefore increase in suction. This can additionally result in a diffuse flux in the clay shale in radial direction towards the tunnel. Experimentally, the advective flux is simulated by water saturation and the diffusive flux by a stepwise vapor saturation of the samples.

In this frame, the mechanical interactions between the swelling clay shale and the tunnel structure in terms of deformation tolerability leads to different volumetric boundary conditions for the swelling clay shale at the tunnel as well as at the experimental scale: 1) unsupported tunnel = free swelling, 2) stiff tunnel support = constant volume swelling and 3) deformable tunnel lining = swelling under controlled volumetric deformations.

To consider all different saturation modes and volumetric boundary conditions in the same device, a new swelling pressure cell was developed. While controlling and measuring swelling pressure and deformation, the experimental data allows to develop a swelling law which takes into account not only suction and time, but also volumetric deformations.

First tests on remolded clay shales (powder) in the new cells show an exponential decrease in swelling pressure with released volumetric deformations (heave), which is qualitatively and quantitatively in good accordance with various constant volume swelling pressure tests on samples with different initial dry densities. Additionally, the stiffness of the saturated clay shale was determined from a reloading after the test, again being in a good accordance with the previous oedometer tests. Swelling pressure tests with controlled stepwise volumetric deformations on intact clay shales are currently running and multistep vapor saturation tests are up next.

Characterization and beneficiation of local bentonite clay for use as drilling fluids

Abayomi Olatunde, Chiemena Okoroafor*

University of Lagos, Department of Chemical Engineering, Akoka, Lagos, Nigeria

*150401002@live.unilag.edu.ng

The need to develop local content by sourcing components locally for oil drilling operations in Nigeria has necessitated an evaluation of properties of local clays from Abia state, Nigeria for its suitability for drilling fluids. The clay is sourced locally and the suitability is evaluated by characterizing the clay sample and beneficiating it with various additives to improves it properties. The clay was characterized using X-ray Diffraction (XRD) to identify the mineralogical compositions, X-ray Fluorescence Spectrophotometer (XRF) which was used to determine the chemical compositions of the sample, Scanning Electron Microscopy for bulk microstructure and Fourier Transform infrared for surface chemistry. The Xray diffractogram confirmed the presence of montmorillonite with traces of quartz meaning the sample contained bentonite and the elemental analysis showed that the ratio of Al_2O_3/SiO_2 is 1/3 which indicated a montmorillonite that is also Ca-based rather than Na-based used for drilling purpose thus the need for beneficiation. The beneficiation of the bentonite was done by ion exchange with sodium carbonate followed by addition with different compositions of viscosifiers namely: carboxymethyl cellulose (CMC), drispac and guar gum. The rheological properties together with the gel strength and filter loss of the clay were determined. The drilling mud formulated with the ion-exchanged bentonite clay without the additives resulted in a poor performance while most of the bentonite compositions met the required standard for the formulation with the combination of 22 g bentonite + 2. g guar gum + 1 g CMC was the optimum local clay and additives concentrations that gave the best result for both rheological and filtration properties.

Study of the flocculation phenomenon over different bentonite-type materials within vertical fractures

Kenji Ishii[1], Hanna Kronberg[2], Heikki Laitinen[2], Macarena Leal-Olloqui[2], Patrik Sellin[2,*], Daniel Svensson[2]

[1]Kajima Technical Research Institute, Tokyo 1820036, Japan
[2]Svensk Kärnbränslehantering AB, Äspö Hard Rock Laboratory, 572 95 Figeholm, Sweden

*patrik.sellin@skb.se

Internationally selected as the primary buffer and backfill material for the final disposal of high level radioactive waste (HLW) is bentonite, a natural occurring geomaterial characterized by its high content in montmorillonite. The montmorillonite clay mineral component in bentonite provides the ability to absorb large volumes of water, whilst keeping some shear strength and ductile behavior. Hence, bentonite is considered the most suitable material to fulfil the desired safety functions at the KBS3 design.

In the KBS3 system, the waste containers will be deposited in drilled boreholes within the host rock and surrounded by the bentonite buffer (Shelton et al., 2018). Thus, the ensuing swelling of bentonite through water up-take is constrained by the walls of the deposition holes. Nevertheless, the existence of fractures interfering with the deposition holes could ultimately facilitate bentonite free swelling, resulting in the separation of adjacent montmorillonite layers while promoting its dispersion and transport by groundwaters mean (Hedström et al., 2016). Once released, eroded clay particles tend to form flocs which will be carried away by the flow. Moreover, as a result of this phenomenon, those flocs sedimented in sloping fractures may originate more severe erosion than the caused by the inflowing waters (Alonso et al., 2019).

In view of the flocculation phenomena importance, SKB initiated a pilot programme with the purpose of further exploring such phenomenon over different bentonite-type materials. SKB experimental work was conducted by using an artificial fracture of 0,20mm to simulate the intrusion of water. Compacted bentonite rings, with a 35,20mm and 14,80mm outer and inner diameter, and 10,20mm total thickness, were 'sandwiched' between two Plexiglas plates, vertically placed under no water flow conditions, favoring bentonite swelling, the subsequent gel formation and its expansion through the fracture. Obtained results allowed to draw conclusions regarding the mass loss and expansion over different bentonite-type materials.

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Libertad Clay: Expansion pressure reduced by lime adding

Marcos Musso

Universidad de la República, Facultad de Ingeniería, Departamento de Ing. Geotécnica, Montevideo, Uruguay

mmusso@fing.edu.uy

Older civilization used lime to obtain better behavior in soil. The Romans used volcanic ash and lime in soil for increase mechanical strength in Via Apia. Improve soil using some additive is a common practice in geotechnics. Fine soils have low strength then it is necessary to adapt modified engineering designs or improve strength values using an additive. Lime was a common additive to improve fine soil to engineering proposes as clay or silt (CL, CH, ML, MH). In these soil limes produce a volume change stabilization, modified plasticity and increase workability and strength. When the soil has enough moisture the lime increase pH, dissolve clay border releasing aluminum and siliceous ions generating a gel that produce new calcium aluminum silicate when crystallize. These pozzolanic reactions are time and temperature dependent.

The behavior of fine soils of Libertad Clay (clays, silty clays and loess deposits generated in continental environments associated with Quaternary glaciations) in the south of Uruguay is analyzed in this work. Different expansive behaviors were determined in previous researches developed by the author. These soils were composed by clays, silty clay and clayey silt with Smectite and Illite as main minerals. Pressure expansions measured were variable between 100 kPa to 1000 kPa.

Four samples were analyzed (ML, CH, CL) with 16 % and 45 % of clay. Soil CEC was obtained by blue methylene (8 a 35 cmol/kg), then CEC clay varies between 50 a 78 cmol/kg. Smectite and Illite are domain clay minerals. Expansion pressure was carrying out in oedemeter, in constant volume process. Some changes in mineralogical composition was observed with new weak peak in X-Ray Diffraction (XRD) associated calcium aluminum silicate hydroxide (CAH) gels.

In natural condition pressure expansion obtained were 60 kPa, 250 kPa and 1000 kPa (samples m1, m2 and m4 respectively). When lime was added the pressure expansion were reduced to 10 kPa, 12 kPa and 500 kPa in 7 aging days (samples m1, m2 and m4 respectively).

In 14 aging day m4 pressure expansion was reduced to 250 kPa. Then some differences were observed because soil compositions are variable and all soils have a reduction in pressure values and this reduce increase with aging.

In the future the samples will be aging more days to evaluate changes in mineralogical composition when the pozzolanic reactions will have completed. Also pressure expansion and other geomechanics properties as strength could be evaluate when mineralogical changes happened.

TS34 General Session

ORAL PRESENTATIONS

How selective can be synthesis of iron bearing clay minerals?

Amira Doggaz[1*], Liva Dzene[1], Patrick Dutourni[1], Jocelyne Brendl[1], Christelle Martin[2], Nicolas Michau[2]

[1]Institut de Science de Matériaux de Mulhouse CNRS UMR 7361, Université de Haute- Alsace, Université de Strasbourg, 3b rue Alfred Werner, 68093 Mulhouse, Cedex, France

[2]Andra, R&D division, Materials & Waste packages Department, 1 :7 rue Jean Monnet, F-92298 Chtenay-Malabry, Cedex, France

*amira.doggaz@uha.fr

Iron-bearing 1:1 phyllosilicates (serpentines) are present in various geologic environments such as ocean floor or may form at the interface between iron components and either vitrified waste or deep-geological formations foreseen for radioactive waste disposal [1]. To predict the long-term behavior of these formations, synthetized iron-rich clay minerals are used as analogues to naturally formed minerals in order to investigate the thermodynamic properties necessary formodelling purposes. It has been previously reported that hydrothermal synthesis is the most preferred method, and that the pH is the key parameter governing the nature of the synthesized products [2]. Therefore, this study aims to find optimum pH conditions favoring the formation of 1:1 phyllosilicates.

A set of experiments were carried out by varying the initial pH from 8.50 to 11.50 with molar ratio $(Fe/Si)_{ini} = 1.5$. The temperature and the duration of the hydrothermal treatment were fixed to 160 °C and 2 days, respectively. pH and redox potential were measured in each stage of the preparation of the precursor and after the synthesis. The products were characterized by Raman spectroscopy and X-Ray diffraction.

Results showed 3 distinct predominance fields that differed by the pH and Eh evolution after the hydrothermal treatment. The first zone with $pH_{ini} > 11.00$ favored the formation of 2:1 and1:1 phyllosilicates. The second zone of pH_{ini} approximately 10.00 was suitable for the formation of 1:1 phyllosilicates. In the third zone, where $pH_{ini} < 9.60$, only iron oxides were obtained. In order to better understand the selective process of 1:1 phyllosilicates formation, additional investigations were conducted such as the influence ofthe precursor aging stage and the concentrations of dissolved species of silica.

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Colloidal amorphous silica nanosheets and their two-dimensional assembly

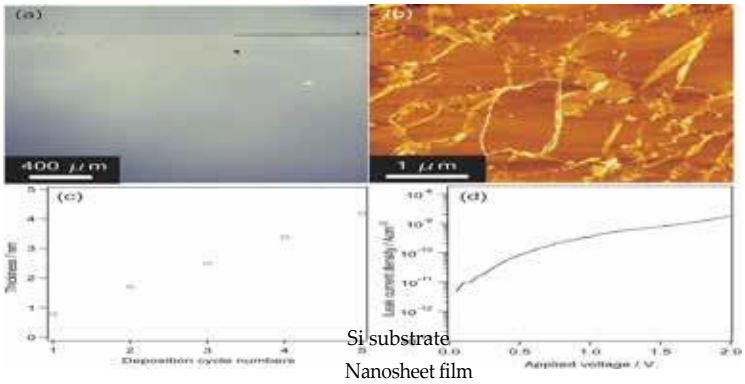
Eisuke Yamamoto[1,2,*], Kosuke Fujihara[3], Yue Shi[1], Makoto Kobayashi[1], Minoru Osada[1,4]

[1]Institute of Materials and Systems for Sustainability, Nagoya University, Japan
[2]PRESTO, Japan Science and Technology Agency (JST), Japan
[3]Graduate School of Engineering, Nagoya University, Japan
[4]National Institute for Materials Science (NIMS), Japan

[*]e-yamamoto@imass.nagoya-u.ac.jp

Amorphous nanosheets have attracted much attention because they exhibit unique properties distinct from bulk counterparts (Toh, 2020). In particular, amorphous silica nanosheets have been prepared through various templating methods based on wet chemical processes (Toussaint, 2009; Singh, 2019); however, those amorphous silica nanosheets had rather thick and aggregated, and the atomically thin (>1nm) nanosheets have never been synthesized. In this study, surfactant-silica lamellar hybrids were exfoliated into colloidal nanosheets as monolayer form using surfactant non-ionic surfactant as a template, and the neatly packed monolayer film was successfully fabricated.

Surfactant-silica lamellar hybrid was synthesized using a Brij52 ($C_{16}H_{33}(OCH_2CH_2)_2OH$) as a template (Zhao, 1998). The obtained surfactant-silica lamellar hybrid was exfoliated by sonication in ethanolic solution for obtaining nanosheets dispersion. The Langmuir film was
prepared by spreading the colloidal suspension carefully on the water surface, and was transferred onto the substrates for preparing nanosheets film.



The formation of the surfactant-silica lamellar hybrid was confirmed by the FT-IR spectrum and XRD pattern. The obtained colloidal suspension was transparent and showed an apparent Tyndall phenomenon. TEM image and SAED pattern showed the formation of amorphous nanosheets. The thickness of the obtained nanosheets after removing the surfactant was 0.9 nm as con-firmed by AFM observation. In addition, the confocal laser microscope image of the film showed that the amorphous silica nanosheets were homogeneously deposited on the substrate (Figure 1 (a)). The AFM image clearly resolved individual nanosheets arranged edge to edge in a monolayer with negli- gible gaps (Figure 1 (b)). Furthermore, multi-layered films were also fabricated through repeating the deposition process, which are expected to be used for various devices.

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Geochemical alteration occurring during multiple cation exchange process provoked in-situ in the case of Na-rich montmorillonite: effect of cation ionic potential and electronegativity

Chadha Mejri*, Walid Oueslati, Abdsslem Ben Haj Amara

University of Carthage, Faculty of Sciences of Bizerte, LR19ES20: Resources, Materials and Ecosystems (RME), 7021 Bizerte, Tunisia

*chadha.mejri@fsb.ucar.tn

One of the fundamental properties of clays is the intrinsic cation exchange capacity (CEC) which provides a means for estimating the general chemical properties. Clays are used as geological barrier for industrial and radioactive waste confinement. Therefore, the performance limits of these minerals towards the external stresses must be evaluated according to the real use conditions. in this case a series of constraints with different nature appear as well as their variable coupling level. From this complex configuration, only the effect of a series of multiple cation exchange process (heavy metals cation) is investigated, according to the electronegativity and the cation ionic potential. The starting material is the Na-rich montmorillonite and the structural analysis is achieved using the XRD profile modeling approach to quantify the interlayer space (IS) deformation and to highlight the geochemical alteration. The quantitative XRD analysis, which consists of the comparison of experimental 00ℓ reflections with the calculated ones deduced from structural models, allowed us to determine the optimal structural parameters describing IS configuration along the c^o axis before and after applying constraint. The obtained result shows and heterogeneous mixed layer structure MLS for all exchanged cation indicating partial CEC saturation. The 0W, 1W and 2W hydration behavior is observed and omnipresent regardless of the exchangeable cation type. For Co(II), Ni(II), Mg(II), Cu(II) and Zn(II) cation, the hydration sphere appears unaffected by the created chemical constraint. A very remarkable interlamellar water molecule evolution (following the process of multiple cation exchange) in the case of Cd(II), Pb(II) and Ba(II) cations is observed. Quantitatively, an elevated hydration heterogeneities degree (great fluctuations in discretization of the hydration states) appears. By the fact of the change in the nature of the exchangeable cation and for Cd(II), Pb(II) and Ba(II) cations, a limited and thwarted CEC performance is showed. The coexistence of the different layer type populations and their stacking mode were identified by the theoretical decomposition of the experimental XRD profiles. A segregated stacking mode trends dominate all studied samples.

Layered silicate-polymer nanocomposite hydrogels – an investigation into polymer chemistry and layered silicate types

Francis Clegg*, Hassan Judah, Chris Sammon

Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield, S1 1WB, UK

*f.clegg@shu.ac.uk

Nanocomposites are multiphase solid materials incorporating two or more individual components, were one of the phases has one or more dimensions less than 100 nm. The high surface area interactions offered by the nano-sized components not only offer an enhanced combination of component properties but also a unique property profile.

Layered silicate-polymer nanocomposite hydrogels are a unique class of nanocomposite, which offer a range of applications and performance characteristics as smart materials. Within these, the layered silicate acts as a crosslink to provide a stable, three-dimensional polymeric network forming a soft material. They are capable of retaining substantial amounts of water up to thousands of times their dry weight, which fills the interstitial space of the network. Moreover, layered silicate acts as physical crosslinks (rather than covalent) enabling the polymer chains to be free and flexible allowing solvent casting and ease of fabrication.

A research study has been conducted to investigate and understand the physical and chemical properties of layered silicate-polymer nanocomposite hydrogels through changing different polymer chemistries, layered silicate type (natural bentonite, Cloisite® Na^+, and various synthetic Laponite® grades) and percentage composition.

Layered silicate dispersion was assessed using X-ray diffraction, Fourier transform infrared spectroscopy and thermogravimetric analysis. This data was correlated to morphological and mechanical behaviour assessed by rheological studies and scanning electron microscopy of freeze fractured nanocomposites.

Synthesis of polymer-talc like composite *in-situ*

Liva Dzene[1,*], Frdryck Tidas[1,2], Anne-Sophie-Schuller[2], Jocelyne Brendle[1], Christelle Delaite[2], Sverinne Rigolet[1]

[1]Institut de Science des Matriaux de Mulhouse CNRS UMR 7361, Universit de Haute-Alsace,Universit de Strasbourg, 3b rue Alfred Werner, 68093 Mulhouse, France

[2]Laboratoire de Photochimie et d'Ingnierie Macromolculaires, Universit de Haute-Alsace, Universitde Strasbourg, 3b rue Alfred Werner, 68093 Mulhouse, France

*liva.dzene@uha.fr

The dispersion of layered fillers in polymers at nanoscale can significantly improve many properties of composite material (Kojima et al., 1993). In order to achieve such dispersion in the polymer matrix several techniques are described (Alexandre & Dubois, 2000) with natural or synthetic fillers already functionnalized or not. Here we report an innovative way i.e., the *in situ* synthesis of the filler within polymer matrix. Such concept is based on the emergence of a novel class of hybrid organic-inorganic compounds having a talc-like structure (Brendl, 2018). This latter can be prepared via sol-gel process from magnesium salts and alkoxysilanes. In this study, a series of silanized polyethylene glycols having different chain lengths was prepared and used as one of the silicon sources together with tetraethyl orthosilicate. The magnesium nitrate was used as a source of metal salt. X-ray Diffraction and ^{29}Si solid state Nuclear Magnetic Resonance indicated that a layered structure can be formed, paving the route to applications of our approach.

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Physico-chemical classification of fine-grained soil using artificial neural network model

N. Saranya[1]*, G. Manavaalan[2], V. Manikandan[2], M. Vijay[3]

[1]Coimbatore Institute of Technology, Department of Civil Engineering, India
[2]Coimbatore Institute of Technology, Department of Electrical and Electronic Engineering, India
[3]Coimbatore Institute of Technology, Department of Physics, India

*saranyan@cit.edu.in

The knowledge on Atterberg's Limit (liquid limit [LL]; plastic limit [PL] and plasticity index [PI]), activity, clay mineralogy and clay content are highly important for understanding the engineering application of fine-grained soil [1]. However, in the recent research works, it has been observed that in addition to Atterberg's limit and other soil properties, the engineering behaviour of fine-grained soil is strongly influenced by its physico-chemical characteristics such as specific surface area, SSA and cation exchange capacity, CEC [3,6,7,10,13]. Furthermore, few research works have also concluded that there is a strong inter-relationship between the physico-chemical characteristics and index properties of fine-grained soil [4, 8, 9, 11, 12]. Based on the above observations it is evident that the Atterberg's limit, activity, clay mineralogy, clay content and physico-chemical characteristics need to be considered while assessing the engineering behavior of fine-grained soil [2, 5]. In this regard, the present study has attempted to develop a new soil classification based on LL, PI, activity, clay content, SSA and CEC, using Artificial Neural Network (ANN) model. Around 430 datasets from various literatures have been used for the analysis. The datasets are split into 50:50 (training/validation:testing) with two hidden layers. The neural network structure is boiled down to 6:12:6:3. The convergence rate of data's is 87% and 70% during training/validation and testing respectively. In addition, the sensitivity of individual input parameters is also considered during the analysis. From the results, it is observed that the proposed model gives an encouraging output compared to the conventional practice adopted for soil classification.

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Mechanism of diagenetic reorganization of weathering hematite crystals

Marek Szczerba*, Jan Środoń, Katarzyna Luberda-Durnaś, Barbara Barylska

Institute of Geological Sciences PAS, Research Centre in Kraków, ul. Senacka 1, 31-002 Kraków, Poland

*ndszczer@cyf-kr.edu.pl

Hematite is a common component of sedimentary rocks deposited under oxidizing conditions. It originates mostly from erosion of lateritic tropical soils, and/or from the lateritic-type weathering of the sediment *in situ*. During burial diagenesis, significant changes of powder diffraction patterns of sedimentary hematite have been observed. The main aim of this study was to investigate the reorganization mechanism of hematite, which is reflected in decreasing broadening of its peaks and in the evolution of crystallite size distribution (CSD), calculated from peak shapes of the X-ray powder diffraction patterns.

A series of 83 samples from the Ediacaran redbeds, paleosols, and hydrothermally altered basalt and tuffs of the East European Craton, representing wide range of origin and of diagenetic conditions, was analyzed using X-ray powder diffraction. Additionally, a series of 10 younger sedimentary rocks of different ages, diagenetic conditions, and from different localities were analyzed for verification of the received trends. The results indicate that hematite formed during weathering has platy crystallite shape and the main direction of diagenetic growth is [001], accompanied by the decrease of micro-strain in [100] and [010]. Evaluation of CSD in [104] direction indicates that with the progress of diagenesis the distributions fitted with lognormal function have parameters that are spread in relatively broad range but generally the values of beta^2 are slightly increasing with increase of alpha. This indicates that surface/supply-controlled growth mixed with random ripening is the mechanism responsible for thickening of crystallites. Hematite growth according only to the Oswald ripening model is much less probable, since in all cases, except one, significant deterioration of (104) reflection fits were observed if distributions corresponding to this model were used. In rare cases, bimodal distribution gives the best agreement, which indicates a contribution of separate population of thicker hematite crystallites.

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Presenting a global quantification of clay minerals on Earth

Laurence N. Warr

Institute of Geography & Geology, University of Greifswald, Greifswald, Germany

warr@uni-greifswald.de

A database is presented compiling clay mineral (phyllosilicate) quantifications for 21 lithological units of the Earth's brittle continental and oceanic crust. Published mineral abundances for >23 000 samples determined largely by the Rietveld XRD-based technique indicate 21.5 weight (wt.) % of the brittle crustis composed of clay minerals and associated phyllosilicates: 12.8 wt.% is located in the upper (< 12 km) continental crust and 8.6 wt.% in the thinner oceanic crust down to average depths of 6.57 km. In terms of clay mineral types, the 2:1 clay minerals with little or low expandability (commonly illite) are most abundant in upper crustal environments and total 7.7 wt.%. The remaining 13.8 wt.% is distributed more equally between the 1:1 kaolinite-serpentine minerals (5.3 wt.%), the highly expandable 2:1 smectites (3.4 wt%) and the 2:1:1 chlorites (5.1 wt.%). Continental soils and the underlying regolith represent only a small part of the clay mineral inventory (just 0.016 wt.%), but they do constitute important generating zones. These minerals and other products of surface weathering are redistributed to the main depositional sinks of sedimentary basins where 8.13 wt.% of hydrous sheet silicates reside and are further modified during diagenesis or hydrothermal activity. A further 1.38 wt.% is redistributed as deep ocean floor sediment. The remaining 5.58 wt.% of clay minerals in the continental crust are located in the altered igneous and crystalline rocks. Although less well quantified, the altered basalts, gabbros and ultramafic rocks of the oceanic crust, together with the overlying oceanic sediments, represent a significant and rather overlookedpart of the inventory characterized by notably high amounts of smectite, chlorite and serpentine minerals.The total amount of stored water (adsorbed and crystalline water) held in the brittle crust by these mineralsis estimated to be equivalent in volume to ca. 22% of today's surface water with approximately half located in the oceanic crust. The trapping and release of surface water is likely to have played a key role inboth crustal processes and climate change throughout most of Earth's history. The global quantificationsmade are discussed within the context of our rather unique planetary "dynamic clay factory".

Nano-remediation: starch functionalized magnetite for As sequestration

R. Coustel*, **M. Rakotomalala Robinson, M. Abdelmoula, M. Mallet**

Université de Lorraine, CNRS, LCPME, F-54000 Nancy, France

*romain.coustel@univ-lorraine.fr

This study is devoted to further understanding the role of polysaccharide upon the formation of divided oxide designed for As sequestration application. Magnetic nanoparticles have generated a continual interest due to their potential applications in environmental processes. Among magnetic material magnetite (Fe_3O_4) exhibits attractive properties: high saturation magnetizations and Curie-temperature, good biocompatibility, low toxicity. Moreover, below ~30 nm in diameter magnetite particles present superparamagnetic behaviour at room temperature. Surface functionalization prevents particles agglomeration, which is of prime interest to preserve adsorption properties for nanoremediation applications. In this study, we focused on the role of starch functionalization of magnetite nanoparticles. Starch was chosen as an abundant and eco-friendly polysaccharide.

Starch-functionalized magnetite nanoparticles were prepared by both the oxidation-precipitation (OP) method (Schwertmann et Cornell 2000; Rakotomalala Robinson et al. 2019) where Fe^{2+} is partially oxidised by NO_3^- in alkaline medium and the coprecipitation (CP) (Chang et al. 2011) method where Fe^{2+}:Fe^{3+} (1:2) solution is steeply alkalinized. Obtained materials were probed by transmission electron microscopy (TEM), powder X-ray diffraction (PXRD), Raman, Fourier transform infrared (FTIR) and Mössbauer spectroscopies. In particular, Mössbauer spectrometry (see Fig. 1) evidences that how magnetic properties of magnetite particles can be thoroughly changed depending on the choice of synthesis conditions.
The adsorption properties of the materials obtained by oxidation-precipitation or coprecipitation with or without starch were examined. As(V) (respectively, As(III)) sorption capacities up to 1.3 mmol g_{Fe}^{-1} (respectively, 1.0 mmol g_{Fe}^{-1}) were determined (Robinson et al. 2020). It comes that a wide range of easy-to-prepare nanostructured materials for pollutant sequestration is at hands by using polysaccharide to control oxide synthesis.

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Quantification of smectites in an altered basalt by VNIR-SWIR spectroradiometry

Mercedes Suárez[1,*], Emilia García-Romero[2,3]

[1] Department of Geology, University of Salamanca. Plaza de la Merced, S/N, 37008 Salamanca
[2] Department of Mineralogy and Petrology, Complutense University of Madrid. C/José Antonio Novais, 12, 28040 Madrid
[3]Institute of Geoscience (UCM-CSIC). C/Doctor Severo Ochoa 7, 28040 Madrid

*msuarez@usal.es

The third set of looks of the Panama Canal, one the most impressive civil constructions around the world, was constructed using the local basalt from the Miraflores Formation as raw material. The cost overruns in billions dollars and the delay in the construction of the new canal were related in large part to the extraction, storage and use of the basalt as the raw material (aggregates and sand) for concrete. A detailed study revealed that the presence of dioctahedral smectites filling a dense network of micro and nanocracks intensely connected caused the unexpected behaviour of the basaltic rocks (Suárez et al., 2021). During the study of the Miraflores Basalt was necessary the quantification of the smectites content in hundreds ofsamples and the VNIR-SWIR spectroradiometry was used to obtain semiquantitative data.

A portable ASD fieldspec 4 HR spectroradiometer was used to obtain more than 700 spectra on cores and samples from quarries from the Miraflores Basalt. To be able to use data from the spectra for quantification a regression model was developed considering data from the Thermal Analysis (thermogrametric analysis) and the structural formulae obtained by point analysis obtained with Analytical Electron Microscopy.

Clay minerals in general and specially smectites are hydrated minerals and the NIR-SWIR spectroradiometry is a good technique to study them because they have characteristic bands related to the absorptions of H_2O molecules and OH^- groups. These bands are easily identified and can be used for comparing samples with the same mineralogical composition. The regression model was developed from data of a small group of samples and later applied to the quantification.

The results shown that all spectra evidenced the presence of smectites, that appear widespread in the area with a mean content of 17.1%. The VNIR-SWIR spectroradiometry resulted an excellent technique to obtain semiquantitative data in a very short time and without any pre-treatment of the sample.

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Thermal analysis of kaolinite group minerals

Andrea García-Vicente[1,*], Adrián Lorenzo Hernández[1], Juan Morales Sánchez Migallón[1], Emilia García-Romero[2,3], Mercedes Suárez[1]

[1] Department of Geology, University of Salamanca. Plaza de la Merced, S/N, 37008Salamanca.
[2] Department of Mineralogy and Petrology, Complutense University of Madrid.
[3]Institute of Geoscience (UCM-CSIC). C/Doctor Severo Ochoa 7, 28040 Madrid.

*andrea_gar@usal.es

The thermal decomposition of layer silicates, and in particular the dehydroxylation of kaolinite minerals, has been examined with precision in the last decades. The dehydroxylation temperature is persuaded by the degree of disorder of the kaolinite structure. Contrasting the temperature of dehydroxylation, it is noticed that low-ordered kaolinite dehydroxylated at lower temperatures. More detailed research is necessary to define the influencing factor in dehydroxylation at elevated temperatures among diverse kaolinite poly- types, such as dickite (Cheng et al., 2010). In fact, stacking sequence in each mineral and orientation of OH^- groups makes it easier to deduce the different kaolin polytypes through DTA and TG analysis.

A characterization by thermal analysis of 14 kaolin samples was carried out. A characterization of these kaolins was also performed by X-Ray Diffraction and Transmission Electron Microscopy. From XRD, 5 kaolinites, 4 dickites and 5 halloysites were identified. Among the kaolinites differences in the crystallini- ty were observed. It could be noticed that kaolinite give a single symmetric peak at 500°C, which becomes asymmetric with an increase in stacking faults. However, dickite exhibit a double dehydroxylation peak at 600°C, although it is noticeable that the thermal behavior of dickites differs among the studied samples, in parallel with the differences found in the XRD-patterns. Halloysite dehydroxylates at 450°C, allowing distinction from kaolinite samples. The typical morphology of kaolinite and halloysite was observed to beplaty-like and nanotubes, respectively, and influenced thermal decomposition.

The results of thermal analysis clearly indicate that the dehydroxylation temperature differs in each case, as correspond to different kaolinite polytypes and that crystallinity influences on the thermal behavior.

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Clay minerals of western Baltica Proterozoic as climatic indicators

Jan Środoń[1*], Sirle Liivamägi[1,2], Maciej J. Bojanowski[3], Karol Jewuła[1]

[1]Institute of Geological Sciences PAS, Research Centre in Kraków, Senacka 1, 31-002 Kraków, Poland
[2]Current address:Geological Survey of Estonia, Kreutzwaldi 5, Rakvere, Estonia
[3]Institute of Geological Sciences PAS, Twarda 51/55, 00- 818 Warsaw, Poland

*ndsrodon@cyf-kr.edu.pl

Baltica crystalline basement is covered by the Mesoproterozoic sedimentary rocks, preserved locally in tectonic depressions, and by the Neoproterozoic rocks covering most of the craton within the central basin and basins on the cratonic edges. The central basin rocks underwent only shallow burial and weak diagenetic alterations, as evidenced by porosity measurements, and both clay and organic diagenesis studies. These rock sequences offer a unique opportunity for studying Precambrian clays, preserved in the sedimentary rocks, in altered volcanics, and in paleosols of different ages, developed on the crystalline basement, on the Ediacaran volcanics, and on the Ediacaran sediments.

Precambrian paleosols are known since Mesoproterozoic till Ediacaran, and they all represent lateritic type weathering, leading towards kaolinite plus hematite assemblage, via the intermediate stage of dioctahedral smectite. Occasionally, pure smectites have been preserved, but most often they underwent Paleozoic illitization, reaching ca. 25%. Locally, aluminoceladonite was another product of this process. Ediacaran volcanics of the Volyn Large Igneous Province underwent syndepositional hydrothermal alteration, which produced di and trioctahedral smectite, chlorite and mixed-layer chlorite-smectite plus hematite.

Oxidized sediments (redbeds) dominate and they preserve the composition of eroded paleosols and hydrothermally altered volcanics. Such sediments locally underwent additional lateritic weathering *in situ*, evidenced by authigenic kaolinite and hematite. Two sedimentary sequences (Bortnikov and Orsha) are extremely mature, composed only of quartz, kaolinite and hematite. Third, the Paleoproterozoic sequence of this kind (Ovruch Series), has been metamorphosed and is preserved as quartz, pyrophyllite, and hematite assemblage.

Reduced sediments are known from the upper Ediacaran and are characterized by the massive development of berthierine replacing kaolinite, dominant in all identified sedimentary environments from continental to marine, including glacial sediments (diamictites).
Both lateritic-type weathering, recorded by the composition of paleosols and redbeds, and berthierine as dominant product of mineral authigenesis in reduced sediments indicate hot and humid tropical climate on Baltica for over 1 Ga years, even during a glacial period.

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Restoration of Moroccan historical heritage with a geopolymer binder

Anass El Khomsi[1,*], Ameni Gharzouni[1], Noureddine Idrissi Kandri[2], Abdelaziz Zerouale[2], Sylvie Rossignol[1]

[1]Institute of Research on Ceramics (UMR7315), 87068 Limoges Cedex, France
[2]Laboratory of Signals Systems and Components, Faculty of Sciences and Technics, 3000 Fez-Morocco

*anass.el_khomsi@unilim.fr

The historical monuments of the Old Medina of Fez city in Morocco, were built from clays and sands available around. Nowadays, this historical heritage is restored using a cement-lime mortar that may cause irreversible damages to the monuments, as a result of efflorescence and the high rigidity of the cement. To palliate these issues, geopolymer binders could be an alternative, indeed, these binders can be obtained using natural calcined clays. Consequently, the aim of this study is to develop a geopolymer coating, based on Moroccan raw materials for historical heritage restoration. To achieve this objective, different Moroccan sands and calcined clays were used.

The experimental procedure consists on mixing the calcined clay with a potassium silicate solution, after that, the reactive mixture is applied on different substrates by projection. Microstructural analysis and adhesion tests were performed on the applied coatings.

The results show that geopolymer materials can be obtained from calcined Moroccan clays, it also shows that this geopolymer coatings exhibits an adherence varying between 1 and 9 MPa depending on the used substrate, and their interactions with the substrates are limited, manifested by a weak diffusion of the alkaline element of the order of 8 µm.

Fluorescence enhancement of molecules on the clay surface and its environmental responses

Shinsuke Takagi

Tokyo Metropolitan University, Department of Applied Chemistry, Tokyo, Japan

takagi-shinsuke@tmu.ac.jp

In photo-functional organic/inorganic composites, it is possible to develop its functionalities such as absorption and emission abilities, redox activities, and environmental response capabilities, by combining the advantages of them. For example, dye-sensitized solar cells and artificial photosynthesis systems, which convert solar energy to electric and chemical one, are typical examples of organic/inorganic composites. Among the inorganic host materials, layered materials (LM) such as synthetic saponite (SSA) and titania nanosheet, are known as unique host materials, because of their flat and negatively charged surface. Research groups, including us, have reported a variety of dye/LM composites from a view point of surface- and photo-chemistry. For example, cationic porphyrins were adsorbed on SSA and TNS without aggregation even at high density adsorption conditions. This phenomenon was named “size-matching effect” [Takagi (2013), Takagi (2017)]. Because an aggregation tends to decrease the excited lifetime of sensitizer, this high-density adsorption structure without aggregation is suitable for a construction of photochemical reaction systems. In addition, the physical property of dyes and proteins on the surface shows unique phenomena such as emission enhancement and reactivity change [Tokieda (2017), Ishida (2014)]. In some cases, non- or weak emissive molecule becomes fluorescent on the clay surface and/or the fluorescence becomes much stronger. Based on its mechanism, we name this effect of nano-sheet as “Surface-Fixation Induced Emission (S-FIE)” [Tokieda (2017), Ishida (2014)]. In this talk, the examples of such S-FIE behavior and its mechanism will be presented.

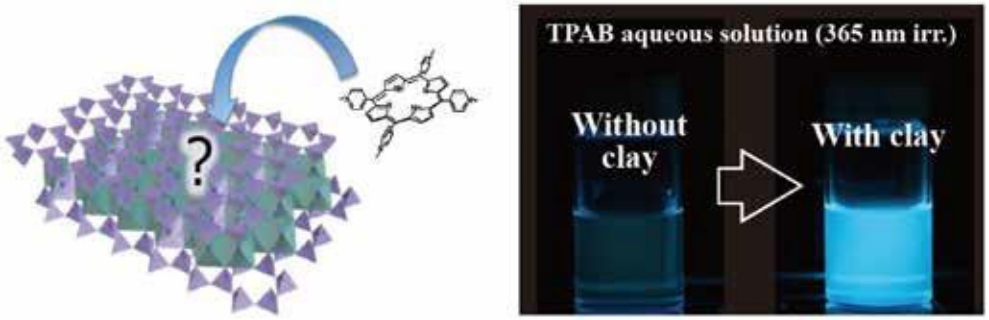


Fig. The fluorescence enhancement of dyes on the clay surface.

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3D printability of three-component photoinitiating systems in a diacrylate resin containing Laponite® as filler

Christian Ley[1], Antoine Ishak[1], Boris Metral[1], Jocelyne Brendlé[2,*], Xavier Allonas[1]

[1]Laboratoire de Photochimie et d'Ingénierie Macrololéculaires, EA 4567, Université de Haute- Alsace, 68083 Mulhouse, France

[2]Institut de Science de Matériaux de Mulhouse, CNRS UMR 7361, Université de Haute-Alsace, Université de Strasbourg, 68083 Mulhouse, France

*jocelyne.brendle@uha.fr

Additive manufacturing (3D printing) is a technic allowing fabrication of objects with complex shapes and intricate features that cannot be achieved with conventional injection molding or subtractive manufacturing techniques. Technologies make use of a (liquid) photopolymer resin which is able to cure (solidify) under a light source which can be a laser tracing a layer in the case of stereolitography (SLA) or a projected light source allowing the illumination of the whole printed whole printed area at once with the pattern of the layer in the case of digital light processing (DLP). In this case, a polychromatic Xenon arc lamp with full visible spectrum (leading to a broader range of usable photoinitiating systems (PIS)) or a monochromatic LED, mostly in the 385-405nm area up to Liquid Crystal Displays can be used, printing time being often reduced compared to SLA. Type I photoinitiating systems (PIS), which convert light into radical by photocleavage of molecules, are mostly used in vat photopolymerization 3D printing, however they absorb only UV to near UV light. Some Type II PIS, which are based on a bimolecular photoreaction (photoinduced electron transfer, H abstraction…) between a dye and a coinitiator are employed as well. Th innovative approach of this study stands in the use of Laponite® to improve the efficiency of type IIPSI by tuning the photoinduced electron transfer reaction between an organic dye and two coinitiators. The three component photoinitiating systems are based on an anionic dye Rose Bengal and a cationic dye Safranine O, N-phenylglycine as an electron donor co-initiator and a Iodonium salt as an electron acceptorredox additive. The effect of Laponite® on the photophysic and the photochemsitry on the two dyes was studied by steady state and time resolved spectroscopies showing that only the cationic dye properties areimpacted. With a simple diffusion model we try to figure out the effect of viscosity on the photoinduced electron transfer reactions which are underlying the photocyclic behavior of the two dyes PIS. The ef- ficiency of the PIS were then compared by RT-FTIR exemplifying the positive effect (nearly by a factor2) of the clay content on the PIS efficiency which can be ascribed to the fact that cationic molecules are attracted by the negatively charged nanoparticles surface leading to a local increase of concentrations. This positive effect of clay content on polymerization efficiency effect was confirmed in DLP 3D printing: a reduction by a factor three of the layer exposure time was obtained. This reactivity increase is very important because it reduced the long printing time of 3D objects. Therefore, this three-component initiating system based on SFH^+/NPG/I250 is suitable for DLP 3D printing of acrylate resins with and without Laponite® with high part quality and low printing time.

Fluorescent dyes encapsulated in organic-inorganic hybrids having a talc-likestructure as fillers for photopolymers: preparation, surface characterizations and photophysical properties

Jocelyne Brendlé[1,*], Christian Ley[2], Eric Brendlé[3], Adrian Beda[1,2]

[1]Institut de Science de Matériaux de Mulhouse, CNRS UMR 7361, Université de Haute-Alsace, Univer-sité de Strasbourg, 68083 Mulhouse, France

[2]Laboratoire de Photochimie et d'Ingénierie Macrololéculaires, EA 4567, Université deHaute- Alsace, 68083 Mulhouse, France

[3]Adscientis, 68310, Wittelsheim, France

*jocelyne.brendle@uha.fr

The sol-gel process enables the formation of clay-mimicking compounds with unique properties. This one- step method is performed at room temperature involves the use of organotrialkoxysilanes (R-Si(OR')$_3$) were R stands for an organic moiety and R' for a methyl orethyl group with different functionalities, an aqueous or organic-solvent based solution of a magnesium salt, and in some case, an aqueous solution of sodium hydroxide. By this way, the organic chains are covalently bonded to the silicon of the tetrahedral sheets, pointing in the interlayer space and present at the surface.

In this study we focused first on the synthesis of (TLH) starting from organotrialcoxysilanes having different functionalities (mercaptopropyl, phenyl, and mixture of both), an ethanolic solution of a mag-nesium salt and thioxanthone (TX) a chromophore which has often been used as triplet sensitizers and photoinitiators of polymerization and has interesting photophysical properties. In a second step, a special attention was paid to the effectof TX confinement on its photophysical properties prior preparing photopolymer-TX-TLH composites. A special attention was paid to the surface characterization of the different samples by Inverse Gas Chromatography (IGC), a powerful tool to gather information on the dispersive component of the surface energy (g^d), surface nanoroughness and morphology as well as on the acid-base character.

The fine tuning of the key parameters gove rning the synthesis enables the formation of lamellar structures at 20°C in less than 24h. The samples wera characterized by X-Ray diffraction. X- Ray fluorescence spectrometry thermogravimetric analysis, Fourier Transformed Infrared spectroscopy. Structural investigations performed by ^{13}C and ^{29}Si solid state NMR confirmed the integrity of the pendant organic chainsto the inorganic framework as well as on the integrity of TX and the degree of polycondensation of silicon species. Femtosecond pump-probe and steady state UV-Visible measurements gave information about the the photophysical properties. Photopolymer-TX-TLH composites were obtained with different fillerscontent.

This set of experiments showed that the the combination of TX and TLH leads to very interesting hybrid materials showing original properties and having a high potential as fillers for polymers and photopoly-mers.

Hybridization of organic compound onto optically manipulated clay surface

Takumi Harada[1,2,*], **Masahiro Yahara**[2], **Yasutaka Suzuki**[1,2], **Jun Kawamata**[1,2]

[1]Graduate School of Sciences and Technology for Innovation, Yamaguchi University, Yamaguchi 753-8511, Japan
[2]Facultyof Science, Yamaguchi University, Yamaguchi 753-8511, Japan

*i059df@yamaguchi-u.ac.jp

When aqueous solution of a cationic organic compound is mixed with an aqueous dispersion of exfoliated clay layers, organic compound is typically adsorbed on all clay layers. In this study, we aimed at hybridization of organic compounds onto a specific clay layer in aqueous dispersion. To this end, water-organic solvent interface was utilized. When solution of an organic compound dissolved in a water immiscible solvent is poured on a water phase, organic compound gradually dispersed into the water phase. This creates a situation in which small amount of organic compound exists only nearby the interface in the water phase. One specific clay specimen was then transported near to the interface by the optical manipulation technique. As a result, only the transported clay specimen could selectively be hybridized with the organic compound.

Water-organic solvent interfaces consisting of aqueous dispersion of fluorohectorite (FHT) and toluene solution of 1,3-dimethyl-4,4-(9,9-diethyl-2,7-fluorenediyl-2,1-ethe-nediyl)-dipyridinium iodide (FL), (1-pyrenedi-2,1-ethanediyl) pyridinium iodide (mono-PY), and 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21H,23H-porphine tetra-p-tosylate (TMPyP) were prepared. One FHT specimen exfoliated into single layer was optically transported to the interface according to the previous report (Higashi, 2018).

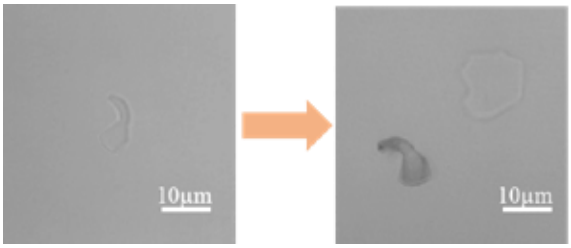


Figure 1 Microscope images of FHT before (left) and after (right) optical transportation.

Microscope images of FHT before and after optical transportation to (toluene solution of FL)-(water dispersion of FHT) interface are exemplified in Figure 1. Before transportation, FHT appears in Figure 1 (left) was transparent (colorless). Figure 1 (right) shows an image when one FHT specimen transported to interface was further transported to the water phase far from the interface. Transported FHT specimen looks black reflecting the adsorption of organic compound. Together with the black FHT, colorless FHT can be seen in the same focal plane. Thus, the selective adsorption of an organic compound onto only one specific clay specimen can be realized by utilizing the water-organic solvent interface and the optical manipulation technique.

Y. Higashi et al. *Clay Sci.*, 22(3), 79-83, 2018

Fabrication of ordered interstratification phased hybrids consisting of several photo-functional amphiphiles with different length of alkyl chains

Mahito Shintaku*, Yasutaka Suzuki, Jun Kawamata

Graduate School of Sciences and Technology for Innovation, Yamaguchi University, Yamaguchi 753-8512, Japan

*i037df@yamaguchi-u.ac.jp

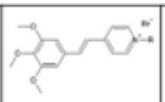
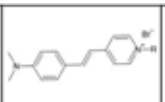
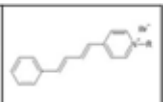
When cationic organic compounds are adsorbed on a clay in an aqueous dispersion, obtained clay-organic compound hybrids tend to form aggregation. Although the hybridization of organic compounds brings the com- pounds on unique electronic properties, different from those in solution and/or in the solid state, the aggregation of hybrid often hinders such electronic properties. Therefore, preparation of colloids of hybrid without aggregation is indispensable for maximizing electronic properties of hybrids. It is reported that ordered interstratification(OI) phased hybrids can be well dispersed in water even at a high concentration (1). The OI phased hybrids can be prepared using amphiphilic organic compounds as the guest. To reveal structural features of the functional organic compounds which favor to form OI phase, we attempted prepared of OI phased hybrids byemploying several amphiphilic photo-functional organic compounds.

OI phased hybrids were prepared by employing three kinds of cationic chromophores equipped with an alkylchain with different lengths. Sodium-fluorohectorite (FHT) provided from Prof.

J. Breu was used as the host clay. The hybridization was conducted according to [1]. Formation of OI phase was evaluated using microscope observation and X-ray diffraction (XRD) measurements.

Structures of chromophores are illustrated in Table 1, where R denotes alkyl chain. The presence or absence of OI phased hybrid when employing each chromophore are summarized in Table 1. Obtained colloids were classified into three types. In table 1, circle denotes colloids in which OI phased hybrid was the main component. Triangles indicate colloids in which OI phased hybrid, aggregated hybrid and unhybridized FHT coexisted. Cross indicates colloid in which aggregated hybrid and unhybridized FHT coexisted and no OI phased hybrid was found. As shown in Table 1, OI phased hybrids were main component for all chromophores when the length of the alkyl chain was 16 or 18. This suggests that the length of the alkyl chain, rather than the molecular structure of the chromophore, is the dominant factor in the formation of OI phased hybrids.

Table 1. The presence or absence of OI phased hybrid when employing various chromophores.

Carbon numbers (*n*)			
10	△	△	×
14	○	△	○
16	○	○	○
18	○	○	○
22	△	△	△

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Genesis of smectites associated with coal seams succession in the Neogene Orhaneli and Keles coal deposits (Bursa), NW Turkey

Hülya Erkoyun[1], Selahattin Kadir[1], Tacit Külah[2,*]

[1]Eskişehir Osmangazi University, Department of Geological Engineering, TR-26040 Turkey
[2]Kütahya Dumlupınar University, Department of Geological Engineering, TR-43100 Turkey

*tacitkulah@gmail.com

The Bursa-Orhaneli and Keles-Harmanalan coal deposits were developed in the swampy and lacustrine environments in western Anatolia under the E-W trending graben zone during the Neogene period. The aim of this study was to determine the detailed mineralogical and geochemical properties, and genesis of smectites and associated clays interlaying the coal seams in order to determine the deposition environment. These deposits comprised of argillaceous sediment, marl, coal seam, mudstone, organic-rich shale, sandstone, and conglomerate were deposited in a lacustrine environment accompanied by volcanogenic materials. Rhyolitic tuff and andesitic tuffite, sandstone, organic-rich-sandstone, and organic-rich shale host rocks of the coal deposits are characterized by partially to completely argillized and sericitized sanidine and plagioclase, muscovite, rock fragments, and organic matter in carbonate and clay groundmass. Smectite, kaolinite, illite, and heulandite/clinoptilolite are the main alteration minerals associated with quartz, feldspar, pyrite, aragonite/calcite, dolomite, siderite, and amphibole. Flaky authigenic smectite formed by the devitrified volcanic glass and resorbed feldspar in tuffaceous volcanic units and detritic irregular outlined cementing the volcanogenic fluvial sediments such as organic-rich shale, sandstone, and mudstone. The slight enrichment of light rare earth elements (LREE) compared to heavy rare earth elements (HREE) with positive Eu and Ce anomalies reflects fractional crystallization of feldspar and amphibole. The negative correlation of Al_2O_3 vs. SiO_2 and the positive correlation of Zr/Ni vs. Zr/Co and K_2O vs. Rb reveal that plagioclase, alkali feldspar, biotite was replaced with smectite, kaolinite, and illite during the alteration processes. Alteration of feldspar and volcanic glass resulted in the concentration of Al, Fe, Mg, and K in a stagnant environment, favored the precipitation of smectite in tuff/tuffite in organic-rich shale, mudstone, and sandstone, and illite in an alkaline environment. The chemical analyses of smectite-rich clay fractions show montmorillonite composition with the average structural formula of: $(Ca_{0.42}Na_{0.25}K_{0.08})(Al_{2.76}Fe_{0.47}Mg_{0.59}Ti_{0.07}Mn_{0.002})(Si_{7.65}Al_{0.35})O_{20}(OH)_4$

Kaolinite precipitated in an acidic open hydrological system. An increase in Ni/Co and V/(V+Ni) ratios in the altered units also suggest oxic, suboxic to anoxic conditions. Association of the argillization and silicification with coal, pyrite, and chalcopyrite indicates a swampy environment and partial influence of hydrothermal processes. The calculated formation temperature of 106.7–233 °C for smectite, 135.8 °C for illite, and the wide range $d^{34}S$ isotope values (–1.5–15‰) indicate a signature of both diagenetic and hydrothermal origin for the clay and sulfide minerals.

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Preparation of antimicrobial thermoplastic starch/clay films by using different starch sources

Ayşe Tuğce Çokkuvvetli[1,*], Öznur Yolaçan[1], Ceren Alpaslan Güler[1,2], Sennur Deniz[1]

[1]Yıldız Technical University, Department of Chemical Engineering, 34210 Turkey
[2]Elif Plastik Ambalaj San. ve Tic. A.Ş.

*ayse.tugce.cokkuvvetli@elif.com

Thermoplastic starch (TPS) is the form of starch, which is a biopolymer of natural origin, which can be processed by traditional polymer processing methods as a result of heat treatment with helping by plasticizers. The main reasons why thermoplastic starch is preferred in the production of bionanocomposite flexible packaging are its renewable, toxin-free, compostable and 68% less greenhouse gas emissions compared to traditional plastic production [1]. Pure starch films are brittle due to strong intra- and intermolecular hydrogen bonding. Therefore, it needs to be plasticized. Starch films are known to be effective barriers to O_2 and CO_2, but they are highly permeable to water vapor. So, final thermoplasticized starch films need to be improve barrier properties [2-4].

The aim of this study, thermoplasticization process was to be conceived for two different starch types (corn and potatoes) in accordance with hydrolization parameters which are consisting of hydrolysis temperature, time, plasticizer ratio by using experimental design program. The pure thermoplasticized starch films obtained were subjected to mechanical, optical and thermal characterizations. After determining of optimum hydrolysis conditions, antimicrobial agent (Turkish Oregano natural essential oil) is integrated into film structure. At last stage, clay is added with different ratios (1-5 wt%) into optimum antimicrobial TPS formulation. Mechanical, thermal and barrier characterization tests of the final antimicrobial TPS/ clay bionanocomposite films were performed. The effect of three differet types of clay additives on antimicrobial bionanocomposite films properties was investigated.

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The effect of different clay types on the barrier properties of PLA/PBAT biocomposite packaging films

Ceren Alpaslan Güler[1,2,*], Öznur Yolaçan[1], Ayşe Tuğçe Çokkuvvetli[1], Sennur Deniz[1]

[1]Yıldız Technical University, Department of Chemical Engineering, 34210 Turkey
[2]Elif Plastik Ambalaj San. ve Tic. A.Ş.Esenyurt, 34538 İstanbul, Turkey

*ceren.alpaslan@elif.com

Disposal of petroleum based plastic packages leads to a serious environmental problem worldwide because of nonbiodegradable. In addition, using of petroleum-based plastics are avoided because the formation of microplastics has a negative effect on human health. Therefore, biodegradable packaging is gaining importance for their daily use [1-3].

In this study, firstly neat binary biopolymer blends which are consisting of PLA/PBAT is first compounded by using a lab-scale twin screw extrusion. At this point it is important to determine the optimum PLA/PBAT blend ratio and extrusion conditions. Compounding of PLA blends are performed for various blend ratios (in the range of 20-40 wt.% PLA) and twin screw rotation rate and then PLA/PBAT films blends films are prepared by using a lab-scale single screw blown film extruder. For all blend films, characterization tests are carried out to obtain mechanical, optical, barrier and thermal properties. The properties of PLA/PBAT films are compared with industrial PE (poly ethylene) film as a reference food packaging film. Optimum blend ratio is found when below of 25 wt.% of PLA. According to optimum blend ratio five types of clay are added during compounding process and bionanocomposite film are obtain by blown film extrusion. The effects of five different clay (1-5 wt.%) types and their ratios on the barrier properties of the films were investigated.

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The effect of pyrolysis temperature on the physochemical properties of smectite mineral from Çanakkale -Turkey

Davut Laçin[1], **Ayşe Zehra Aroğuz**[2]

[1] Department of Geological Engineering, Faculty of Engineering, İstanbul University-Cerrahpasa, 34320 İstanbul, Turkey
[2] Department of Chemistry, Faculty of Engineering, İstanbul University-Cerrahpasa, 34320 İstanbul, Turkey

davut@iuc.edu.tr

A thick volcanogenic sequence of Lower-Middle Miocene consisting of rhyolite, rhyodacite and andesite characterized by lavas, tuff and agglomerates (Biga Volcanics) located the east of Biga, Çanakkale. The smectite mineral (montmorillonite) developed along the cracks of the perlites at certain levels of the rhyolites in this sequence. Alteration levels montmorillonite-bearing are pink colored, quite pure and their oriented and non-oriented XRD records did not reveal the presence of any other mineral other than montmorillonite. Moreover, their electron microscope (SEM) studies indicate that they had a typical smectite appearance.

In this study, the mineralogical behavior of natural pink smectite gathered from the Çanakkale region was investigated by X-ray diffraction (XRD) method at different pyrolysis temperatures in both oxidizing (with oxygen) and reducing (without oxygen) environments. In reducing environment, four different pyrolysis temperatures were selected as 200°C, 300°C, 400°C and 550°C, respectively. Based on XRD data, it was observed that the same smectite sample have obvious changes at different pyrolysis temperatures in the reducing environment, while the usual smectite-mica structure transformation (Paragonite) and the presence of rutile mineral is observed at 550°C in an oxidizing environment. At low pyrolysis temperature as 200°C, the structure and mineralogical composition of smectite mineral did not notable change, while significant changes were observed at high pyrolysis temperatures between 300 and 550°C.

The smectite mineral with different compositions and different XRD patterns at various pyrolysis temperatures shows that the pyrolysis temperature strongly affects some physicochemical properties and surface structure related to the increase of surface area as a result of pyrolysis. In the literature, the properties of some materials at different pyrolysis temperatures have been investigated and similar results were proposed which support the results obtained in this study.



Figure 1. Folded perlite levels and smectite minerals between them (north of Işıkeli Village).

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TS34 General Session

POSTER PRESENTATIONS

Electrocatalytic behavior of pillared montmorillonite-supported cobalt oxide doped with Cu, Zn, Fe, and Ni for glucose sensing

Biljana Milovanović[1,*], Rada Petrović[2], Sanja Marinović[1], Aleksandra Milutinović-Nikolić[1], Predrag Banković[1], Tihana Mudrinić[1]

[1]University of Belgrade - Institute of Chemistry, Technology and Metallurgy, National Institute of the Republic of Serbia Department of Catalysis and Chemical Engineering, Njegoševa 12, Belgrade, Serbia

[2]University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia

*biljana.milovanovic@ihtm.bg.ac.rs

Aluminum pillared montmorillonite-supported cobalt (Co/AP) has proven to be a suitable non-enzymatic sensing material (Mudrinić, 2019). Beside low cost, Co/AP exhibited adequate electrocatalytic performance toward glucose. However, further improvements of electrocatalytic performances are needed, especially regarding increasing sensitivity and widening the linear range of glucose detection.

In this regard, in addition to the monometallic cobalt oxide catalyst, a series of bimetallic catalysts supported on AP (Co+Cu/AP, Co+Zn/AP, Co+Fe/AP, and Co+Ni/AP) have been synthesized by the incipient wetness impregnation method (Pinna, 1998). The total amount of supported metal was fixed at 4 mass%, while cobalt:dopant molar ratio was 9:1 for all samples. The synthesized materials were prepared in the form of carbon paste electrode (Co+dopant/AP-CPE) with the same mass ratio of Co+dopant/AP to carbon black (CB) and applied as a working electrode.

All the electrochemical measurements of each Co+dopant/AP-CPE were conducted using an Autolab PGSTAT302N potentiostat with Nova 2.1 software. The experiments were carried out in a three-electrode cell with prepared electrodes as working, Ag/AgCl (3 M KCl) as a reference electrode, and platinum rod as a counter electrode. Electrochemical behavior of the working electrodes for glucose detection was studied by the cyclic voltammetry and chronoamperometry in alkaline solution, with and without glucose. Among investigated electrodes for glucose electrooxidation, the Co+Fe/AP-CPE exhibited the highest current response with the best sensitivity. These very first results indicated a vital role of Fe in enhancing the glucose-sensing performance of aluminum pillared montmorillonite-supported cobalt. The physical chemical characterization of all Co+dopant/AP materials is ongoing.

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Mudrinić, T., Marinović, S., Milutinović-Nikolić, A., Jović-Jovičić, N., Mojović, Z., & Banković, P. (2019). Novel non-enzymatic glucose sensing material based on pillared clay modified with cobalt. *Sensors and Actuators B: Chemical*, https://doi.org/10.1016/j.snb.2019.126976.

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Electrocatalytic activity of different cobalt oxides supported on mineral oxides toward glucose oxidation

Tihana Mudrinić*, Biljana Milovanović, Sanja Marinović, Srđan Petrović, Jugoslav Krstić, Predrag Banković, Aleksandra Milutinović-Nikolić

University of Belgrade - Institute of Chemistry, Technology and Metallurgy, National Institute of the Republic of Serbia, Department of Catalysis and Chemical Engineering, Njegoševa 12, Belgrade, Serbia

*tihana@nanosys.ihtm.bg.ac.rs; tihana.mudrinic@ihtm.bg.ac.rs

In recent years, mineral oxides (i.e. zeolite, alumina and clay minerals)-supported non-precious transition metals have extensively studied as highly promising sustainable and green glucose-sensing materials (Hassaninejad–Darzi 2016; Li 2009; Mudrinić 2019). The reason for that is their low cost, easiness of synthesis, low negative environmental impact, and desirable electrochemical properties toward glucose oxidation.

It is widely accepted that the catalytic activity of the mineral oxides-supported cobalt is strongly influenced by cobalt-mineral oxide interaction. As a consequence of this interaction different cobalt oxides (Wang 1991) could be formed: Co_3O_4-contains both cobalt ions in tetrahedral (Co^{2+}_{Td}) and octahedral (Co^{3+}_{Oh}) coordination and $CoAl_2O_4$-contains only Co^{2+}_{Td}. However, little is known about the catalytic activity of these cobalt oxides (i.e. cobalt ions) in the reaction of the electro-oxidation of glucose.

In this work, cobalt oxides in both tetrahedral (Co^{2+}_{Td}) and octahedral (Co^{3+}_{Oh}) coordination and with only Co^{2+}_{Td} were synthesized on aluminum pillared clay (AP) and alumina (A). The obtained materials were characterized by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and temperature-programmed reduction (TPR). Electrochemical measurements were performed in alkaline solution with and without glucose using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronoamperometry (CA). TPR and XPS along with the results of electrochemical measurements in alkaline solutions without glucose confirmed the successful synthesis of the different cobalt oxides on both AP and A. The electrochemical measurements in glucose-containing solutions showed the enhanced electrocatalytic activity of AP and A with Co^{2+}_{Td} in comparison to their counterparts with both Co^{2+}_{Td} and Co^{3+}_{Oh}. This result suggested that the Co^{2+}_{Td} acted as the main active site for the glucose oxidation.

Acknowledgement: This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. Grant No. 451-03-68/2022-14/200026).

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Valorization of furfural in one-pot reaction using Al- and Zr-PILCs as catalysts

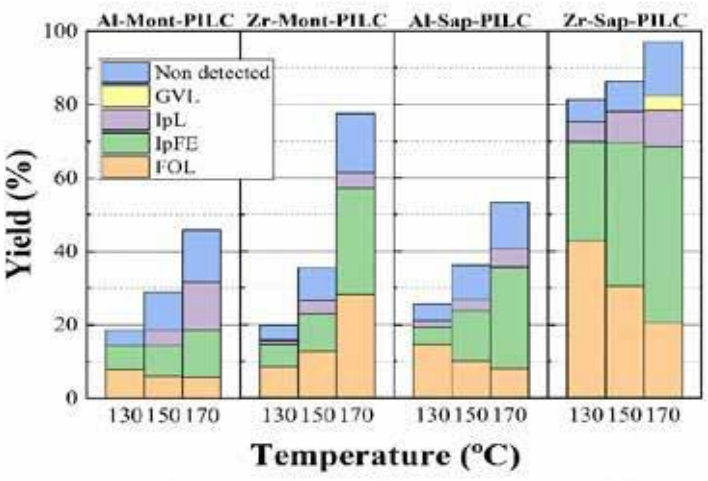
Salima Es Sih[1], Juan Antonio Cecilia[1*], Carmen Pilar Jiménez Gómez[1], Cristina García-Sancho[1], Francisco Franco-Duro[1], Ramn Moreno-Tost[1], Pedro Maireles-Torres[1]

[1]Universidad de Málaga, Department of Inorganic chemistry, mineralogy and crystallography, Málaga 29071, Spain

*jacecilia@uma.es

The depletion of fossil fuels has given rise to the search and development of new sources of energy and chemical products. In this sense, lignocellulosic biomass has emerged as interesting alternative due to its high availability and low cost. Focusing on the hemicellulose fraction, its hydrolysis leads to their respective monomers, mainly xylans, which can be dehydrate with the use of acid catalyst, obtaining furfural.

Furfural is considered as valuable product since a wide range of valuable products can be obtained from different reactions. In the case of the hydrogenation reactions, furfural can be hydrogenated to form furfuryl alcohol using a Lewis catalyst. This compound shows high interest since it is used in the field of polymer field. However, it the strength of these acid is strong, it is possible to obtain other interesting products such as alkyl levulinates, or valerolactones, which are also considered as valuable products.
In the present study, two smectites (montmorillonite and saponite) have been selected to incorporate Al- and Zr-polyoxocations to form pillared clays. These materials have shown high proportion of acid sites and high activity in the valorization of furfural in a one-pot reaction [1].



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Whole rock and clay mineralogy of Oligocene sedimentary rocks outcropped in Muş Basin (Eastern Anatolia)

Turker Yakupoğlu[1,*], Safa Serdar[2]

[1]Van Yuzuncu Yil University, Department of Geological Engineering, 65080 Van, Turkey
[2]Municipality of Bitlis, 1300 Bitlis, Turkey

*turkery@yyu.edu.tr

The study area is located in in the northeast of Korkut district of Muş province and covers an area of approximately 200 km². Three stratigraphic sections were measured from the area as Kelereeşdre, Taıçşla and Gltepe. A total of 506 m thick sedimentary sequence was measured along these sections and a total of 80 samples were collected as the material to be studied. All of the samples were analyzed by X-ray diffraction method, and the mineralogical compositions of the whole rock and clay fraction were determined. Quartz, feldspar, mica, calcite, amphibole and clay minerals were determined in whole rock compositions of the samples. In the clay fractions, smectite, illite, chlorite, chlorite-smectite, illite-smectite and serpentine minerals were detected as clay minerals. Scanning electron microscopy and energy dispersive spectroscopy studies were conducted on five selected samples. The presence of clay minerals such as serpentine, chlorite and smectite was observed in these samples. In this study, semi-quantitative percentage ratios of whole rock components by X-ray diffraction were also calculated. Pipette analysis was performed on selected samples and specific surface area was determined by BET method. Although the clay percentages obtained from the pipette analysis results and the specific surface area determination results were compatible, it was determined that they were not compatible with the semi-quantitative percentages.

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Paleoclimatic records from the Fuente Nueva 1 Section (Orce, Guadix-Baza Basin, Ne Granada, Spain): preliminary mineralogical data

Mara-Dolores Rodrguez-Ruiz[1*], Alejandro Granados[2], Mara-Patrocinio Espigares[2], Sergio Ros- Montoya[2], Paul Palmqvist[2], Bienvenido Martnez-Navarro[3], ngel Santamara[4], Antonio Guerra- Merchn[2]

[1]Departamento de Qumica Inorgnica, Cristalografa y Mineraloga. Universidad de Mlaga, 29071Mlaga, Spain
[2]Departamento de Ecologa y Geologa. Universidad de Mlaga. Campus de Teatinos, 29071 Mlaga, Spain
[3]ICREA, IPHES-CERCA. Universitat Rovira i Virgili, 43007 Tarragona, Spain
[4]Departamento de Geologa. Universidad de Salamanca, 37008 Salamanca, Spain

*mdrodriguez@uma.es

The mineralogical study of forty-five samples collected from the Fuente Nueva 1 (FN1 section (Orce, NE Granada, Spain has been carried out using X-ray diffraction data on bulk powder and <2 mm fraction to the establishment the paleoclimatic record and the origin of the inputs into the basin. The FN1 section is located in the north-eastern part of the post-orogenic Guadix-Baza Basin, located in the central sector of the Betic Cordillera. During the Pliocene and Pleistocene, the Guadix sub-basin was dominated by alluvial and fluvial sediments, while the Baza sub-basin was dominated by lacustrine deposits. The FN1 section (in Baza basin comprises a lower unit of Pliocene age consisting of lacustrine limestones and marls. Discordant on it, the Pleistocene is characterized by an alternation of two alluvial and two lacustrine episodes. In the first lacustrine episode is located the paleontological site of FN1 (approx. 2.3 Ma, which represents the oldest Pleistocene macrovertebrate site of Baza sub-basin. Moreover, this basin preserves some of the earliest evidences of human presence in Europe in several archaeo-paleontological sites correlated with the second Pleistocene lacustrine episode of FN1 section.

The climate during the deposition of FN1 section was temperate to warm-subarid with seasonal contrast as suggested the high occurrence of 2:1 layer phyllosilicates. The subarid conditions were more remarkable in the first Pleistocene alluvial episode as attested by an increase in palygorskite and precipitation of gypsum. Whereas, at the end of the second alluvial episode, the humid conditions were established as showed by lack in palygorskite and increase in illite and kaolinite. The variable quartz/phyllosilicate (Qz/Phy relation suggests changing source areas along the deposited. Specifically, the high Qz/Phy and occurrence of muscovite and paragonite in samples at the end of the second Pleistocene lacustrine episode indicate a high detrital input from the Internal Zone outcrop in the south of the basin. Further studies include a precise characterization of morphology and geochemistry of the clay minerals in order to provide better paleoclimatical and paleoenvironmental characterization of basin.

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Modification and change in the distribution of Si-Al network toward Pb- rich mining waste incorporation into metakaolin-based geomaterial by XASinvestigations

Emmanuel Joussein[1,*], Alexandra Courtin[2], Erwan Paineau[3], Marilyne Soubrand[1], Solenn Reguer[4], Delphine Vantelon[5]

[1]Université de Limoges, FST, E2Lim, 123 avenue Albert Thomas, 87060 Limoges, France
[2]Université Paris Saclay, Géosciences Paris Sud GEOPS UMR CNRS-UPS 8148, 91400 Orsay, France
[3]Laboratoire de Physique des Solides, CNRS, Université Paris-Saclay, 91405 Orsay, France
[4]Synchrotron Soleil, Diffabs Beamline, L'Orme des Merisiers, 91190 Saint-Aubin, France
[5]Synchrotron Soleil, Lucia Beamline, L'Orme des Merisiers, 91190 Saint-Aubin,France

*emmanuel.joussein@unilim.fr

Since the beginning of industrialization, smelting and/or mining activities allow many various contaminatedmineral wastes to be released in the environment without management. Although contaminated, these materials represent an excellent source of raw materials for manufacturing new compounds, if the contaminants can beinerted. Alkaline activation technology provides an ideal binder for the immobilization of toxic contaminants because of its low permeability, resistance to acid attack and long-term durability. The geomaterials result from the dissolution under alkaline conditions (Na or K-based) of reactive aluminosilicate precursors (metakaolin) following by a polycondensation reaction ($Si[OH]_4$ and $Al[OH]_4$ oligomers), which generates an amorphous 3D network. Moreover, the role of metallic elements in geomaterial networks can increase the structural strength. In the case of Pb-rich waste materials, the mechanisms of underpinning immobilization and distribution of Pb in geopolymers is also primordial to understand the relation with Si-Al networks. In this context, different formulations have been explored, according to (i) the % of Pb-rich mining waste (1 and 3 wt.% Pb) and (ii) the counter ion Na or K for the alkaline dissolution. To go further, an overall description of the structural transformation of the Si-Al network (then their distribution) has been obtained during the incorporation of waste and the dissolution of Pb-rich phases. It was indeed proposed that Pb act as network former in the Si-Al matrix (sup-posed like glass material). Microfocus experiments will be performed at the Al, Si, Na and K K-edge on LUCIA beamline whereas Pb K-edge from DIFFABS beamline (synchrotron Soleil).

These experiments provide a deep insight of the mechanisms of Si, Al distribution into geomaterial network. In particular, the modification involved in this network, the role of Na and K, as well as the influence of toxic element (Pb) incorporation and distribution into the geomaterial matrix have been unraveled thanks to the combination of XAS measurements at different K-edges (Al, Si, K and Pb). About Pb, the results show that (i) the local environment around lead atoms is strongly altered during/after the reaction, (ii) as the Pb phase is incorporated, the sulfate form gradually evolved to an oxide form, which reveals the Pb-phases dissolution and reorganization, and finally (iii) the counter-ion used for activation has a significant effect. At the Si and Al K-edge, the results clearly show differences relative to (i) the cation used, and (ii) the amount of mining waste. Finally, the results of speciation and distribution of elements will be discussed toward mechanical properties and leaching tests.

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ORAL PRESENTATIONS

Geochemical signatures and intensity of hydrothermal alteration in the interpretation of the origin of Ahırözü (Mihalıççık-Eskişehir) kaolin deposits

Işıl Ömeroğlu Sayıt[1,*], Asuman Günal Türkmenoğlu[1], Ş. Ali Sayın[2], Kaan Sayıt[1]

[1]Middle East Technical University, Department of Geological Engineering, Ankara, Turkey
[2]Turkish Association of Economic Geologists, Kilis Sok. No:7/Çankaya/Ankara, Turkey

[*]isilomeroglu@yahoo.com

Hydrothermally originated kaolin deposits occur at the contact of granite-serpentinite rocks, situated to the southeast of Ahırözü-Hamidiye villages, Mihalıççık, Eskişehir-Turkey. The kaolin deposits were studied in two different locations, which are the Ayının Tepe kaolin pit and Hamidiye kaolins. Petrographical analyses, ICP-MS, ICP-ES, XRD, SEM-EDX, and O-H stable isotope analyses were performed to investigate chemical and alteration characteristics of the deposits (Ömeroğlu-Sayıt, 2018).

In the study area, argillic and propylitic alterations are attributed to secondary mineralizations. The first is peculiar to the granitic parent rock and is characterized by the presence of kaolinite, halloysite, natroalunite, and accessory pyrite (Ömeroğlu-Sayıt et al., 2018). Metamorphic/ultramafic igneous rocks in contact with the granitic intrusion are exposed to propylitic alteration for which chlorite-smectite-illite and carbonate minerals are the major alteration products (Ömeroğlu-Sayıt et al., 2018). The Alteration Index (AI) and Chlorite-Carbonate-Pyrite Index (CCPI) highlight the alteration types in the study area. The AI values are between 54-80 and 9-46 respectively from the Hamidiye and Ayının Tepe kaolins originated by the hydrothermally alteration of granitic rocks (Ömeroğlu & Günal-Türkmenoğlu, 2017; Ömeroğlu-Sayıt, 2018).

Chondrite-normalized trace and REE diagrams of the kaolin samples from both locations show significant characteristics that reflect the effects of the parent rock composition and the hydrothermal processes. While the variation of Cs, Ba, Rb, Th, U, Pb, and Nb is almost similar, higher values for Ce, Sr, Zr, Tb, Y, and Ta are characteristic of the Hamidiye samples (Ömeroğlu-Sayıt et al., 2018). The ΣREE concentration is also higher in the Hamidiye kaolin samples (Ömeroğlu-Sayıt et. al, 2018).

Considering the stable isotope values of the kaolin samples, the δD and $\delta^{18}O$ values varying between -80.86 and -88.81, and 5.03 to 8.73, respectively, indicate the influence of magmatic waters in the hydrothermal system and the parent rock alteration (Ömeroğlu-Sayıt, 2018).

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Mineralogy and geochemistry of hydrothermal alteration associated with the Triassic volcanogenic massive sulfide deposit in the Küre, Kastamonu, NE Turkey

Hülya Erkoyun[1,*], Selahattin Kadir[1], Tacit Külah[2], Mohamed El Hady Jdou[1]

[1]Eskişehir Osmangazi University, Department of Geological Engineering, TR-26040 Turkey
[2]Kütahya Dumlupınar University, Department of Geological Engineering, TR-43100 Turkey

*herkoyun@ogu.edu.tr

The Küre volcanogenic massive sulfide (VMS) deposit is the third-largest copper deposit (37.35 Mt) in Turkey, located in the Kastamonu region. The VMS deposit is being hosted by basalt and bituminous shale of the Triassic Küre ophiolitic complex of the Central Pontides which were altered by hydrothermal fluids under control of the seafloor volcanic activities. The chloritization, serpentinization, silicification, sericitization, carbonatization, and epidotization is abundant in the volcanic units hosted by the Küre VMS deposit. The gossan zone outcropped at the uppermost of the VMS deposit. The massive sulfide orebody consists of abundant pyrite and chalcopyrite, and few amounts of marcasite, magnetite, hematite, and sphalerite. The abundance of chlorite, locally smectite, and illite increase in the upper and outer zones. Pyrite and hematite/goethite associations with the silicified zone (quartz), locally talc and their precursor's olivine, pyroxene, amphibole, and feldspar. Micromorphologically, chlorite has an oriented platy form associated with flaky smectite/smectite-illite and sub-rounded iron oxide phases resembling goethite/hematite, blocky pyrite/chalcopyrite, and volcanogenic materials. Chlorite, iron oxide phases, and pyrite/chalcopyrite are also evidenced by their individual sharp EDX spectrum of Si/Fe/Al/Mg, Fe/ Co, and Fe±Cu/S, respectively. Local enhance of Ca, Ba, Sr, Pb, Zn, Ni, and V are detected. The slight enrichment of light rare earth elements (LREE) compared to heavy rare earth elements (HREE) with positive/negative Eu and positive Ce anomalies based on chondrite normalized rare elements reflect the different degrees of hydrothermal alteration and fractional crystallization of plagioclase. N-MORB normalized spider diagram demonstrates the depletion of HFSE (Nb, Zr, Y) relative to LILE (Rb, Ba, Sr). The enhancement of Ishikawa alteration indexes (AI) to the max. 99.55, resulted in gains of K_2O and depleted in Na_2O and the chlorite-carbonate-pyrite index (CCPI) to the max. 99.95 in the claystone and gossan zone show the intensity of the alteration process(es). The enrichment of Fe and loss of Mg are related to the concentration of chlorite and pyrite in the alteration and gossan zones. The enhance of K suggests the sericitization of K-feldspar. The enrichment of Pb, Zn, Cu, Co, Ni, As, V, and Ba, and the depletion of Na, Ca, Zr, Hf, Y, and Nb, and Co/Ni ratio>1 indicate the hydrothermal alteration during and following the VMS deposit.

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Geology, mineralogy and genesis of alteration in Tekneli (Niğde) and Delikkaya (Kayseri carbonate-hosted Pb-Zn deposits

Hülya Erkoyun*, Ali Jawadi

Eskişehir Osmangazi University, Department of Geological Engineering, TR-26040, Turkey

*herkoyun@ogu.edu.tr

Tekneli (Çamardı-Niğde) and Delikkaya (Yahyalı-Kayseri) carbonate-hosted Pb-Zn deposits are found in the Aladağ region, located northeast of eastern Taurus. These deposits are formed in faults and karstic caves with the effect of hydrothermal fluids and later supergene oxidation in Upper Permian and Jura limestones, argillaceous limestone and dolomitic limestones. The micritic and microspharitic limestones have locally coated clay and Fe oxy-hyroxide and consist of pellects, fragments of algae and foraminifera that high organic matter. Primary ore minerals are galena, sphalerite, pyrite, a lesser magnetite, secondary supergene minerals such as smitsonite, ceriusite, limonite, goethite and hematite, gangue minerals are calcite, dolomite, quartz, kaolinite, illite and smectite. The smectites are occur in the compact, bended flaky kaolinite and illite is located on the edge of kaolinite associated with star like goethite. The low silicification in the carbonate rocks indicate that Mississippi Valley Type (MVT deposit. The high Fe_2O_3 contents are 8.27-75.52% in iron oxidation zone and claystone shows associated with goethite, limonite, hematite, pyrite and marchasite and the high chemical index of alteration (CIA average values (71.51 and 76.52, respectively deposits show that intense chemical weathering. The high Ba, As, Cu, Co, Ni, Sb, and Mo ratios in iron oxide units and claystones indicate that the effect of hydrothermal fluid. The light rare earth elements (LREE exhibit slight enrichment relative to heavy rare earth element (HREE to claystones and the negative Eu and Ce anomalies indicate that oxidation of pyrite, precipated with from sea water. The low $\delta^{13}C$ values demonstrated shallow sea water carbonates and there is an external hydrothermal fluid flow in the Mississippi Valley Type (MVT) deposit. The high positive $\delta^{34}S$ values of galena and sphalerite show that galena and sphalerite were formed during under the influence of hydrothermal solutions, and indicate that the sulfur source comes from seawater and suggested the formation temperature of 127–243°C. The detritic kaolinite was formed effect of moderately acidic meteoric waters contact of limestones, nontronite that at low temperature (< 70ºC and mixture of hydrothermal fluids and ambient seawater and detritic illite was formed from K^+ that derived from seawater under supergene conditions.

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Geochemistry and mineralogy of clay-rich volcanic rocks related with Pb-Zn mineralization (Kirazlıyayla-Bursa, NW Turkey)

Farhad Jawid[1], Emin Çiftçi[1,*], Fahri Esenli[1], Şenel Özdamar[1], Bala Ekinci Şans[1], Naşide Merve Sütçü[1], Selahattin Kadir[2]

[1]İstanbul Technical University, Department of Geological Engineering, TR-34469 Turkey
[2]Eskişehir Osmangazi University, Department of Geological Engineering, TR-26040 Turkey

*eciftci@itu.edu.tr

Acidic hydrothermal solutions related to structurally controlled Eocene volcanism resulted in the formation of a number of clay minerals in and around Kirazlıyayla Zn-Pb deposit (Bursa, NW Turkey) owned by a local mining company. A total of 14 samples collected from the mine site (open pit) and ponds within the site were studied for mineralogical (by XRD) and geochemical characteristics (WD-XRF & ICP-MS). The ore deposit is hosted by highly altered andesitic volcanics of Eocene age, cutting through the base- ment metamorphics. Averages of the major oxide chemical analyses of altered volcanic rocks are (wt.%) SiO_2: 42.83 %, Al_2O_3: 20.04 %, Fe_2O_3: 7.56 %, TiO_2: 1.17, CaO: 4.71, MgO: 4.44, Na_2O: 0.75, K_2O: 3.46, SO_3: 1.35% and the loss on ignition (LOI): 13.24. In the open pit area, argillization has occurred as a result of alteration of the volcanic rocks as the main rock. The clay formation in the volcanic rocks in the open pit area has a clay mineral association that can be summarized as kaolinite + illite. Clay mineral content is below 50% in parent rock in general, whereas fine-grained material contains higher clay mineral asso- ciation (up to 80%). The general mineralogical composition of this material, which represents the whole area, is as follow: kaolinite (30-40%) + illite (15-40%) + carbonate minerals (<5-10%) + quartz (15-30%) + feldspar (<5-15%) + (other-trace phases including amorphous iron oxide-hydroxide, pyrite, allophane, anatase, amorphous opal). Except for one sample that was taken from the basement metamorphics, none of the samples contained smectite. Kaolinite and illite dominated along with quartz and feldspar relicts in the majority of the samples. Carbonate minerals are found to be dominantly dolomite along with minor to trace calcite, ankerite, magnesite, and smithsonite. Comparing to the parent volcanics, SiO_2, Al_2O_3 and K_2O increased in clay-rich material, whereas Fe_2O_3, CaO, MgO and LOI decreased. Hf, U, Th, Cd, Rb, Tl, La, Cs, Pb and Zn also increased in clay-rich material. Pb (0.042 %) and Zn (0.27%) in clay-rich material are approximately 20 and 10 times higher, respectively than that of parent volcanic rocks. Both kaolinite and illite are related to the pre-mineralization in the andesitic volcanics in the Kirazlıyayla deposit. On the other hand, there are two types of clay formations in the basement metamorphic rocks: First, bluish-black-ish clay formations attributed to hydrothermal origin and contained kaolinite, chlorite, illite, smectite, quartz, feldspar, dolomite, and calcite and second, brown colored clay formations found in the weathering zones of metamorphics that contained kaolinite, illite, quartz, feldspar and calcite.

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Occurrence and genesis of the hydrothermal Oysu kaolinite deposit in Miocene Karacahisar volcanics, Kütahya, western Anatolia, Turkey

Tacit Külah[1,*], Selahattin Kadir[2], Dur Mohammad Sakhizada[2]

[1]Kütahya Dumlupınar University, Department of Geological Engineering, TR-43100 Turkey
[2]Eskişehir Osmangazi University, Department of Geological Engineering, TR-26040 Turkey

*tacitkulah@gmail.com

The Oysu kaolinite deposit represents a potential source of raw material for tiles and glaze industries in Turkey. This study comprises the detailed mineralogical, geochemical, and isotopic characteristics of this kaolinite and discusses its origin, which has not been examined to date. The Oysu kaolinite was developed by hydrothermal alteration of Miocene Karacahisar volcanics that are composed of trachyandesitic, andesitic, dacitic, rhyodacitic tuffs, and lava flow, through the NW–SE trending dip-slip normal fault. The characteristics of the altered and fresh volcanic units were examined using polarized-light microscopy, X-ray powder diffractometry (XRD), scanning electron microscopy (SEM–EDX), and chemical (ICP–AES and –MS) and isotopic (H–O) methods. Mineralogical zonation, such as the abundance of kaolinite with silica veins and Fe-oxide stains close to the fault zone, at the central part of the deposit, an increase of illite and smectite outward, and occurrence of silica cap (opal-CT) upward sequence suggest that the kaolinization and associated alunitization were formed by the hydrothermal alteration process(es). Oysu kaolinite is identified by sharp peaks at 7.17 and 3.57 Å and alunite by 4.92 and 2.97 Å. Micromorphologically, kaolinite shows book-like and vermiform character edges devitrified volcanic glass and altered feldspar suggest *in situ* dissolution and precipitation mechanism. The positive correlation of SiO_2 vs. each of Zr and Nb and negative vs. Al_2O_3+Fe_2O_3+TiO_2. The leaching of Si, Mg, Ca, Na, K, Ba, Rb, Cs, and Zr, enrichment of Fe, Al, Mn, Ti, Sr, Zn, Pb, Cr, Ni, and V, an increase of *LREE*/*HREE* ratio, and the negative Eu anomaly reveal that the alteration of feldspar, hornblende, and devitrification of volcanic glass within the andesitic and dacitic tuffs. The δD and $\delta^{18}O$ compositions range from –94.32 to –69.63‰ and from 1.77 to 8.47‰, respectively, suggest an epithermal alteration process(es) and local contribution of meteoric water mixed with magmatic fluid during the hydrothermal activity.

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Alteration mineralogy and stable isotope characteristics of carbonate hosted Pb-Zn ore deposits in central and eastern Taurides (S-SE Turkey)

Ahmet Can Özbek[1], Abdurrahman Lermi[2], Selahattin Kadir[3], Emin Çiftçi[1,*]

[1]İstanbul Technical University, Department of Geological Engineering, 34469 Sariyer, İstanbul, Turkey
[2]Niğde Ömer Halisdemir University, Department of Geological Engineering, 51240 Niğde, Turkey
[3]Eskişehir Osmangazi University, Department of Geological Engineering, 26040 Eskişehir, Turkey

*eciftci@itu.edu.tr

Taurides being one of the major tectonic units constituting the Anatolia within the Alpine-Himalayan Orogenic Belt is a host to great number of various types of ore deposits and mineralizations with different sizes and contents. Among those, mostly structurally controlled carbonate-hosted lead and zinc mineralizations are major ones that are primarily epigenetic emplacements and their formations can be considered as structurally controlled in many occurrences. However, these occurrences as they stand are mineralizations of carbonates, silicates and oxides that may and may not contain relict sulfides. Some of them don't have any primary features and can even be considered to be non-sulfidic zinc deposits. The occurrences are hydrothermal Pb-Zn ore deposits; therefore, hydrothermal alteration can be observed near by the ore deposits and between ore and carbonate host rocks. Alteration mineralogy and stable isotope characteristics of the both ore and associated minerals were studied using X-ray diffraction and stable isotope geochemistry were used. Although the primary ore minerals are not diverse, alteration mineralogy shows considerable differences from district to district within the belt. Altered and clay-rich rocks were determined by XRD experiments. XRD study shows presence of kaolinite, dolomite, quartz, and montmorillonite as the important hydrothermal alteration products.

Oxygen isotope values of clay and hemimorphite-rich splits acquired from ore and advanced altered hostrocks vary in the range of -19.18‰ and +30.93‰, while deuterium (D) values fall in the range of -7.53‰ and -147.63‰. These values show scattered pattern on the $\delta^{18}O_{(SMOW)}$‰ vs $D_{(SMOW)}$‰ diagram plotting in meteoric water-sedimentary basin waters-hydrothermal waters fields, but when the data evaluated based on the subdistricts, the plot suggests that solutions have increasing basinal water component within the mixture from the Midwest towards the East Zamanti. Thus, the formation is due to mixed waters from more than one source.

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Supergene and hypogene characterization of clays within hydrothermal kaolin deposits of Etili (Çanakkale-Turkey)

Hatice Ünal Ercan[1], Ö.Işık Ece[2,3], Emin Çiftçi[2*], Ayça Aydın[2]

[1]KOTU, Chemistry and Chemical Processing Technologies, Konya, Turkey
[2]İstanbul Technical University, Department of Geological Engineering, 34469 Sariyer, İstanbul, Turkey
[3]University of Georgia, Department of Geology, Athens, GA 30602-2501 USA

*eciftci@itu.edu.tr

Çanakkale (NW Turkey) hosts numerous hydrothermal ore deposits and associated alteration zones in which clay formations took place at the points where hydrothermal solutions of Late Eocene-Miocene calc-alkaline volcanic rocks interfere with fault zones. Bahadırlı and Duman kaolin quarries are some of the important well-preserved kaolin sites occurring along the Etili fault zone. Distinguishing between the types of hypogene by supergene processes in these kaolins is important because the physical-chemical properties of minerals affected their potential for industrial applications. Mineralogical, geochemical, and geochronologic analyses were performed to identify the origin and formation environments of the solution that caused the formation of the Duman and Bahadırlı kaolin deposits. 29.7±0.1 to 32.4±1.2 Ma ages for alunite are consistent within the Late Eocene-Miocene calc-alkaline volcanic rocks.

Bahadırlı kaolin deposits have abundant kaolinite whereas Duman kaolin deposit is rich in halloysite. Alunite and jarosite minerals are other abundant alteration minerals in the deposits and other alteration mineral assemblages such as feldspars, illites, montmorillonites are subordinate. In Bahadırlı quarry quartz content is also high but in Duman quarry is low. Ba+Sr vs Ce+Y+La binary diagrams suggest hypogene origins for the Bahadırlı kaolin deposits but supergene origin for the Duman kaolins. REE contents of the samples of the Duman quarry are higher than the Bahadırlı quarry. $\delta^{18}O$ and δD isotopic values of Bahadırlı kaolinites ranged from +11,8 to +17.0 ‰ and -93 to -99 ‰ respectively, and +13.3 to +18.3 ‰ and -70 to -102 ‰ respectively for the Duman kaolinites which indicate two different formation types for the kaolin deposits. $\delta^{34}S$ isotopic values ranged from 19.8 to +20.2 ‰ for the Bahadırlı and ranged from -17.2 to +10.5 ‰ for the Duman alunite samples, respectively. These low and high isotopic values are due to bacterial activity.

All these data revealed that although similar hydrothermal processes were effective in the formation of the kaolin deposits of similar age, located very close to each other and on the same fault zone, however, there were mineralogical, chemical, and isotopic differences.

TS35 Hydrothermal Clays

POSTER PRESENTATIONS

Electrocatalytic activity of different cobalt oxides supported on mineral oxides toward glucose oxidation

Tihana Mudrinić*, Biljana Milovanović, Sanja Marinović, Srđan Petrović, Jugoslav Krstić, Predrag Banković, Aleksandra Milutinović-Nikolić

University of Belgrade - Institute of Chemistry, Technology and Metallurgy, National Institute of the Republic of Serbia
Department of Catalysis and Chemical Engineering, Njegoševa 12, Belgrade, Serbia

*tihana@nanosys.ihtm.bg.ac.rs; tihana.mudrinic@ihtm.bg.ac.rs

In recent years, mineral oxides (i.e. zeolite, alumina and clay minerals-supported non-precious transition metals have extensively studied as highly promising sustainable and green glucose-sensing materials (Hassaninejad–Darzi 2016; Li 2009; Mudrinić 2019)The reason for that is their low cost, easiness of synthesis, low negative environmental impact, and desirable electrochemical properties toward glucose oxidation.

It is widely accepted that the catalytic activity of the mineral oxides-supported cobalt is strongly influenced by cobalt-mineral oxide interaction. As a consequence of this interaction different cobalt oxides (Wang 1991 could be formed: Co_3O_4-contains both cobalt ions in tetrahedral (Co^{2+}_{Td} and octahedral (Co^{3+}_{Oh} coordination and $CoAl_2O_4$-contains only Co^{2+}_{Td}. However, little is known about the catalytic activity of these cobalt oxides (i.e. cobalt ions) in the reaction of the electro-oxidation of glucose.

In this work, cobalt oxides in both tetrahedral (Co^{2+}_{Td}) and octahedral (Co^{3+}_{Oh}) coordination and with only Co^{2+}_{Td} were synthesized on aluminum pillared clay (AP) and alumina (A). The obtained materials were characterized by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and temperature-programmed reduction (TPR). Electrochemical measurements were performed in alkaline solution with and without glucose using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronoamperometry (CA). TPR and XPS along with the results of electrochemical measurements in alkaline solutions without glucose confirmed the successful synthesis of the different cobalt oxides on both AP and A. The electrochemical measurements in glucose-containing solutions showed the enhanced electrocatalytic activity of AP and A with Co^{2+}_{Td} in comparison to their counterparts with both Co^{2+}_{Td} and Co^{3+}_{Oh}. This result suggested that the Co^{2+}_{Td} acted as the main active site for the glucose oxidation.

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KAOLIN: GENESIS, SURFACE CHEMISTRY, ADSORPTION, AND RARE EARTH ELEMENTS

New insights about the structure and surface chemistry of kaolinite and halloysite

Cliff T. Johnston

Departments of Earth, Atmospheric and Planetary Sciences and Agronomy, Purdue University, West Lafayette, IN 47907 USA

cliffjohnston@purdue.edu

Kaolin group minerals, which includes kaolinite and halloysite, are among the most distinctive and important members of the materials known as clay minerals. A distinctive feature about kaolinite and halloysite is that these structures are terminated by two different types of surfaces. As shown in Figure 1, the upper surface is referred to as the siloxane surface. The oxygen atoms on this type of surface are relatively weak electron donors (Lewis bases) with a small negative partial charge, and is not capable of having strong interactions with water molecules. Although most clay minerals have an overall hydrophilic character, this type surface is hydrophobic. In addition, kaolinite and halloysite possess a polar (i.e., hydrophilic), the terminating surface of the Al octahedral sheet of kaolinite, referred to as the hydroxyl surface. These hydroxyl groups and their interlayer interactions with the siloxane surface are responsible for a number of important properties, including the resistance of kaolin group minerals to chemical and physical weathering. For comparison, only the siloxane surface is found on the terminating surfaces are found on all members of the 2:1 phyllosilicates (talc, pyrophyllite, smectites vermiculite, mica, brittle micas and chlorites).

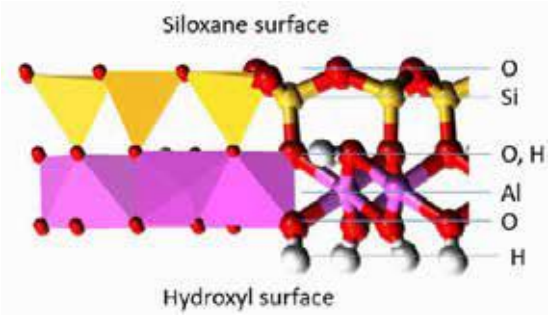


Figure 1

Because kaolinite is terminated by two different types of surfaces, the mineral possesses an overall electrostatic dipole. Related to the contrasting surface character of the siloxane and hydroxyl surfaces, recent years have witnessed an increase in interest about the role of kaolin group minerals stabilizing Pickering emulsions. In fact, kaolinite is a naturally occurring Janus particle. Two examples that illustrate the disparate nature of these surfaces will presented. The first will examine the interaction of complex hydrocarbon mixtures with kaolinite using high-resolution mass spectrometry. These studies revealed that hydrocarbons with no heteroatoms (i.e., non-polar) were preferentially bound to kaolinite over polarcompounds containing heteroatoms. The second will explore the interaction of water with the surfaces present in halloysite. The progressive dehydration of a fully hydrated tubular halloysite (1.0 nm) south- ern Indiana (USA), was investigated using a combination of low temperature differential scanning calorimetry (DSC), X-ray diffraction, electron microscopy, thermogravimetric analysis and attenuated total reflectance (ATR)-FTIR. Consistent with work on other phyllosilicates, interlayer H_2O remains unfrozen at detected by DSC scans down to -75 °C. Interestingly, the data also support a population of 0.31 H_2O molecules per half unit-cell formula of kaolinite that is assigned to a few layers of H_2O molecules bound to the hydrophilic surface found in the inner lumen of halloysite.

Kaolin genesis and alteration mineralogy

Michael C. Cheshire[1,*], David L. Bish[2]

[1]Chevron Technology Company, Houston, Texas 77402 USA
[2]Indiana University, Bloomington, Indiana USA

michael.cheshire@chevron.com

Kaolinite-group minerals consist of kaolinite, dickite, nacrite, and halloysite. The former three are all polymorphs ($Al_2Si_2O_5(OH)_4$) of a 1:1 dioctahedral phyllosilicate having a two-dimensionally continuous octahedral sheet of aluminum bonded to a tetrahedral sheet of silicon. Kaolinite-group minerals form during chemical weathering of micas and feldspars in warm environments with acidic fluids. Saprolitic, soil, sedimentary, and hydrothermal environments are the principal occurrences of the kaolin-group minerals. We will discuss the genesis and alteration geochemistry associated with each of these environments leading to the varied mineralogy that develops.

Kaolinite's main genesis appears to be associated with the chemical alteration of felsic materials, via a process known as saprolization. Rocks with a felsic composition tend to undergo saprolization in warm and humid climates with abundant rainfall that drains into the underlying rocks, leaching more-soluble elements and leaving behind a residuum of less soluble elements. Chemical leaching accelerates through microbial activity and under acidic conditions, especially conditions with high organic acid loads due to associated chelation functions. Parent materials become friable during saprolization facilitating denudation and loading of local transport systems with kaolinite, remnant felsic precursors, and quartz.

Kaolin deposition occurred primarily in coastal areas along deltaic to lagoonal areas. Sorting seems to have separated kaolinitic loads from quartzofeldspatic sediments, leading to kaolinitic lenses within sand-dominated intervals. Variable redox conditions during diagenesis within sedimentary deposits, drives successive mineral and organic transformations facilitated by microbial activity. Sulfate-reducing bacteria oxidize organic matter while producing sulfides, leading to pyrite/marcasite growth, and producing organic acids. Following sulfide crystallization, recrystallization and coarsening of kaolinite occur in the kaolin horizons probably under more oxic conditions leading to differentiated kaolinite properties. Upon erosion of overburden, weathering under oxic conditions proceeds. Further aqueous weathering and leaching leads to bauxitization of kaolins producing Al-(oxy)hydroxides and silica residues in the sedimentary kaolin lenses. Discussions will focus on the various diagenetic chemical reactions within sedimentary and saprolitic kaolin, especially deposits in Atlantic Coastal area as there is a genetic link between the kaolin types, and their similar formation, timing, and climatic conditions.

Dickite and nacrite can form under epithermal (50-200ºC) or mesothermal (200-300ºC) conditions, with nacrite believed to form under high stress conditions. Parent materials are felsic and are usually associated with volcanic-derived hydrothermal fluids. Another form of "hydrothermal" transformation is the kaolinite-to-dickite transition occurring within sandstones. Kaolinite alters to dickite at >120ºC via a complete recrystallization reaction within sandstone pore systems.

Adsorption, retention, and removal of metals and organics by kaolin minerals

Balwant Singh

Sydney Institute of Agriculture, School of Life and Environmental Sciences, The University of Sydney, Sydney, NSW 2006, Australia

balwant.singh@sydney.edu.au

Kaolin is a sub-group of 1:1 phyllosilicates, which have the structure made up of Si in the tetrahedral sheet and Al in the octahedral sheet. The sub-group consists of minerals - kaolinite, halloysite, dickite and nacrite. Kaolinite is ubiquitous clay mineral in many soil types, and it is often the dominant clay mineral in highly weathered soils in the humid tropics. Halloysite is the only other mineral that has been frequently identified in soils, particularly soils formed on volcanic ash and in some weathered soils. Ideally, kaolinite, especially from the geological origin has a little or no isomorphic substitution in the structure and the mineral is considered relatively inert in comparison to 2:1 phyllosilicates that occur in soils. However, research on kaolinite isolated from highly weathered soils demonstrated that soil kaolinites are different from their geological counterparts, having disordered structure, presence of structural Fe, and large specific surface area (Herbillon et al., 1976; Singh and Gilkes, 1992).

Containment of contaminated solid and liquid wastes depends on the adsorptive behaviour of soils. Because of the dominance of kaolinite in many soils, there has been research interest in the adsorption behaviour of kaolinite for both organic and inorganic contaminants. Kaolin minerals contain OH groups at the edge of both octahedral sheet, singly coordinated to Al^{3+}, called aluminol, and tetrahedral sheet, singly coordinated to Si^{4+}, called silanol (Sposito, 1989). The OH groups coordinated to Si^{4+} dissociate only protons, whereas the aluminol groups can dissociate and bind protons. In addition to these reactive sites at the edges, a flat oxygen plane is associated with the Si tetrahedral sheet and a hydroxyl plane is associated with the Al octahedral sheet. These different surfaces of kaolinite contribute and participate in chemical reactions with organic and inorganic compounds.

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The occurrences of the rare-earth elements in the coarse fractions of mined Georgia kaolins

W. Crawford Elliott[1,*], Prakash Malla[2]

[1]Department of Geosciences, Georgia State University, Atlanta, GA 30302 USA
[2]Research & Development Department, Thiele Kaolin Company, Sandersville, GA 31082 USA

*wcelliott@gsu.edu

World class kaolin ore deposits are located in the innermost Coastal Plain adjacent to the Fall Line in Georgia and South Carolina. The REE are found in the fine fraction of the mined kaolin ore (< 45 μm, Cheshire et al., 2018). This fraction is processed further for the kaolinite clay product. REE have also been characterized in the coarse fraction considered gangue or mine waste (grit) (> 45 μm; Elliott et al., 2018; 2019). The heavy subfractions of mine waste/coarse fractions of the mined Georgia kaolins contained sizeable concentrations of REE, enriched in the heavy REE, and select trace elements (Zr, Hf, Nb, Ta, U, and Th). The total REE was 5012 ppm for Buffalo Creek Member and 1648 ppm for the Jeffersonville Member (Elliott et al, 2018). The REE were hosted xenotime in these fractions. These REE are considered a possible coproduced resource from kaolins. The sources for the rare-earth containing mineral are open question(s). Monazite belts, saprolite from granite plutons adjacent to the Coastal Plain, phyllite schist, and, generally, Piedmont, Blue Ridge and Appalachian/Grenville terranes (Mertie, 1953; Cheshire et al., 2018; Bern et al., 2017; Dombrowski, 1993; Epperson et al., 2018) are possible sources for the REE-bearing minerals.

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https://cvent.utexas.edu/2023CMSAnnualMeeting

Contact Info: Michael.Cheshire@clays.org

Saturday (May 20th) Chlorite Short course.
Sunday (May 21st) Council Meeting
Monday-Wednesday (May 22nd – May 24th)
Bailey, Pioneer, Jackson Mid-Career,
Brindley Clay Science Award Lectures
Banquet and Poster Sessions
~120 presentations
Monday (May 22nd) evening poster session.
Tuesday (May 23rd) evening banquet.
Thursday (May 25th) Cave Field Trip.

Short course will cover chlorite geology, geochemistry, and mineralogy through lectures and core viewing.

Field trip will focus on clay mineralogy and geology of cave complexes in the Edwards Limestone near Austin, Texas

Organizing Committee
Meeting Organizers: Michael Cheshire (Chevron) and Timothy Fischer (Chevron)
Short Course: Toti Larson (UT-Austin, BEG) and Rebecca Stokes (USGS).
Field Trip: George Veni (National Cave and Karst Research Laboratory) and Jay Banner (UT-Austin)
Website Design and Facility Coordinator: Soo Teal (UT-Austin)



XVII ICC

ISTANBUL 2022

25 -29 JULY