Program and Abstracts

60th Annual Meeting
The Clay Minerals Society

University of Texas at Austin
May 20 – 25, 2023
60th Annual Meeting
The Clay Minerals Society

Held at the University of Texas-Austin
J.J. Pickle Research Center
May 20 – 25, 2023

Organizing Committee

Michael Cheshire, Chevron
Timothy Fischer, Chevron
Toti Larson, University of Texas-Austin, Texas Bureau of Economic Geology
Rebecca Stokes, U.S. Geological Survey
George Veni, National Cave and Karst Research Institute
Jay Banner, University of Texas-Austin
Vanessa Santo, BYK
Soo Teal, University of Texas, Austin

The Clay Minerals Society Administration

Mary S. Gray
The Clay Minerals Society
3635 Concorde Parkway, Suite 500
Chantilly, VA 20151-1125 USA
Phone: 703-652-9960 | Fax: 703-652-9951 | Email: cms@clay.org
Executive Committee (2022 – 2023)

President: Stephen Hillier (The James Hutton Institute)
Vice-President: Sabine Petit (University de Poitiers)
Secretary: Katerina M. Dontsova (University of Arizona)
Past President: Jeffrey A. Greathouse (Sandia National Laboratories)
Treasurer: Yuji Arai (University of Illinois at Urbana-Champaign)
Editor-in-Chief: Joseph W Stucki (University of Illinois at Urbana-Champaign)
Vice-President Elect: Ian Bourg (Princeton University)

Council members

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<th>Through 2023</th>
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2023 Contribution Sustaining Members

Dr. Richard K. Brown
Dr. Wen-An Chiou
Dr. Randall T. Cygan
Mary and David Gray
Dr. Stephen Guggenheim
Dr. Marc A Herpfer
Dr. Warren D. Huff

Dr. Cliff T. Johnston
Dr. Heather A.W. Kaminsky
Dr. Paul A. Schroeder
Dr. Branimir Segvic
Dr. Joseph W. Stucki
Dr. Lynda B Williams
Prof. Michael A Velbel
Awards

Marilyn and Sturges W. Bailey Distinguished Member Award

The Marilyn and Sturges W. Bailey Award, the highest honor of The Clay Minerals Society (CMS), is awarded solely for scientific eminence in clay mineralogy as evidenced primarily by the publication of outstanding original scientific research and by the impact of this research on the clay sciences. Service to clay mineralogy, teaching, and administrative accomplishments are not considered in the evaluation of nominees.

1968 – Ralph E. Grim  
1969 – C. S. Ross  
1970 – Paul F. Kerr  
1971 – Walter D. Keller  
1972 – G. W. Brindley  
1975 – William F. Bradley  
1975 – Sturges W. Bailey  
1977 – M. L. Jackson  
1979 – Toshio Sudo  
1980 – Haydn H. Murray  
1984 – C. Edmund Marshall  
1985 – Charles E. Weaver  
1988 – Max M. Mortland  
1990 – Joe L. White  
1990 – John Hower  
1991 – Joe B. Dixon  
1992 – Philip F. Low  
1993 – Thomas J. Pinnavaia  
1995 – W. D. Johns  
1996 – Victor A. Drits  
1997 – Udo Schwertmann  
1998 – Brij K. G. Theng  
2000 – Boris Zvyagin  
2001 – Keith Norrish  
2002 – Gerhard Lagaly  
2004 – Benny K. G. Theng  
2005 – M. Jeff Wilson  
2006 – Frederick J. Wicks  
2007 – No Award Made  
2008 – Norbert Clauer  
2009 – Joseph W Stucki  
2010 – J. M. Serratosa  
2011 – Sridhar Komarneni  
2012 – Akihiko Yamagishi  
2013 – Stephen Guggenheim  
2015 – James Kirkpatrick  
2016 – Lisa Keller-Kallai  
2018 – Gordon Churchman  
2019 – Dennis Eberl  
2020 – Eduardo Ruiz-Hitzky  
2021 – David L. Bish  
2022 – Jin-Ho Choy  
2009 – John Hower  
1990 – John Hower  
1990 – John Hower  
2009 – Joseph W Stucki  
2010 – J. M. Serratosa  
2011 – Sridhar Komarneni  
2012 – Akihiko Yamagishi  
2013 – Stephen Guggenheim  
2015 – James Kirkpatrick  
2016 – Lisa Keller-Kallai  
2018 – Gordon Churchman  
2019 – Dennis Eberl  
2020 – Eduardo Ruiz-Hitzky  
2021 – David L. Bish  
2022 – Jin-Ho Choy

George W. Brindley Clay Science Lecture

The G. W. Brindley Clay Science Lecture recognizes a clay scientist who will infuse the Society with new ideas, someone who is both a dynamic speaker and involved in innovative research. Dr. Brindley himself approved the concept of the Lecture, and the speaker should deliver a lecture that Brindley himself would applaud.

1984 – Walter Keller  
1985 – J. J. Fripiat  
1986 – Ralph E. Grim  
1987 – S. W. Bailey  
1988 – M. L. Jackson  
1989 – W. D. Johns  
1990 – Alain Baronnet  
1991 – Thomas J. Pinnavaia  
1992 – Philip Low  
1993 – Dennis D. Eberl  
1995 – Gerhard Lagaly  
1996 – Samuel M. Savin  
1997 – Paul H. Nadeau  
1998 – Bruce Velde  
1999 – Richard Eggleton  
2000 – D. M. Moore  
2001 – Robert Schoonheydt  
2002 – David L. Bish  
2003 – Alain Manceau  
2005 – Maria F. Brigatti  
2008 – Robert Gilkes  
2009 – M. F. Hochella Jr  
2010 – Randall T. Cygan  
2013 – Andrey Kalininchev  
2017 – Sridhar Komarneni  
2018 – Cliff T. Johnston  
2019 – Bruno Lanson  
2020 – No award Made  
2021 – No Award Made  
2022 – Lynda B. Williams
Marion L. and Chrystie M. Jackson Mid-Career Clay Scientist Award

The Award is to recognize mid-career scientists for excellence in the contribution of new knowledge to clay minerals science through original and scholarly research.

2008 – Hailiang Dong     2012 – Jeffery Post
2009 – Lynda B. Williams 2013 – George Christidis

Pioneer in Clay Science Lecture

The Award is to recognize research contributions that have led to important new directions in clay minerals science and technology.

1997 – Koji Wada          2010 – No Award Made
1999 – V. Colin Farmer    2012 – No Award Made
Meeting Sponsors

Platinum Level Sponsorship

Chevron  
Bureau of Economic Geology  
TEXAS Geosciences

CORESPEC ALLIANCE LLC  
NATIONAL CAVE & KARST RESEARCH INSTITUTE

Silver Level Sponsorship

Thiele  
QMINERAL
Parking

Parking fees are included in your registration. Permits have been emailed prior to meeting.

The University of Texas at Austin
Commons Event Services

Parking Map

J.J. Pickle Research Campus (PRC)
2961 Route Granberry Trail, Austin TX 78758
Public Transportation

803 | Burnet/S. Lamar (HIGH FREQUENCY ROUTE)

**803 WEEKDAYS**
- 5 AM - 7 AM: 16 MIN
- 7 AM - 6 PM: 10 MIN
- 6 PM - 8 PM: 15 MIN
- 8 PM - 12:30 AM: 20 MIN

**803 SATURDAYS**
- 6 AM - 8 PM: 15 MIN
- 8 PM - 12 AM: 20 MIN

**803 SUNDAYS**
- 6 AM - 7 PM: 15 MIN
- 7 PM - 11:30 PM: 20 MIN

MetroRapid is a frequency-based service. Real-time arrival/departure times may not be exact and may vary due to vehicular traffic and/or weather-related conditions.
(1) Commons Café: Commons Café is open Monday through Friday 7:30 am – 2 pm.

Off-site Eateries (also check out Google Maps for more food options)

(2) Austin Beerworks
(3) BJ’s Restaurant and Brewhouse
(4) Yucatan Tacos & More
(5) Mighty Fine Burgers
(6) Lupe Tortilla
(7) Jimmy Johns
(8) Many eating choices in the Domain.
(9) Hopsquad Brewing
(10) Oskar Blues Brewery Taproom
(11) Celis Brewery
(12) Starbucks
(13) Taquero Mucho
(14) Dos Salsas
(15) Turnstile
## Schedule at a Glance

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- **Short Course: Sybilla**
- **EX and Council Meeting**
- **Lunch**
- **Bailey Award Lecture**
- **Coffee Social**
- **Isotopes**
- **Energy**
- **Engineered**
- **Ex-Bentonite Field Trip, Gonzales, TX**
- **Lunch on own**
- **Break**
- **Poster Session**
- **Atrium**
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Session Descriptions

Critical materials and clays.
Clay-rich rocks have been shown recently to be new resources for critical materials. Critical materials are the resources (rare-earth elements, lithium, cobalt, manganese, etc) needed to produce key technologies for the energy transition. This session attempts to bring new work on the occurrences of critical materials in clay-rich rocks.
Session Chair: Crawford Elliott (Georgia State University)

Environmental applications of natural and modified clays.
This session is focused on all possible clay-related remediation processes, including, but not limited to adsorption, catalysis, bio or photodegradation, and chemical/fertilizer stabilization.
Session Chair: Rebecca Stokes (USGS), Emily Doyle (Texas Tech University)

Porosity in shales and mudstones.
The relation between the porosity and permeability of clays, claystones and shales is a critical factor in their behavior. Properties such as behaviors as aquitards or aquifers, storage and release of oil and gas, use of such formations as caprocks, and brittle/ductile behavior under stress all depend, at least in part on the nature of the pore structures. These structures can vary in scale from the atomic (i.e., swelling clays) to the macroscopic (i.e., large-scale fractures), and pores at many scales can be present in a given sample. In addition, a number of different techniques are available for measuring such porosity including gas and liquid intrusion, small angle scattering, imaging, and NMR, and these do not always give the same results. Presentations will discuss any of the varied questions involved in the porosity of clay-rich formations or their analysis.
Session Chairs: Timothy Fischer (Chevron), Yiwen Lyu (University of Minnesota)

Importance of clays in the energy sector: petroleum, carbon capture, utilization, and storage. and hydrogen.
Fossil fuels have largely been facilitated the advancement in the quality of life through uninterrupted energy resources since a century. Fossil fuels played significant role in the industrial revolutions, infrastructures, and transportation. The mitigating greenhouse gases, especially carbon dioxide (CO2), is one of the greatest challenges that we must address in the current scenario without compromising the accessibility of affordable energy to all. Hydrogen is considered as medium- and long-term energy resources to partly replace current energy mix and to achieve net-zero transition goals. This session will cover the topics focusing on (1) subterranean CO2 storage in various geologic formation including conventional, unconventional, aquifer and coal, (2) CO2 utilization for enhanced oil and gas recovery, (3) CCUS simulation and CCUS site characterization, and (4) geologic hydrogen storage.

The development in characterization and application of clay minerals in petroleum industries have been one of the key components to meet global energy demand. This session will cover the topics focusing on recent advancement and future direction on utilization and evaluation of clay minerals for efficient production of hydrocarbons. The session will cover talks from the
researchers of academic institutions and industries. A prospective theme of this session will be characterization of clay minerals, use of clay minerals and their modification, computational modeling of clay minerals, application of clay minerals as additives in reservoir fluids and wellbore construction.

Session Chairs: Ibrahim Okunlola (University of Alabama), Michael Cheshire (Chevron)

Current trends in research and development of bentonites for the isolation of spent nuclear fuel.

Smectite clay minerals play an important role in underground nuclear waste repository concepts due to their ability to hinder the transport of aqueous cations through ion exchange and adsorption. In particular, bentonites have been considered for engineered barrier systems and as the primary constituent of surrounding host rock, to prevent or hinder the transport of radionuclides in the subsurface. This session seeks to survey current trends in the research and development activities related to bentonites as barrier materials for isolation of spent nuclear fuel. Examples include, but are not limited to: temperature/humidity/chemical effects, thermomechanical properties, ion, water, and gas (e.g., H2) adsorption and transport. Contributions are welcome from fundamental studies to the industrial development of repository concepts. Methods can involve experimental investigation to molecular, constitutive, and numerical modeling. The aim of this session is to gather experts from multiple disciplines to identify critical research and development needs.

Session Chairs: Jeffery Greathouse (Sandia National Laboratories); Tuan Ho (Sandia National Laboratories); Marcelo Sánchez (Texas A&M University)

Isotopes and clays.

Isotope-based methods can provide information on clay minerals formation conditions and timing which are not accessible by other methods. Traditional (18O/16O, 2H/1H) and non-traditional (e.g., 7Li/6Li, 11B/10B, 26Mg/24Mg, 41K/39K) stable isotope systems offer insights into clay mineral formation conditions and post-formational alteration history. Stable isotope signatures in clays have shown potential in exploration of critical mineral and hydrocarbon resources, and they also have been increasingly used to study important surface processes that control our environment and climate, such as weathering and authigenic clay formation. Radiogenic dating of clays by K-Ar and Rb-Sr systems can help in deciphering geological history of a given material. Isotopes and clays session is meant to provide researchers with a forum to share results and exchange ideas related to the broadly defined topics on isotopes in clays. Both studies of fundamental controls on isotopic signatures in clays and applications of isotopic information in clays to environmental and geological questions, involving stable and radioactive isotope systems are welcomed.

Session Chairs: Artur Kuligiewicz (Polish Academy of Sciences); Crawford Elliott (Georgia State University); Xinyuan Zheng (University of Minnesota)

Industrial application of clays and zeolites.

Clays and zeolites have improved our lives through the use of their physical and chemical properties. This session will highlight the industrial application, processes, and modern modification techniques leading to advanced products. This session will be in honor of Jessica
Engineered layered materials and their interfacial properties.
Layered materials and minerals typically have strong in-plane chemical bonds and weak out-of-plane bonds, which allow them to be exfoliated into high-aspect-ratio 2D nanosheets or form materials with disordered stacking properties. As assembly of 2D materials into 3D structures can lead to innovative behaviors, understanding the structure-property relationships of the layer units is as important as recognizing the interlayer bonding interactions. In the past decade, a myriad of engineered 2D materials with (dis)similar interfacial reactions as to clay minerals has been recognized. This session provides a platform for presenting naturally occurring and chemical engineered materials in the two research fields with emphasis on the interfacial H-bonding and/or ionic interactions in confined geometry, and delineates opportunities for future collaborations.
Session Chairs: Hsiu-Wen Wang (Oak Ridge National Laboratories); Michael Naguib (Tulane University)

Modeling efforts to understand clay structure and chemical properties.
This session will focus on the advances in modeling of processes and geochemistry associated with clay dominated environments.
Session Chairs: Ai Chen (University of Illinois, Champaign-Urbana)

General
We will accept all abstracts on clay related topics that are not covered by the proposed sessions. These will be grouped, and new sessions might be developed.
Session Chair: Anthony Boxleiter (Georgia State University), Ben Urick (California State University at East Bay)
Monday, May 22, 2023

Marilyn and Sturges W. Bailey Distinguished Member Award

Room: Lil Tex
8:30 am - 9:50 am The Very Model of a Modern Major Mineral-Molecular Simulation and the Advancement of Clay Mineralogy. Randall T. Cygan

9:50 am - 11:00 am Coffee Social

Importance of clays in the energy sector: petroleum, carbon capture, utilization, and storage. and hydrogen.

Room: Balcones
11:00 am - 11:30 am Geological gas storage: H₂ and CO₂ intercalation into smectite interlayers. Tuan A. Ho, Yifeng Wang, and Carlos F. Jove-Colon

11:30 am - 11:50 am Laboratory investigation of the impacts of clay on erosion and soil carbon sequestration. Judy Yang

11:50 am - 12:10 pm Effects of clay types on solid bitumen aromatization in pyrolysis experiments. M. Rebecca Stokes, Paul Hackley, Aaron M. Jubb, Bonnie McDevitt

12:10 pm - 12:30 pm Clay Mineral Assemblages and Diagenesis in Upper Cretaceous Eagle Ford Group (Mudrocks). Lucy T. Ko, Rieko Adriaens, Gilles Mertens, Evan Sivil

Isotopes and clays.

Room: Lil Tex
11:00 am - 11:30 am Stable hydrogen and oxygen isotope geochemistry of Fe³⁺-rich, interstratified clay minerals from seafloor hydrothermal sites. Fred J. Longstaffe, Javier Cuadros, Joseph, R. Michalski, and Vesselin Dekov

11:30 am - 11:50 am The hydrogen isotope fractionation in thermally-treated phyllosilicates verifies the models of their dehydroxylation. Arkadiusz Derkowski, Nadine J. Kanik, Jens Dyckmans

11:50 am - 12:10 pm Structural hydrogen isotope alterations of clay minerals during chemical treatments: qualitative and attempted quantitative approaches. Nadine J. Kanik, Artur Kuligiewicz, and Jeffrey T. Cullen.
12:10 pm - 12:30 pm  Clay-Fluid Interaction: Mechanisms and Rates of Hydrogen Exchange.  
Jonathan D. Smolen, Michael T. Hren, Christopher A. Sparacio

**Engineered layered materials and their interfacial properties**

**Room: Stadium**

11:00 am - 11:30 am  Engineering Electrically Conductive Clay-Like MXenes for Energy Storage.  
Michael Naguib

11:30 am - 11:50 am  Automated modelling of 1D XRD profiles based on the recursive algorithm.  
Michael Holmboe

11:50 am - 12:10 pm  Efficient removal of methylene blue from aqueous solution using Charcoal functionated hybrid Mg/Fe LDH.  

12:10 pm - 12:30 pm  Application of multifunctional hydrophobic graphite oxide assisted Mg2Al LDH hydrogel in adsorption of Pb and As from synthetic wastewater.  
Mir T. Rahman, Tomohito Kameda, Farzana Rahman, Yuko Saito, Shogo Kumagai, Toshiaki Yoshioka

12:30 pm - 2:00 pm  Lunch

**Importance of clays in the energy sector: petroleum, carbon capture, utilization, and storage. and hydrogen.**

**Room: Balcones**

2:00 pm - 2:30 pm  Changes in oil shale mineralogy after hydrous pyrolysis.  
Justin E. Birdwell, Adam R. Boehlke, and Michael D. Lewan

2:30 pm - 2:50 pm  Understanding Clay-Mineral Alteration of Silica-Undersaturated Mafic Volcanic Tuffs through Integration of XRD and SEM Analyses.  
Robert M. Reed and Rieko Adriaens

2:50 pm - 3:10 pm  Clay Mineral Control on Organic Matter Distribution in Mudrocks from the Permian Basin, USA.  
Hunter Green and Branimir Šegvić
Isotopes and clays.

**Room: Lil Tex**

2:00 pm - 2:30 pm  
Potassium and argon-isotope measurements of illitic clay: Unfinished work. *J. M. Wampler*


2:30 pm - 2:50 pm  
Experimental constraints on potassium isotope fractionation during cation exchange in clay minerals. *Xin-Yuan Zheng, Xin-Yang Chen, Brian L. Beard, Clark M. Johnson, Noah Brown, and Huifang Xu*

2:50 pm - 3:10 pm  
Experimental constraints on potassium isotope fractionation during cation exchange in clay minerals. *Xin-Yuan Zheng, Xin-Yang Chen, Brian L. Beard, Clark M. Johnson, Noah Brown, and Huifang Xu*

**Engineered layered materials and their interfacial properties.**

**Room: Stadium**

2:00 pm - 2:30 pm  
Influences of particle size, shape, and crystal structure on the oriented attachment of nanoparticles. *Benjamin A. Legg and James J. De Yoreo*

2:30 pm - 2:50 pm  
Roles of hydrogen bonds and lattice alignment on gibbsite-oriented attachment. *Tuan V. Vu and Tuan A. Ho*

2:50 pm - 3:10 pm  

3:10 pm - 3:30 pm  
**Break**

**Isotopes and clays.**

**Room: Lil Tex**

3:30 pm - 3:50 pm  
Exchangeable potassium in fine, smectite-rich size separates: Implications for K-Ar dating. *J. M. Wampler and W. Crawford Elliott*

3:50 pm - 4:10 pm  
Towards understanding of illitization based on stable potassium (K) and magnesium (Mg) isotope systematics. *Yiwen Lyu, Xin-Yuan Zheng, Brian L. Beard, W Crawford Elliott, Clark M. Johnson.*

Potassium isotope behavior during marine authigenic clay formation. *Xiao-Ming Liu, Wenshuai Li, Kun Wang, James McManus, Brian A. Haley, Yoshio Takahashi, Mohsen Shakouri, Yongfeng Hu*
Engineered layered materials and their interfacial properties.

**Room: Stadium**

3:30 pm - 3:50 pm
Local structure of opal-CT: Multiscale modeling of stacking disorder in layered materials. *Hsiu-Wen Wang, Katharine Page, Reinhard Neder, David L. Bish*

3:50 pm - 4:10 pm
Structural Properties of Organically Modified Boehmite Nanomaterials from Molecular Simulation. *Jeffery A. Greathouse, Philippe F. Weck, Nelson S. Bell, Jessica N. Kruichak, and Edward N. Matteo*
Tuesday, May 23, 2023

Pioneer in Clay Science

Room: Lil Tex
8:30 am - 9:50 am
Discovering the Clay Reactions beneath our Feet. **Susan Brantley**, R.Liao, X. Gu

9:50 am - 10:10 am
Break

Current trends in research and development of bentonites for the isolation of spent nuclear fuel.

Room: Lil Tex
10:10 am - 10:30 am

10:30 am - 10:50 am
Computational fluid dynamics simulation of thermal effects in compacted bentonite clay. **Ian C. Bourg**

10:50 am - 11:10 am

Environmental applications of natural and modified clays.

Room: Balcones
10:10 am - 10:30 am
Nitrate elimination from aqueous solution by Fe(II) in electro-chemically reduced ferruginous smectite. **Linda A. Pentrak**, Martin P. Pentrak, and Joseph W. Stucki
The bad and the good though ugly. **Michał Skiba**, Marta Kisiel, Katarzyna Maj-Szeliga, Magdalena Makiel, Sylwester Smoleń, Daniel Kiełbasa, Roksana Woźniak, and Julia Dyrek.

10:30 am - 10:50 am
A comparative photocatalytic study of TiO₂-loaded nanotubes derived from kaolin group minerals: evaluation of degradation efficiency using dyes as model pollutants. **Klaudia Dziewiątka** and **Jakub Matusik**
Modeling efforts to understand clay structure and chemical properties.

**Room: Stadium**

10:10 am - 10:30 am  Development of yet another classical forcefield for molecular modelling of (clay-) minerals. *Michael Holmboe*

10:30 am - 10:50 am  Interpreting Diffusion Data with a Fast, Free, and User-friendly Reactive Transport Modeling Approach. *Christophe Tournassat, Carl Steefel, Patricia Fox, and Ruth Tinnacher*

11:10 am - 11:30 am  Break

**Current trends in research and development of bentonites for the isolation of spent nuclear fuel.**

**Room: Lil Tex**

11:30 am - 11:50 am  The high-pressure (HP) adsorption of molecular hydrogen generated in underground nuclear waste repositories (NWRs) on bentonite barriers. *Arkadiusz Derkowski and Paweł P. Ziemiański*

11:50 am - 12:10 pm  Se(III) Diffusion through Montmorillonite: Comparison of Na and Ca Counterions. *Patricia M. Fox, Christophe Tournassat, Carl Steefel, and Peter S. Nico*

12:10 pm - 12:30 pm  Batch Reactor Alteration of the Hedemünden Nontronite at 180 °C in 0.1 M NaCl Solution: Constraining the Role of Accessory Minerals and K-Oxalate Additives. *Julia Kandler, Ritwick Sudheer Kumar, Laurence N. Warr, and Georg H. Grathoff*

**Environmental applications of natural and modified clays.**

**Room: Balcones**

11:30 am - 11:50 am  Green Magnetic Bentonite Composite for Efficient Removal of Cationic and Anionic Dye in Synthetic and Real Textile Wastewater. *Nur Syafiqah Alisa Mohd Nizam, Ruhaida Rusmin, and Siti Nor Atika Baharin*

11:50 am - 12:10 pm  Nanocellulose-sepiolite bionanocomposite sorbents for removal of hydrophobic pollutants in water. *Amaret Sanguanwong, Adrian E. Flood, Makoto Ogawa, Raquel Martín-Sampedro, Margarita Darder, Bernd Wicklein, Pilar Aranda, Eduardo Ruiz-Hitzky*
Modeling efforts to understand clay structure and chemical properties.

**Room: Stadium**

11:30 am - 11:50 am  Molecular Simulations of Soil Organic Matter at Mineral Interfaces. *Thomas R. Underwood, Kevin M. Rosso, and Ian C. Bourg*

11:50 am - 12:10 pm  Evolution of Bentonite Properties during Progressive Dehydration: A Molecular Dynamics Simulation Study. *Xiaojin Zheng and Ian C. Bourg*

12:30 pm - 2:00 pm  Lunch

Current trends in research and development of bentonites for the isolation of spent nuclear fuel.

**Room: Lil Tex**

2:00 pm - 2:20 pm  Fe(II)-clay interactions: Anaerobic batch and diffusion experiments employing purified montmorillonite SWy-3 and isotopically purified $^{56}$Fe. *Jebril Hadi, Paul Wersin, Mirjam Kiczka, Andreas Jeni, Jean-Marc Grenèche, Olivier Leupin, and Nikitas Diomidis*


2:40 pm - 3:00 pm  Determining layer charge alterations of smectitic wettable surfaces in the Alternate Buffer Materials experiment (Åspö) with the new O-D spectroscopic method: Correlations with cation exchange capacity. *Nadine J. Kanik, Arkadiusz Derkowski, Stephan Kaufhold, Reiner Dohrmann*

Environmental applications of natural and modified clays.

**Room: Balcones**

2:00 pm - 2:20 pm  Activated clay mineral-based beads for pharmaceuticals removal. *Agnieszka Solińska, Natalia Oleksa, Bartosz Możdżeń, and Tomasz Bajda*

2:20 pm - 2:40 pm  Adsorption of the antibiotic ciprofloxacin to montmorillonite - studied by MD simulations. *Rogers Swai and Michael Holmboe*

2:40 pm - 3:00 pm  Layered double hydroxides supported by clay minerals as photocatalysts for visible light-driven degradation of organic pollutants. *Anna Jędras and Jakub Matusik*
General I

Room: Stadium

2:00 pm - 2:20 pm  Effects of subtle structural adjustments in kaolinite and halloysite on their intercalation. Youjun Deng, Bidemi Fashina, Aimee L. Deng, and Chiawei Lin

The Availability of Clay Resources and Ceramic Production Technology in Antiquity: A Case Study of Iron Age Insular Communities of the Eastern Adriatic. Emily Doyle, Marina Ugarković, Goran Durn, and Branimir Šegvić

2:40 pm - 3:00 pm  Solution NMR investigation of phytic acid adsorption mechanisms at the calcite-water interface. Ai Chen, Lingyang Zhu, and Yuji Arai

3:00 pm - 3:20 pm  Break

Industrial application of clays and zeolites.

Room: Balcones

3:20 pm - 3:40 pm  Special note on Dr. Jessica Elzea Kogel. Michael Cheshire

3:40 pm - 4:00 pm  Kaolin uses in the traditional ceramic industry. Murielle C. Perronnet

4:00 pm - 4:20 pm  Effect of incorporated carbonate on cation exchange of sodalite and cancrinite. Chiawei Lin, Youjun Deng, Julie Howe, and Markus Graefe

General I

Room: Stadium

3:20 pm - 3:40 pm  Unleashing the Transformative Power of Science Education at the Elementary Level, Through Engaging and Interactive Experiential Learning. Taniece Thompson-Smith

3:40 pm - 4:00 pm  Revealing surface properties of sepiolite by monitoring dehydration of confined water. Bidemi T. Fashina and Youjun Deng

4:00 pm - 4:20 pm  Sand in tropical and sub-tropical regolith: Clay minerals and textures in sand size aggregates and particles. Paul A. Schroeder, Simone Kilian Salas, Hermann F. Jungkunft, and Daniel D. Richter
Wednesday, May 24, 2023

Marion L. and Chrystie M. Jackson Mid-Career Clay Scientist Award

Room: Lil Tex

8:30 am - 9:50 am
Electrostatic interactions at clay mineral surfaces: At the crossroads between mineralogy, geochemistry, and geophysics. Christophe Tournassat

9:50 am - 10:10 am
Break

Current trends in research and development of bentonites for the isolation of spent nuclear fuel.

Room: Lil Tex

10:10 am - 10:30 am
Thermo-Hydro-Mechanical Behavior of Compacted MX80 Bentonite at High Temperatures above 100°C. John S. McCartney and Yu Lu

10:30 am - 10:50 am
Effect of High Temperature on Swelling and Mineralogy of a Clay-Pellets Intended for Barrier Systems. Abdulvahit Sahin, Roa’a AL-Masri, Youjun Deng, and Marcelo Sanchez

10:50 am - 11:10 am
Dismantling of the bentonite buffer in the inner section of the Prototype Repository at the Åspö Hard Rock Laboratory. Patrik Sellin, Fredrik Vahlund, Daniel Svensson, Mattias Åkesson, and Maria Rasmusson

Critical materials and clays.

Room: Stadium

10:10 am - 10:30 am

10:30 am - 10:50 am
REE remobilization and fractionation in bauxitic kaolin deposits of sedimentary origin in western Georgia, Upper Coastal Plain. Anthony Boxleiter, Yinhao Wen, Yuanzhi Tang, and W. Crawford Elliott

10:50 am - 11:10 am
Porosity in shales and mudstones.

Room: Balcones

10:10 am - 10:30 am
Kenneth C. Littrell

10:30 am - 10:50 am

10:50 am - 11:10 am
Workflow for the digital determination of porosity in tight rocks. Barbara Hill

11:10 am - 11:30 am
Break

Current trends in research and development of bentonites for the isolation of spent nuclear fuel.

Room: Lil Tex

11:30 am - 11:50 am
Changes in U(VI) Sorption Behavior onto Montmorillonite with Temperature and Solution Chemistry. Ben Urick, Christophe Tournassat, Ruth M. Tinnacher

11:50 am - 12:10 pm
Smectite swelling hysteresis is driven by interfacial charge regulation. Yuntian Teng, Benjamin Gilbert, and Michael L. Whittaker

12:10 pm - 12:30 pm
The chemical effect on the swelling of the bentonite: laboratory tests and large-scale modeling. Liange Zheng, Wenming Dong, Jonny Rutqvist, Ayumi Koishi, Chenhui Zhu, Carl I. Steefel, Jens T. Birkholzer

Critical materials and clays.

Room: Stadium

11:30 am - 11:50 am
Diagenetic Control on the REE Budget of Bentonite Clays. Branimir Segvic, Luka Badurina, Adriano H. Braga, Oleg Mandic

11:50 am - 12:10 pm
An approach to Li-clays in continental salars in the Mesa Central, between San Luis Potosi and Zacatecas, Mexico. Vivian Ruiz Mendoza, Sonia A. Torres Sanchez, Rosa L. Tovar Tovar, and Jose R. Torres Hernández
12:10 pm - 12:30 pm  Microstructure of Individual Glauconite Pellets. Wei Sun, Zachary Westgate, Don J. DeGroot, and Guoping Zhang

Porosity in shales and mudstones.

Room: Balcones

11:30 am - 11:50 am  Influence of Clay Minerals on Porosity Measurements: A Case Study from the Third Bone Spring and Wolfcamp Formations, Delaware Basin, Texas. J. Greene, R. Reed, T. Zhang, T. Larson

11:50 am - 12:10 pm  Methane accessibility and densification in the Niobrara Formation at wet-gas thermal maturity conditions. Aaron M. Jubb, Leslie F. Ruppert, Tristan G.A. Youngs, Thomas F. Headen, Justin E. Birdwell, and M. Rebecca Stokes

12:30 pm - 2:00 pm  Lunch

General II

Room: Stadium

2:00 pm - 2:20 pm  HSMQ: a rapid, high-throughput tool for quantitative mineral analysis using FTIR. Rieko Adriaens, Gilles Mertens, and Bram Paredis.

2:20 pm - 2:40 pm  Preliminary mineralogical investigations on clay minerals from Surtsey deposits (SW Iceland). Giovanna Montesano, Concetta Rispoli, Marie D. Jackson, and Piergiulio Cappelletti

2:40 pm - 3:00 pm  Naturally Occurring Microbe-Clay mineral Interaction. Jin-wook Kim, Tae-hee Koo, and Hanbeom Park

Porosity in shales and mudstones.

Room: Balcones

2:00 pm - 2:20 pm  The use of multiple methods to evaluate porosity and pore structure and reduce uncertainty in shale and tight reservoirs. Timothy B. Fischer

2:20 pm - 2:40 pm  Crushed Rock Analysis with Fluid Loss Quantification via Combined Open & Closed Retort. J. Alex Zumberge and Jadranka Milovac

2:40 pm - 3:00 pm  Crushed Rock Analysis—Reservoir Lab Retort and Retort + Chemical Methodologies. Barbara Hill
3:00 pm - 3:20 pm  Break

General II

Room: Stadium  
3:20 pm - 3:40 pm  Evidence for the biotic illitization at the high temperature and high pressure. **Tae-hee Koo, Yuki Morono, Fumio Inagaki, Hanbeom Park, and Jinwook Kim**  
Rapid transformation of biogenic silica to authigenic clay during reverse weathering. **Simin Zhao, Emily M. Saad, Hailiang Dong, Jeffrey W. Krause, and Yuanzhi Tang**

3:40 pm - 4:00 pm  

Porosity in shales and mudstones.

Room: Balcones  
3:20 pm - 4:20 pm  Open round table discussion on the difficulties of porosity measurement in clay-rich rocks. **J. Alex Zumberge (Geomark) and Barbara Hill (SLB)**
Poster Session (Monday, May 22, 2023)

Room: Atrium

Clay Mineralogy of Per- and Polyfluoroalkyl Substances (PFAS) Contaminated Soils from Agricultural Fields in Society Hill, South Carolina. *Adeyemi Oluwaseun* and *Schroeder A. Paul*

Siderite Cementation Controls on Clay Mineral Diagenesis in Pennsylvanian Strata of the Anadarko Basin, OK. *Evans Akuoko Ansah* and *Branimir Šegvić*


Clay mineral characterization of lacustrine sediments from alkaline lakes on the Cariboo Plateau, BC. *Maria L. Arizaleta, Nina Zeyen, Maija J. Raudsepp, and Siobhan A. Wilson*

Detailed mineralogical characterization and nanoporosity evaluation of USGS Shale Geochemical Reference Materials. *Justin E. Birdwell, M. Rebecca Stokes, Aaron M. Jubb, and Brett J. Valentine*


Understanding Rare Earth Element Distribution in Low/Medium Grade Hydrothermal Chlorite. *Kevin Byerly, Damir Slovenec, and Branimir Šegvić*

Geology and mineralogy of the S’Aliderru bentonite deposit (Sardinia, Italy): preliminary data. *Sebastiano Coticelli, Piergiulio Cappelletti, Concetta Rispoli, Giuseppina Balassone, Fabio Granitzio, and Nicola Mondillo*

NMR investigation of the phosphorus mineralization affected by the calcite-water interfacial chemistry. *Ai Chen and Yuji Arai.*

Mineral diagenesis of proximal Cutler Group (CO): signatures of climate and fluid alteration from a chemical and textural analysis. *Brock S. Dumont, Andrew S. Elwood Madden, Gerilyn S. Soreghan, Gilby Jepson, and Sarah W.M. George*

Effect of γ-irradiation on the redox state of the structural iron in Montmorillonite. *Michael Holmboe, and Mats Jonsson*

Atomistic simulations of smectite interlayer entry of anions and the relevance for nuclear waste applications. *Michael Holmboe, Christophe Tournassat, and Ruth M. Tinnacher*

Statistical method to understand the sediment provenance in the Amundsen Sea, West Antarctica. *Insung Kang, Young Kyu Park, Kyu-cheul Yoo, Minkyung Lee, Jinwook Kim*
Study of Dongchang illite from Yeongdong, South Korea: Candidate for a new potential source clay. **Namgu Lee, Hanbeom Park, Sei Jei Seong, Dong Heun Han, Hwa Jin Kim, and Jinwook Kim**

The effect of synthesis conditions on formation and properties of kaolinite-based nanotubes. **Jakub Matusik and Klaudia Dziewiątka**

Preparations, characterization and use of a Chitosan-clay biocomposite in glyphosate removal. **Abdelhak Mesbah, Imene Feddal, Safia Taleb, and Monica Brienza**

Sorano (Tuscany - Italy) zeolitized tuffs mining waste, a resource for countless technological applications: preliminary results. **Sossio Fabio Graziano, Mariano Mercurio, Alessio Langella, Francesco Izzo, Davide Santaniello, Concetta Rispoli, and Piergiulio Cappelletti**

Swelling pressure of a compacted Ca-bentonite with different pore fluid. **Ro’a AL-Masri, Camilo Sanchez, Jeffery A. Greathouse, Edward N. Matteo, Thomas Dewers, Youjun Deng, and Marcelo Sanchez**

Molecular modeling to predict the optimal mineralogy of smectites as binders of aflatoxin. **Marek Szczereba, Youjun Deng, and Mariola Kowalik-Hyla**

Cross heating of samples during IR-laser argon extraction. **Marek Szczereba, Michal Banaś, Zuzanna Ciesielska, Aleksander Skala, and Hocine Djouder**
ABSTRACTS

Oral Program
Quantification of mineral assemblages is traditionally performed using laboratory X-ray powder diffraction tools (XRPD). In order to acquire an accurate mineral quantification, an adequate sample preparation is a critical prerequisite of the actual XRD measurement. Even more prone to errors is the data interpretation required by a data analyst.

Although XRPD is the best primary method for quantitative analysis, as documented by the Reynolds Cup round robin, it has many disadvantages. First of all, the analysis requires a lab environment to be processed. Secondly, the accurate analysis of clay-bearing samples is often complex and therefore both time- and work-consuming. As a result, XRD analyses are relatively expensive and the number of analyses performed is often limited to the absolute minimum.

In the industry, there is a growing demand for getting results faster, optionally even while on-site, in order to facilitate decision-making. To anticipate this demand, High Speed Mineralogical Quantification (HSMQ) was developed – an automatic application tool for rapid but still accurate mineral quantification using Fourier Transform Infrared Spectroscopy (FTIR).

Measurements require very little sample preparation and are performed using a compact and mobile FTIR spectrometer that can be used on-site. The measurement itself is very fast (<1 min.) and is performed using an ATR (Attenuated Total Reflection) module able to analyze low sample volumes. The HSMQ application requires virtually no user input, runs on a cloud server and is easy accessible. The entire operation, from sampling until data interpretation, takes less than 10 minutes per sample.

The HSMQ software model is a customized application developed by creating an FTIR inversion based on Qmineral’s high-accuracy XRD data, documented in previous Reynolds Cup editions. HSMQ provides high-quality data both for main and minor phases and also allows clay speciation (see Figures 1 and 2).

HSMQ is preferably deployed after XRD calibration on a limited number of samples to optimize accuracy. The versatility and speed of the technique allows the user to gather almost continuous data and it provides more complete mineralogical information to users which in turn can drive faster and better-informed decisions.
Figure 1. Comparison between the HSMQ-FTIR model performance (orange) and the reference XRD data (blue) for the main minerals Quartz, Calcite and total Clays in an unconventional well.

Figure 2. Comparison between the HSMQ-FTIR model performance (orange) and the reference XRD data (blue) for feldspars and individual clay phases in an unconventional well.
Thermal Conductivity of Pellets-Clay Mixtures Intended for the Isolation of High-Level Nuclear Waste.

Roa’a AL-Masri (Texas A&M University, College Station, TX USA), Abdulvahit Sahin (Texas A&M University, College Station, TX USA), and Marcelo Sanchez (Texas A&M University, College Station, TX USA)

Pelletized clay mixtures are being considered as potential materials for the construction of engineered barrier systems (EBS) and seals in the context of deep geological disposals envisaged for the isolation of high-level nuclear waste (HLW) and spent nuclear fuel (SNF). Such type of facility contemplates placing the HLW/SNF encapsulated in a metallic container in horizontal drifts or vertical boreholes excavated in deep and good-quality rocks. The empty space between the rock and the canister will be filled with the manmade EBS. One key function of the EBS is to dissipate the heat emitted by the HLW/SNF. An advantage of high-density clay-pellets mixtures is that its emplacement is relatively easy because the clay pellets are directly projected into the openings without the need for compacting them, enabling filling the technical voids typically found in this type of system (e.g., at the rock-barrier interface), or achieving EBS target dry densities ($\rho_d$) without the need of in-situ compaction. However, clay pellet mixtures produce large macropores (i.e., the inter-aggregate voids between the clay pellets [1]) that strongly affect the thermal conductivity of the buffer system, particularly during the first operational stages. When the EBS is unsaturated. One possible solution to enhance the heat dissipation around the canister containing HLW/SNF is to mix highly heat conductive material (e.g., graphite) with clay pellets.

In recent years, there has been an interest in optimizing the disposal of HLW/SNF and higher temperatures are being considered up to 200 °C [2]. Furthermore, previous research has mainly focused on the thermal properties of compacted clays This work investigates the thermal conductivity of clay-pellets mixture at different temperatures up to 200 °C and saturations.

Nanocellulose-sepiolite bionanocomposite sorbents for removal of hydrophobic pollutants in water

Amaret Sanguanwong (Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong, Thailand & Materials Science Institute of Madrid (ICMM-CSIC), Madrid, Spain); Adrian E. Flood (VISTEC, Rayong, Thailand); Makoto Ogawa (VISTEC, Rayong, Thailand); Raquel Martín-Sampedro (ICMM-CSIC, Madrid, Spain); Margarita Darder (ICMM-CSIC, Madrid, Spain), Bernd Wicklein (ICMM-CSIC, Madrid, Spain), Pilar Aranda (ICMM-CSIC, Madrid, Spain), Eduardo Ruiz-Hitzky (ICMM-CSIC, Madrid, Spain)

One of the great concerns connected to the pollution of the seas is related to oil spills due to the irreversible damage they cause to the environment. The efficiency of clays, particularly when they are suitably modified, is well known in pollutant adsorption processes, including the removal of hydrophobic and amphoteric compounds such as hydrocarbons and oils. In this context, this communication addresses the preparation and exploration of the properties of bionanocomposites that combine nanocellulose and sepiolite for application in the removal of oils present in water. In particular, various approaches have been explored for the production of bionanocomposite foams that may operate as highly efficient biosorbents for use in open water and with the capacity to be reused after the recovery of retained contaminants (Sanguanwong et al., 2021).

In our study, we have confirmed that it is possible to produce CNF-sepiolite bionanocomposite foams with various characteristics depending on the liophilization method applied, which could involve a normal freezing, a directional freezing or a two-step process with a first directional freezing followed by thawing and then a normal freezing (refreezing) before the drying. The presence of clay favors the improvement of mechanical properties and can be advantageous in the foam hydrophobization process through treatment with silane vapors. Thus, for example, after silanization with methyltrimethoxysilane, the foams become hydrophobic and can be satisfactorily used for oil sorption, with the possibility of recovering it simply by compressing the foam. The satisfactory results, especially using foams prepared by the refreezing method, open the way to explore the use of other bionanocomposites based on cellulosic precursors to produce foams for oil removal applications in open waters.

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Changes in oil shale mineralogy after hydrous pyrolysis

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Laboratory pyrolysis experiments designed to mimic the effects of heating during deep burial in the subsurface are utilized to evaluate a variety of geologic processes. One widely used approach is hydrous pyrolysis (HP). This closed-system pyrolysis technique is particularly useful for studying rock interactions under subcritical, liquid water conditions. HP is most often employed with organic-rich mudstones, which are often petroleum source rocks, to study the effects of thermal maturation on the various forms of organic matter. Although most studies utilizing HP focus on organic phases, under HP conditions changes in the mineral matrix also occur. As part of a larger study on oil shales from around the world, twelve very organic-rich mudstones (organic carbon content 10 – 60 wt. %), collected on five continents and representing source rocks from the Early Cambrian though the Eocene, were evaluated prior to and after HP (360°C, 72 hours) to assess mineralogical alteration induced by the process. Major and trace element measurements were made on the original and post-pyrolysis oil shales along with whole rock and clay mineral characterization using Fourier transform infrared spectroscopy and X-ray diffractometry. On an organic-free basis, all samples showed some alteration following HP with illite, kaolinite, calcite, and dolomite concentrations being altered and mineral concentrations reduced by the largest amounts due to alteration or dissolution and reprecipitation as other phases. Feldspar minerals, in particular albite, appeared to be generated during HP, increasing in relative content by up to 30%. Quartz was variably affected by HP treatment. The most altered mudstones examined were from the Carboniferous Pumpherston Shale, the Permian Irati Formation, the Upper Cretaceous Timahdit oil shale, and the Eocene Green River Formation. These four showed the greatest shifts in mineralogy, mainly conversion of dolomite to calcite or loss of carbonate minerals and loss of illite and kaolinite accompanied by the formation of albite. These results suggest that elevated expulsion of hydrocarbons from source rocks observed in HP relative to natural systems may be driven in part by matrix alteration due to concomitant mineral reactions during pyrolysis.
Clay reactions are important from industry to natural systems. This talk will focus on natural systems and how weathering transforms clays in the subsurface through reactions with water, oxygen, and carbon dioxide. Such reactions are important at least partly because they affect our drinking water resources over short timeframes and because they buffer atmospheric concentrations of the gases over geologic timeframes. These reactions also affect mineral distribution in the subsurface because meteoric waters infiltrate downward, creating reaction fronts where one mineral disappears and another forms. However, we know almost nothing about the distribution of reaction fronts at depth. We studied reactions in a shale weathering in a watershed to map clay reactions using chemical analyses, microscopies, scattering, diffraction, and geophysical techniques. The main reactions investigated were oxidation of pyrite and the weathering of iron-rich chlorite to hydroxy-interlayered vermiculite, vermiculite, and goethite. Oxidation of pyrite and chlorite commence near the water table across narrow depth intervals under the upper-catchment ridges, but well below the water table across wide depth intervals under the valley. The front for chlorite under the valley is wide because groundwater flows downward and laterally under the stream axis at the watershed outlet. We need to map such clay reactions in the subsurface in many locations to illuminate the mechanisms and distributions of natural transformation of clays while also demonstrating how groundwater and dissolved gases (CO$_2$, O$_2$) affect the chemistry and mineralogy of rock at depth.
Computational fluid dynamics simulation of thermal effects in compacted bentonite clay

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Bentonite clay has been extensively studied as an engineered barrier material for use in geologic repositories for high-level radioactive waste. A key challenge in this application is that the barrier will be exposed to gradients in saturation, fluid chemistry, and temperature that may give rise to complex coupled phenomena, such as thermally-induced cracking. Efforts to simulate these phenomena at the scale of the engineered barrier rely largely on approaches developed for brittle poro-elastic materials, whereas compacted clay exhibits a ductile poro-viscoplastic behavior.

Here, we build upon our recent development of a computational fluid dynamics (CFD) treatment of single- and two-phase flow in compacted clay (Fig. 1; Carrillo and Bourg, 2021). Specifically, we implement an additional heat conservation equation that enables representation of the couplings between fluid flow, solid deformation, and heat transport in compacted bentonite at the scale of an engineered barrier. The parameterization of sub-grid-scale properties (including the heat capacity, thermal conductivity, and thermal expansion coefficient of bentonite) is guided in part by all-atom molecular dynamics (MD) simulations of smectite-water mixtures (Zheng et al., 2023). Preliminary results are presented and compared with large-scale experimental results, and remaining challenges are identified and discussed.

Fig.1. Left: CFD simulation of multiphase flow in a viscoplastic porous material showing the formation of desiccation cracks (white) during displacement of a wetting fluid (red) by a non-wetting fluid (blue). Right: sub-grid-scale simulation parameters are constrained based on a combination of all-atom MD simulation predictions and previous experimental results.

REE remobilization and fractionation in bauxitic kaolin deposits of sedimentary origin in western Georgia, Upper Coastal Plain

Anthony Boxleiter, Yinghao Wen, Yuanzhi Tang, and W. Crawford Elliott (Georgia State University, Atlanta, GA, USA)

Rare-earth elements (REEs) are critical materials for a wide range of applications and high-tech industry. Understanding REE geological occurrences is important for their exploration and extraction. Compared to the well-established REE occurrence as ion-adsorption clays (IACs) in granite regolith-hosted deposits (in-situ granite weathering profiles), bauxitized kaolin deposits and their connection to REE fractionation is underexplored and the hosting potential for IACs remains unclear.

This study examines the occurrence of the REEs in the highly weathered environment of bauxitized kaolin deposits of sedimentary origin in western Georgia. Geologic drill core samples from the Andersonville area were sampled from a complete section of a bauxite-kaolin clay bed. X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses were conducted to characterize the mineralogical and elemental compositions, respectively. Results showed a gradual increase in gibbsite content from 0% at the top of the bed (“pre-bauxite” zone), to up to 67 wt.% in the center of the bed (“bauxite” zone), and a gradual decrease to 0% at the bottom of the bed (“post-bauxite” zone).

Ion-exchange experiments were conducted to understand the presence of the REE in these bauxites. Leachates were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). Results showed that light REE (LREE) and heavy REE (HREE) concentrations relative to Upper Continental Crust (UCC) remain stable in the pre-bauxite zone (~0.8–1.3 times UCC) and post-bauxite zone (~0.6–1.4 times UCC), accompanied with a stable content of exchangeable REE (~2–12%) throughout both zones. Interestingly, the bauxite zone showed a depletion in LREE (<0.4 times UCC) and highly fluctuating values of exchangeable LREE at different depth (~8 to 46%), whereas the HREEs showed little change relative to UCC and a stable range of exchangeable HREE (~10–15%).

These results suggested REE remobilization and fractionation during bauxitization of the kaolin-clay bed resulting from weathering. Ongoing work involves sequential leaching experiments and spectroscopic characterizations to determine the REE phases and speciation throughout the bauxite-kaolin.
Fe-Saponite growth at the bentonite / steel canister interface.
Repository corrosion implications

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The United States has initiated the Spent Fuel and Waste Storage and Transport (SFWST) Disposition campaign to evaluate various generic geological repositories for the disposal of spent nuclear fuel. Most previous international work (Swiss, French) describes Engineered Barrier Systems (EBS) for repositories focused on low temperature and pressure conditions. Our hydrothermal experiments on EBS materials were conducted to characterize high temperature interactions of bentonite clay with candidate waste container steels (304SS, 316SS, low-C steel).

The hydrothermal experiments were performed using Dickson reaction cells at temperatures and pressure of up to 300°C and 15 – 16 MPa, respectively, for five to eight weeks. Wyoming bentonite was saturated with a 1,900 ppm K-Ca-Na-Cl solution in combination with stainless and low-C steel coupons.

No smectite illitization was observed in these reactions. However, a partial K-enrichment of smectite occurred, providing a precursor to illitization. It would appear that illitization was retarded due to a limitation of K⁺ in the closed-system.

Notable clay mineral reactions occurred at the steel surfaces. Authigenic chlorite and Fe-saponite grew with their basal planes near perpendicular to the steel plate, forming a 10 – 100 μm thick ‘growth’ layer. Partial dissolution of the steel plates was likely the iron source for chlorite/saponite formation with steel plates acting as a substrate for chlorite/saponite growth. XRD and microprobe analyses of the silicate mantling on the low-carbon steel indicates the phase is a Fe-saponite with a composition of (Na₀.⁰⁹,Ca₀.⁰³) (Fe₂.²₀Mg₀.₁₂Al₀.₈₆) (Al₀.₅₈ Si₃.₄₂)O₁₀(OH)₂. Stainless steel (304) is mantled by a chlorite/Fe-saponite mixture. This phyllosilicate mix is high in Fe (33.₉₉ wt% FeO), Cr (1.₃₅ wt % Cr₂O₃) and Ni (1.₃₄ wt % NiO).

Mineral growth on the waste containers was influenced by the container, buffer, and fluid compositions, in addition to pressure and temperature conditions. No significant clay mineral alteration was apparent away from the steel-smectite interface. Results of this research show that the waste container may act as a substrate for mineral growth in response to corrosion. The role of these Fe-rich minerals as passivating agents on steel canisters at elevated heat loads is currently under investigation.
Solution NMR investigation of phytic acid adsorption mechanisms at the calcite-water interface

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As one of the most stable and thus predominant organic phosphorus (P) species in many soils, phytic acid could serve as an important mineralizable P reservoir in soils and sediments. The predominance of phytic acid has been largely attributed to its adsorption by clay minerals, which inhibits P mineralization in soils and controls the solubility and bioavailability of phosphate in soils. However, the adsorption mechanisms of phytic acid on the mineral surface are not clearly understood. Calcite is widely distributed in neutral to alkaline soils and calcareous soils and contribute significantly to phytic acid retention. Therefore, the objective of this study was to investigate the adsorption mechanism of phytic acid at the calcite-water interface at pH 6.0 and 8.0 using solution $^{31}$P, $^1$H nuclear magnetic resonance (NMR) and $^1$H-$^{31}$P two-dimensional NMR. Phytic acid adsorption isotherm revealed maximum phytic acid adsorption of 3.07mmol/g, 2.60mmol/g, 2.39mmol/g at pH 6.0, 8.0, and 9.5, respectively. The presence of outer-sphere surface complex was indicated by a lack of significant change in the zeta-potentials of phytic acid-reacted calcite at pH 6 and 8.0. Solution NMR results corroborated the outer-sphere complexation mechanism. $^{31}$P spectra showed fast exchange between adsorbed and unreacted phytic acid at the mineral surface on an NMR time scale, also indicating the major contribution from outer-sphere complexation at both pH values. Additionally, P5 and P4,6 was preferable in interacting with calcite surface at pH 6.0. Adsorbed phytic acid on the calcite surface should therefore be labile and is not limiting P mineralization and bioavailability in the terrestrial environment.
Molecular understanding of interfacial structure and reactivity of clay minerals in aqueous environments is critical for the treatment of chemical contaminants, safe disposal of radioactive waste, improved gas and oil extraction, and carbon sequestration to mitigate climate change. Basal surfaces and interlayers of clay minerals provide structurally-constrained interfacial environments to advance our understanding of these complex processes. We use large-scale classical molecular dynamics simulations to examine the interfacial structure and adsorption behavior of smectite, kaolinite, and other hydrated mineral phases. The models offer insights into the mechanisms controlling adsorption, hydration, wetting, interlayer swelling, electrical double layer, diffusion, and related phenomena. Specifically, molecular dynamics simulations involving clay interlayers provide models of nanopores where confinement and limited transport can impact interfacial structure and aqueous behavior. Combined with analytical methods such as NMR and neutron spectroscopies, molecular simulation offers a powerful approach for interpreting complex structure and dynamics of important environmental phases.

Early efforts in computational chemistry—beginning in the mid-1980s—focused on the analysis of organic compounds and how they interact with protein surfaces to develop new pharmaceuticals. Much of this software was later modified to be used in the evaluation of inorganic compounds and related materials, with special effort devoted to understanding the mechanisms of catalysis and gas separation. Molecular simulations typically involve the use of empirically-derived parameters based on crystal structures, spectroscopies, and other experimental data to derive interatomic potentials, which collectively are referred to as an energy force field. Clayff is one of several such force fields developed to accurately model clay mineral systems (see figure). These classical models rely on evaluating all possible atom-atom interactions based on the force field potentials to derive the total potential energy for the molecular model. Accurate determination of the potential energy is critical for obtaining optimized structures, and in performing various molecular dynamics and Monte Carlo-based molecular simulations. These topics, along with various musings about research in clay mineralogy, provide context for a scientific career.
Effects of subtle structural adjustments in kaolinite and halloysite on their intercalation

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Intercalation of kaolin minerals is important in manufacturing advanced organic-kaolin nanocomposites. The intercalation of kaolin minerals, particularly kaolinite, have shown some anomalous behavior that do not follow the common laws of physical chemistry. It is more difficult to intercalate the smaller kaolinite particles than to intercalate the larger particles. It was recently observed that 1) the kaolinite residue after dissolution by 4 M NaOH at 80 °C was difficult to intercalate and 2) increasing temperature reduced the extent of the intercalation of kaolinite by N-methylformamide (NMF). The objective of this study is to test a hypothesis that these unusual behaviors in kaolin intercalation are caused by the subtle atomic position adjustments in the 1:1 layers in an effort to better compensate the misfit of the tetrahedral sheet and the octahedral sheet.

The 1-2 µm fraction of a kaolinite (Georgia) could be intercalated by KOAc at room T, but heating the sample in the temperature range of 100 to 400 °C, and then cooling to room T, reduced intercalation rate when the heating temperature was increased. No intercalation was observed in 14 days after the 400 °C heating treatment. Variable temperature IR analysis indicated that the H-bonding between neighboring 1:1 layers enhanced at higher T, an indication of minor structural adjustments within the 1:1 layers. The IR patterns also suggested the adjustments were reversible when the temperature was varied between -195 °C and 300 °C.

A partially hydrated halloysite (Utah), could be easily intercalated by KOAC at room temperature but when this halloysite was heated to 300 °C for one hour and then cooled to room temperature, the halloysite could not be intercalated in two weeks. One explanation for the cease of intercalation of dehydrated halloysite could be the result of 1) the diminished open at the edges and ends of the tubes after losing the interlayer water and 2) the reduced structural stress caused by rolling the 1:1 layers to the tubular morphology.

These intercalation rate changes observed on the heated halloysite and kaolinite, along with the in-situ high temperature intercalation results reported in the literature, and the well documented effect of particle size on the intercalation, appeared to point to one common cause: the minor structural adjustments of the tetrahedra and octahedra in the 1:1 layers at higher T or during morphology changes to minimize the structural stress caused by the misfit of the tetrahedral sheet and octahedral sheet and to maximize the H-bonding between the 1:1 layers.
The hydrogen isotope fractionation in thermally-treated phyllosilicates verifies the models of their dehydroxylation

Arkadiusz Derkowski, Nadine J. Kanik (Institute of Geological Sciences, Polish Academy of Sciences, Senacka 1, Krakow, Poland), Jens Dyckmans (Centre for Stable Isotope Research and Analysis, University of Gottingen, Gottingen, Germany)

The dehydroxylation of phyllosilicate minerals quantitatively follows the reaction: $2(OH) \rightarrow H_2O + Or$ (residual $O$ in the structure). The known models of phyllosilicates’ dehydroxylation involve either a one-step reaction proceeding from pristine to the fully dehydroxylated phase, or a multi-step reaction that includes an intermediate phase. The reaction is speculated to proceed either by an instantaneous dehydroxylation of the entire layer (or even a crystallite) and sudden interlayer opening due to the $H_2O$ pressure, or by $H_2O$ molecule-by-molecule formation and their subsequent individual diffusion through the interlayer.

By analysing partially dehydroxylated, various 1:1 and 2:1 layer type phyllosilicates for their H isotope composition, we found two, distinctive, pronounced patterns of the H isotope evolution in the residual OH groups. In dioctahedral and trioctahedral micas - structures with a relatively large interlayer space, filled by potassium cations - H isotopes undergo strong fractionation during dehydroxylation. In the structures devoid of interlayer cations (1:1 type layer minerals and pyrophyllite), thus, with a narrow interlayer space, the fractionation is negligible or non-existent. Dehydrogenation, occurring along dehydroxylation in Fe(II)-bearing phyllosilicates, leads to even stronger H isotope fractionation in the residual OH groups than dehydroxylation.

Internal fractionation of H isotopes is possible only in the model of dehydroxylation that involves a molecule after molecule removal from the octahedral sheet, and with an interlayer space wide enough for $H_2O$ diffusion. Therefore, the fractionation observed in muscovite and illite questions the entire model of dehydroxylation based on structural studies. The lack of fractionation in interlayer cation-free phyllosilicates provides insight into H migration and removal during dehydroxylation, implying the layer-by-layer reaction model.

This is the first time that H isotope determination has been used for the verification of the models dehydroxylation in phyllosilicates. Also, we suggest using kaolinite and serpentine as H isotope mineral reference materials. The currently available reference materials (muscovite - USGS 58 and biotite - USGS 57) undergo H isotope fractionation during heating, making them unreliable for particular protocols for H isotope ratio determination.

The study was supported by the National Science Centre, Poland (grant No. 2021/41/B/ST10/01951).
The high-pressure (HP) adsorption of molecular hydrogen generated in underground nuclear waste repositories (NWRs) on bentonite barriers.

Arkadiusz Derkowski & Paweł P. Ziemiański (Institute of Geological Sciences, Polish Academy of Sciences, Senacka 1, Krakow, Poland)

The reaction of water with metal canisters leads to the generation of H₂ gas and its release into the bentonite barrier hosting radioactive material in NWRs. The bentonite’s extremely low permeability to gases will cause the buildup of up to 100 bar of H₂ pressure present around the canisters for thousands of years. A significant portion of the generated H₂ can be adsorbed physically within the bentonite barrier.

This study presents the textural and structural control of H₂ adsorption on smectite minerals, by combining the HP-H₂ adsorption with low-pressure N₂ and CO₂ adsorption techniques, and transmission electron microscopy. The HP adsorption isotherms of H₂ were recorded on various cationic forms and hydration states of smectites and illites at ambient and elevated temperatures relevant to those predicted for NWRs.

In kerogen-poor clays, clay minerals form the microporosity available for gases to adsorb, whereas the mesopore surface area and volume play an insignificant role. The H₂ adsorption is primarily controlled by the texture of the clay particles represented by the crystallites’ planar dimensions and their aggregation pattern. The adsorption sites are located outside the interlayer space unless it is open wide enough for H₂ to diffuse. Therefore, HP-H₂ adsorption volume in bentonites can be accurately approximated by N₂-accessible (at 77°K) micropore volume only if H₂ does not intercalate the smectite interlayers, as at 77°K they are not available for N₂ molecules.

We found that H₂ intercalates the interlayers of smectite with a basal spacing larger than 10.8 Å. Under specific conditions, the interlayer pillared by organic cations or incompletely dried cations of high hydration enthalpy can accommodate more H₂ than the adsorption sites at the external features of crystallites. Most of the H₂ would be adsorbed in micropores accessible to CO₂. However, interlayer expandability under CO₂ (measured at 273°K) and probably not under HP-H₂ makes CO₂ useless as a proxy for H₂.

Despite weak interactions of H₂ with minerals, the density of adsorbed H₂ is about double that of free H₂ gas at given geologic conditions, effectively increasing the gas storage capacities in bentonite and decreasing the H₂ pressure buildup in NWRs.
The Availability of Clay Resources and Ceramic Production Technology in Antiquity: A Case Study of Iron Age Insular Communities of the Eastern Adriatic

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Compositional properties of clay resources used in ceramic manufacture have long been a matter of interest of archaeometric community. Kaolinite and illite clays are normally the common raw material choices in the traditional pottery production due to their availability and comportment during firing giving rise to the optimal technological properties of thermally altered clays. The choice of the raw material and its preparation recipes are also culture specific and can be used to learn about the behavior of our prehistoric ancestors especially when written sources are elusive. The Iron Age communities that lived on the island of Hvar in the Eastern Adriatic are a prime example of this. Clay-rich sediment sources were obtained from the island and the neighboring mainland. Three sediment groups emerged from this prospection: terra rossa soil, Eocene flysch, and Cretaceous paleosols (Fig. 1). These sediments were analyzed for mineralogy, geochemistry, and granulometry. The island was home to both indigenous hillfort communities and Greek colonists who left behind a material record. Fragments of their locally made ceramic vessels were excavated and underwent similar analyses to then be compared to the sediments. This allowed for analysis of prospection and production techniques that would provide insights into their respective cultures and technological aptitudes.

![Figure 1. Prospective clay-rich raw materials. Left to right: terra rossa soil, Eocene flysch, and Cretaceous paleosols.](image)

The Cretaceous paleosols were determined to have the optimal properties for ceramic production. The dominant clay mineral is illite with some illite-smectite. There was also a lower amount of carbonate in the paleosols than in the other two sediment types. High concentrations of carbonates will cause breakage in the vessel while a small amount acts as a flux to cause sintering. The utilization of this material would not have required much temper material and showed a strong understanding of ancient potters what materials would be beneficial for ceramics.
A comparative photocatalytic study of TiO$_2$-loaded nanotubes derived from kaolin group minerals: evaluation of degradation efficiency using dyes as model pollutants

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Mesoporous phyllosilicate materials with nanotubular morphology have drawn much attention lately. Such structures play an important role as supports for photocatalysts. The transformation of lamellar kaolinite into mesoporous nanoscrolls enables the production of inexpensive material of high purity. This research compares the photodegradation efficiency of TiO$_2$-loaded 1:1 layered supports of different morphology using dyes as model pollutants.

Kaolinite nanotubes (MN) were prepared using kaolinite-rich sample (M) from Maria III deposit (Poland). The obtained MN material was calcined at 600°C for 3 h (MNC). Further, the M, MN, MNC, halloysite-containing sample from Polish Dunino deposit (HD) and halloysite purchased from Sigma Aldrich (HS) were impregnated with TiO$_2$. This procedure gave: MT, MNT, MNCT, HST and HDT materials containing ~30-40 wt.% of TiO$_2$. The synthesized samples, as well as commercial P25 photocatalyst (Evonik), were examined in UV photodegradation reactions (365 nm, 10 mW/cm$^2$) against methylene blue (MB), safranin O (SO) and acid blue 129 (AB129).

The XRD pattern of MN showed an 8.85 Å basal reflection attributed to methoxy-kaolinite. The tubular morphology of MN was preserved after calcination (MNC sample) as attested by STEM micrographs. The N$_2$ adsorption/desorption proved the mesoporous character of MN and MNC with high S$_{BET}$ of 72.8 m$^2$/g and 75.7 m$^2$/g, respectively. The TiO$_2$-loaded samples contained various anatase/rutile ratios identified with Raman spectroscopy. The photocatalytic experiments showed the advantage of MNCT and HST in dyes degradation. These samples demonstrated MB degradation rates of 0.035 and 0.033 (1/min) correspondingly, which was close to the P25 rate - 0.042 (1/min). The fastest AB129 removal was observed for the MNCT where the degradation rate reached 0.009 (1/min), while the rate for P25 was slightly lower - 0.008 (1/min). The SO degradation was faster than for the AB129. In this case, the dye removal by the HST was faster than for the MNCT with a degradation rate of 0.019 and 0.015 (1/min), respectively. Considering the ratio of photodegradation efficiency to TiO$_2$ content, the MNCT and HST samples showed a better photocatalytic effect than P25.

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Revealing surface properties of sepiolite by monitoring dehydration of confined water

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The physiochemical properties of water in the confinements of clay minerals and mesoporous materials are characteristically different from those of bulk water. Sepiolite, a modulated 2:1 clay mineral, has confinements (tunnels) that run along the length of the tubular morphology. At optimum moisture conditions, each confinement holds 8 zeolitic water (Zw) that can be reversibly lost upon mild drying by heating or purging with N₂. Earlier studies have revealed the number of sites and the distribution of the sites of Zw in the confinements of sepiolite. Yet, little is known about the re-arrangement of the confined Zw and the re-distribution of sites during the dehydration of the confinements or the chemical properties (e.g., pH) of these confinements.

Using in situ variable temperature infrared (Fig. 1) and molecular dynamics (MD) simulation, detailed investigation on the zeolitic dehydration of the confinements of sepiolite was performed. Pyocyanin (a tricyclic zwitterion with pKa 4.9) was used as a molecular probe of the chemical properties of the confinement of sepiolite. Pyocyanin is red at pH < pKa (i.e., protonated pyocyanin) and blue at pH > pKa (i.e., neutral pyocyanin).

The responses of the infrared spectrum of sepiolite to mild heating from 25 to 300 °C suggests that the confinements have four zeolitic hydration states (Fig 2): (I) a fully hydrated state (7-8 Zw), (II) a transition (intermediate) state (4–6 Zw), (III) a more stable phase hosting ~ 2 Zw, and (IV) dry state which hosts 0-1 Zw. The loss of Zw causes a relaxation of the Si-O-Si linkages. The MD results suggest that in fully hydrated confinement (i.e., 8Zw), there are 4 sites for Zw, 2.5 sites for 4Zw, and 2 sites for 2Zw. Both neutral and protonated pyocyanin came out blue on sepiolite which implies that the confinement of sepiolite was basic (Fig 3).

These results elucidated the hydration states, the distribution, and sites of zeolitic water and, the surface chemistry of the confinement of sepiolite.
The use of multiple methods to evaluate porosity and pore structure and reduce uncertainty in shale and tight reservoirs

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Multiple complications exist in measuring porosity in shale and tight (S&T) reservoirs and, because there is not a lot of pore space to begin with, even small errors in this fundamental parameter can lead to significant misinterpretation of volumetric estimates. Prior to the development of novel methods for evaluating saturation and porosity in S&T via integration of traditional and NMR techniques, the industry used methods originally developed for conventional reservoirs (i.e., pycnometry, Dean Stark, retort, water-immersion). Each of these methods, though, came with its own challenges when applied to S&T rocks and their accuracy is dependent on the types and maturity of organic matter, the amount of clay-bound water, and the variety of mobilities of different fluids hosted in the rock. Further complicating matters, the pore structure of these reservoirs can vary greatly between clay- and OM-rich porosity to matrix-dominated porosity.

One approach to evaluate this data is to avoid use of any one technique. Rather, by measuring the porosity of the rocks with different methods, and understanding the relationships between those methods, it is possible to bracket the porosity between high and low bounds. For example, in one set of wells, we conducted Dean Stark, Water Immersion Porosity (WIP), NMR, and retort (summation of fluids) porosity measurements. The WIP values were typically the lowest measured with the values obtained from Dean Stark at the high-end and the NMR and retort values scattered in between. The multiplicity (and variability) of measurements allows the practitioner to better understand when they have arrived at a reasonable value for porosity.

In addition to the measurement of the actual value of porosity, pore structure analysis gives insight into potential flow regimes and whether the porosity is OM- or matrix-hosted. This information has been used to correlate to electro-facies and used to propagate pore structure analysis to petrophysics workflows.
Se(VI) Diffusion through Montmorillonite: Comparison of Na and Ca Counterions

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Bentonite is commonly used in engineered barrier systems for nuclear waste disposal due to its unique swelling properties and high cation exchange capacity, which arise primarily from the high smectite (e.g., montmorillonite) content. Solute transport in barrier systems is controlled by diffusion, and adsorption of solutes to the clay can significantly retard transport of radionuclides. Furthermore, the cation composition of montmorillonite is known to affect its microstructure and swelling behavior. While a relatively minor component of spent nuclear fuel, $^{79}$Se is a major driver of the safety case for spent fuel disposal due to its long half-life ($3.3 \times 10^5$ yr) and its low adsorption to clay ($K_d<10$ L/kg), thus a thorough understanding of Se diffusion through clay is critical for understanding the long-term safety of spent fuel disposal systems. Through-diffusion experiments with tritiated water (HTO) and Se(VI) were conducted with a well-characterized, purified montmorillonite source clay (SWy-2) under a constant ionic strength (0.1 M) and three different electrolyte compositions: Na, Ca, and a Na-Ca mixture, in order to probe the effects of electrolyte composition on clay microstructure, Se(VI) aqueous speciation, and ultimately diffusion. HTO served as a conservative tracer, providing insights into the montmorillonite structure under the different electrolyte compositions. HTO flux was 40% higher in the Ca cell compared to the Na cell, despite only an 8% increase in the total porosity. This increase in flux is likely due to a greater degree of clay layer stacking in the presence of Ca compared to Na, which leads to larger inter-particle pores. The difference in Se(VI) flux was even greater, with the flux in the Ca cell being six times higher than in the Na cell. These differences in Se(VI) flux cannot be explained by differences in clay structure alone. Rather, differences in Se(VI) aqueous speciation and adsorption must be invoked to explain the results. Using a combination of experimental and modeling work, this study highlights the compounding effects that electrolyte and counterion compositions can have on radionuclide transport through clay.
Batch Reactor Alteration of the Hedemünden Nontronite at 180 °C in 0.1 M NaCl Solution: Constraining the Role of Accessory Minerals and K-Oxalate Additives

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The search for a suitable repository for high-level radioactive waste (HLRW) represents a major challenge for all nations that use nuclear energy. In Germany a suitable location is being searched for that can safely store the highly radioactive waste for at least 1 million years. There are various concepts for final disposal, for most of which bentonites play a key role. In this study we focused on nontronite, the di-octahedral Fe rich smectite, in order to experimentally investigate the influence of high Fe-contents in smectites regarding alteration processes. We purified the Hedemünden nontronite and investigated how the presence of calcite, pyrite and K-oxalate influences the stability of the nontronite. The batch reactor experiments of the nontronite were conducted at 180 °C in a rotary oven (20 rpm) for 31 days, with 10 % of accessory minerals (calcite and/or pyrite) with and without 0.03 M K-Oxalate in 0.1 M NaCl solution. The products were analyzed by XRD, XRF, IR, SEM-EDX, MP-AES and pH.

The results show significant changes in the state of the nontronite occurred after the 31 days of batch reaction. The degree of alteration was particularly influenced by the presence of K-oxalate solution. The pH and the type of accessory minerals play a role as well and will be discussed. The K-oxalate caused permanent K-fixation by forming ordered mixed layered structures even after Ca exchange of the products. Chemically these changes were expressed in both the interlayer and the tetrahedral sheet (Si⁴⁺ by Fe³⁺), as well as a general increase of the total layer charge. In addition, all the experiments led to the formation of hematite and some formed whewellite.

The transformation of expandable smectite, at 180°C, 0.03 M K-oxalate concentration and a high fluid to rock ratio, to non-expandable minerals leads to a reduction in the swelling capacity. If this reaction were prominent, it could jeopardize the safe storage of HRLW in repositories.
Structural Properties of Organically Modified Boehmite Nanomaterials from Molecular Simulation

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Novel sorbents are needed for selective adsorption of anionic radionuclides in engineered barrier systems for underground nuclear waste repositories. Layered geomaterials such as clays and metal (oxy)hydroxides offer a platform to develop hybrid materials with modified interlayers that can be tuned for high selectivity for specific radionuclides. Here we consider glycoboehmite (GB) materials, which consist of layered g-AlOOH (boehmite) with intercalated ethane (C2), butane (C4) and hexane (C6) diols. These hybrid materials have been synthesized via several methods, but the exact interlayer structure has not been determined. In this work, molecular models of boehmite interlayers modified by C2 – C6 alkanediols are simulated using classical (force field) and quantum (density functional theory, DFT) methods. As loading is increased, the boehmite interlayer expands in stepwise fashion, similar to smectite hydrates. The interlayer initially expands to accommodate the first diol molecules, then the spacing remains nearly constant as the gallery is filled up to a monolayer on each basal surface. These monolayers can remain separated with a hydrophilic midplane lined with alcohol groups (GB2), or the monolayers can comingle forming a hydrophobic interlayer (GB4, GB6). A subsequent expansion occurs to accommodate an additional disordered layer, up to a bilayer at each surface. As seen below, simulated basal spacings are in good agreement with experimental X-ray diffraction results. The effect of temperature on the interlayer structure of monolayer and bilayer intercalates is compared with quantum calculations and experiment.

Interlayer expansion with increasing diol loading from force field simulations of glycoboehmites formed from intercalated ethanediol (GB2), butanediol (GB4), and hexanediol (GB6). Experimental values for GB2, GB4, and GB6 are shown as red, blue, and green asterisks, respectively. Diamonds represent layer spacings from DFT geometry optimization.


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Influence of Clay Minerals on Porosity Measurements: A Case Study from the Third Bone Spring and Wolfcamp Formations, Delaware Basin, Texas

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Clay minerals and their associated porosity play a significant role in unconventional hydrocarbon production. The accurate understanding of resource in-place requires the simple, yet challenging quantification of porosity. In many cases, various porosity techniques provide different answers, which introduces the question – which porosity is correct?

Whole core from the Permian Third Bone Spring Sand and Wolfcamp XY formations of the East Vermejo #1 well in Ward County, Texas highlights the occurrence of cyclic hybrid event beds. X-ray diffraction (XRD) quantifies the range of clay mineral content to vary between 3 and 45 weight %, with an average of 17%. Mercury injection capillary pressure (MICP), N₂ adsorption, helium porosity, and scanning electron microscopy (SEM) measurements were acquired on subsamples taken from the whole core to understand porosity and pore distributions.

SEM imaging on Ar-ion-milled samples showcases the interplay of inorganic and organic pore systems, the former comprised of both clay-mineral-associated and non-clay-mineral-associated interparticle porosity. The dependency of the various porosity measurements to capture the full range of pores is dependent on both the sample condition and measurement technique. Crushed sample material can be advantageous for high clay content facies to provide sufficient surface area for both residual fluid removal and pore access. For intrusive-based measurements, smaller molecular size of measurement fluids aids pore access concerns. Clay-rich samples also present stress-sensitivity due to weaker mechanical strength and slot-like pore structures, which influence applied pressure measurements such as MICP. Due to the additional presence of non-clay mineral associated porosity, distribution measurements such as N₂ adsorption and MICP offer additional characterization on the size range and abundance of clay-mineral-associated porosity.

The results of this targeted case study emphasize the need for multiple porosity measurement integration, especially for characterization of clay-rich facies. This process allows for implementation of a “Three Point Stance” approach. The convergence of results from multiple methods and resolutions indicates property constraint and accuracy. Whereas the non-similarities of integrative values provide additional qualitative understanding based on the advantages and limitations of the respective methodology and measurement resolution.
Figure 1: Backscatter scanning electron microscope image of clay mineral-associated porosity from a laminated siltstone. Clay mineral-associated porosity is observed to be slot-like in form with maximum pore width apertures less than 3 micron.

![Backscatter scanning electron microscope image](image)

Figure 2: Comparison of pore size distributions from mercury injection capillary pressure (MICP) and N\textsubscript{2} adsorption techniques. The N\textsubscript{2} adsorption distribution more accurately characterizes the clay porosity and distribution of the laminated siltstone, while the MICP distribution covers the range of clay mineral-associated and non-clay mineral-associated interparticle porosity.
Fe(II)-clay interactions: Anaerobic batch and diffusion experiments employing purified montmorillonite SWy-3 and isotopically purified $^{56}$Fe

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Swiss and French HLW repository concepts for radioactive waste will employ steel waste-containing canisters and bentonite (as backfilling material). Upon repository closure, steel canister corrosion will eventually release mobile Fe(II) into the bentonite clay. Several corrosion-related processes potentially affecting the barrier function of the bentonite backfill have been recognized, including (1) local cementation of bentonite via precipitation of Fe (oxyhydr)oxides (2) destabilization of the dioctahedral smectite leading to dissolution, or (3) transformation to a non-swelling Fe phyllosilicate by incorporation of diffusing Fe into the structure, and (4) Fe sorption on smectite, possibly followed by reduction of smectite structural Fe ($\text{Fe}_{\text{str}}$).

A mechanism of steel-bentonite interaction was recently proposed (Hadi et al., 2019) occurring in two main phases. In the first “pre-anaerobic” phase, the Fe(II) generated by anaerobic steel corrosion is oxidised in situ by residual $\text{O}_2$ as it diffuses into the bentonite, generating a goethite rich rim at the vicinity of the interface. The “truly-anaerobic” phase begins as $\text{O}_2$ is depleted and Fe(II) diffuses deeper into the bentonite, further interacting with it (through ion-exchange, sorption, and possible electron transfer to $\text{Fe}_{\text{str}}$). This second sequence is envisioned to be the dominant process over long term interaction, following closure of repository and rapid depletion of $\text{O}_2$ trapped in the bentonite.

The present study is focused on the truly-anaerobic phase. Fe(II) interactions with a pure montmorillonite (SWy-3) are investigated in batch and diffusion experiments (Figure 1), focusing on the impact on smectite properties ($\text{Fe}_{\text{str}}$ reduction level and swelling properties), in repository like conditions (anaerobic, pH 7.3, high ionic strength, low liquid-solid ratio). Post mortem analyses include solution assays, and $^{57}$Fe Mössbauer spectrometry of the reacted clay. Isotopically purified $^{56}$Fe(II) solutions (transparent to Mössbauer spectrometry) are employed in order to focus on eventual redox alterations of $\text{Fe}_{\text{str}}$. Our data show great contrasts between batch (diluted) and diffusion (compacted) experiments. In diluted conditions, high Fe(II) uptake by the clay is observed (through both sorption and surface precipitation), accompanied by extensive electron transfers from sorbed Fe to $\text{Fe}_{\text{str}}$. Instead, in compacted conditions, Fe(II) uptake is notably lower, and no electron transfers are observed.
Figure 1: Experimental set-up for diffusion experiment, and profiles of Fe(II) concentration in the reservoirs and clay cores of two diffusion experiments.

References:
Workflow for digital determination of porosity in tight rocks

Barbara Hill (SLB Reservoir Lab)

Due to the size of the pores and pore throats, mudstone and shales represent unique difficulties in determining porosity via conventional methods due to the size of the pores and pore throats, pore hosts (matrix vs organic), and open ionic bonds on the surface of clay minerals.

Digital rock analysis (DRA) overcomes these challenges through a unique workflow which begins with careful sample selection from core (whole core or sidewall cores) and/or cuttings. Samples are affixed to an aluminum stub and initially polished manually, but ultimately through ion milling. The surface of the prepared sample is then imaged in backscattered electron mode (BSE) using a 2D scanning electron microscope (SEM). Once imaging is complete, all images are stitched together to form a large mosaic of the entire surface. Digital analysis of the stitched mosaic yields porosity and an evaluation of the heterogeneity. To clarify which minerals are hosting pores, we use automated mineral mapping software to create a mineral map that encompasses the entire stitched surface.

To apply SEM image analysis to core and field scale, subsections from the stitched image are chosen to best represent the rock. Each subsection is imaged at a resolution that is higher than the initial stitched image resolution and the resulting stitched mosaic of the subsection is then digitally processed to determine organic-hosted, matrix-hosted, and total porosity. The results are then compared to the initial larger scale mosaic image and the mineral map, and a determination is made as to which location within the subsections will be used for high resolution 3D imaging and volume rendering. Once the location for the 3D imaging is chosen, it is imaged using focused ion beam SEM (FIB SEM) providing high resolution images which are stacked together to form a 3D volume of the subsection which best represents the original sample. As with the 2D SEM images, organic-hosted, matrix-hosted, and total porosity are determined at a high level of accuracy, such that the SEM subsample matches the macro sample. By paying close attention to minor details, we are able to obtain a representative sample at the micron to nano scale which allows us to upscale the volumetric data to core scale and ultimately to field scale.
Crushed Rock Analysis—Reservoir Lab Retort and Retort + Chemical Methodologies

Barbara Hill (SLB Reservoir Lab)

To calculate hydrocarbon reserves, clients must know the oil, gas, and water saturations of their reservoir. While the saturations may be estimated from wireline logs, many clients look to core analysis to help them adjust their petrophysics models for a better estimate of the reserves. For porous and permeable rocks such as clean sandstones, deriving saturations from the samples is a relatively straightforward process that involves taking a plug from a whole core or using an intact sidewall core that undergoes a distillation process to extract the water content, cleaning in solvents to extract soluble hydrocarbons, pressure tests, bulk volume measurements, etc. Once the data are derived, calculations are made and reasonable estimates of porosity, permeability, and saturations are determined. With organic-rich tight rocks, however, the determination of these properties is not as straightforward. For tight rocks, the distillation process may take weeks or months just to establish a stable water content from a plug or intact sidewall core. Alternate methods using crushed rock samples instead of intact plugs or sidewall cores were derived to expedite water and hydrocarbon extraction and to thus determine porosity and saturations. Two of the most commonly used methods today are chemical extraction using solvents (GRI method and modifications thereof) and thermal extraction (retort) using heat. For this presentation, the Tight Rock Analysis (TRA) and the modified TRA methods used at SLB Reservoir Labs for the derivation of porosity, permeability, and saturations of a typical organic-rich, tight mudstone sample will be explained.
Development of yet another classical forcefield for molecular modelling of (clay-) minerals

Michael Holmboe (Umeå University, Umeå, Sweden)

Molecular simulations techniques, based on electronic or classical DFT, \textit{ab initio}, classical Monte Carlo (MC) and molecular dynamics (MD) simulations, have emerged as useful tools to obtain detailed insights into the structure, thermodynamics and dynamics of hydrated clay minerals and other geochemical systems [1]. However, classical MC and MD simulations approaches rely on the ability of pre-defined forcefields to accurately represent the unit cell metrics and the angles and bond distances of atomic structures (\textit{i.e.} the mineral lattices), typically obtained from X-ray diffraction or other experimental methods. The motivation for a new mechanistic forcefield for mineral and layered hydroxides was simply to improve the agreement between simulated and experimental structural data compared to existing forcefields such as Clayff and the Interface FF [1,2], as revealed by Bond Valence Sum (BVS) analysis and a direct comparison to reference unit cell data.

This new forcefield, called MinFF, uses angle terms but no bonded terms between all metal-oxygen sites, which also if used with Clayff also improves its ability to represent the unit cell metrics of layered hydroxides. The overall forcefield optimization was obtained from iterative simulations using the MD package Gromacs, controlled by the \textit{atom} MATLAB Toolbox [3] acting as a wrapper. The optimization was performed with respect to the Lennard-Jones potential (\textit{i.e.} the \textit{VdW} interactions), with fixed or starting values for the partial charges and C6 dispersion coefficients taken from the Chargemol, MCLF and DFT-D3 programs [4,5]. To assure generality of the new forcefield, this was done synchronously for different minerals lattices sharing oxygen atomtypes.

Automated modelling of 1D XRD profiles based on the recursive algorithm

Michael Holmboe (Umeå University, Umeå, Sweden)

X-ray diffraction of clay minerals has intrigued the scientific community for nearly a century, since give information about the clay mineral crystallinity, or lack thereof. Especially for samples containing smectite clay minerals, one-dimensional mixed layered modelling (also denoted 1D XRD modelling) is a useful technique that can reveal the irrational series of 00l X-ray reflections, the (small) crystallite size, mean particle orientation, as well as the unit cell metrics and composition (along [001]) of coexisting phases [1]. A handful of studies in the last decade using Monte Carlo (MC) or molecular dynamics (MD) simulations has demonstrated the power of classical molecular simulations in generating averaged unit cell data of the interlayer material (water, cations and organics), resulting in nearly perfect crystal layer structure factors (F(hkl) or preferably the continuous G(2θ)) needed for the 1D XRD modelling [2], using mainly the matrix formalism.

Here we present a 1D XRD modelling of montmorillonite and vermiculite, using a code called 1DXRD2C which allows mixing of four main phases, each consisting of two interstratified subphases. 1DXRD2C is based on Reynolds recursive algorithm used in the code Newmod [3], here implemented in MATLAB using several new features, such as full optimization of phase relative weights, basal spacings, particle size distribution, interparticle diffraction, microstructural strain using custom layer types (e.g. custom phases), taken either from tabulated structural data or molecular modelling entirely. Since 1DXRD2C can be run in manual as well as in fully automatic mode, a trial-and-error analysis and brute force iterative method can be used to perform a sensitivity analysis on the modelled variables, granting more rational fine-tuning in 1D XRD modelling.

(3) Reynolds, R.C., Jr. NEWMOD© a Computer Program for the Calculation of One-Dimensional Diffraction Patterns of Mixed-Layered Clays.
Geological gas storage: $\text{H}_2$ and $\text{CO}_2$ intercalation into smectite interlayers

Tuan A. Ho, Yifeng Wang, and Carlos F. Jove-Colon (Sandia National Laboratories, Albuquerque, NM)

Gas ($\text{H}_2$ and $\text{CO}_2$) geological storage has been considered an important strategy for meeting our energy demands and reducing the greenhouse gas effect to the environment. The safety and economic feasibility of geological gas storage depends on gas interactions with earth materials including gas intercalation into smectite that is present in caprock. Intercalation traps $\text{CO}_2$ and induces swelling that can lead to closure of fractures in caprock, thus improving seal integrity. However, for hydrogen, intercalation causes $\text{H}_2$ loss, thus affecting the economic feasibility of a storage. $\text{H}_2$ intercalation into clay interlayers may also find its importance in a nuclear waste repository, where $\text{H}_2$ can be generated from metal corrosion of nuclear waste canisters. The $\text{H}_2$ uptake and transport across a clay-based engineered barrier is an important process that needs to be considered for nuclear waste disposal. Using molecular dynamics (MD) simulation, we calculate free energy landscapes of gas intercalation into montmorillonite interlayers as a function of structural charge distributions and interlayer hydration states. Our results reveal that hydrated clay interlayers promote gas uptake into the hydrophobic (e.g., siloxane groups) domain, while inhibiting gas sorption near the hydrophilic sites (e.g., charge sites). On average, the $\text{CO}_2$/water ratio in interlayers is higher than $\text{CO}_2$/water ratio in bulk water. However, $\text{H}_2$/water ratio in interlayers is comparable or less than $\text{H}_2$/water ratio in bulk water. Compared to $\text{CO}_2$, the amount of $\text{H}_2$ intercalated into hydrated interlayers is about one to two orders of magnitude smaller. Our results qualitatively predict that $\text{H}_2$ loss due to intercalation into clay-rich caprock and leak through clay interlayers, if any, is limited.

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Laboratory Spectral Analysis of Abandoned Mine Waste from the Former Katherine Gold Mine, Arizona: Mineralogical and Textural Characteristics with Implications for Future Remote Sensing Studies

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The Katherine Au-Ag mine, in Lake Mead National Recreation Area, Arizona, was in operation from 1903 to 1943. Gold and silver were mined primarily from Comstock-type epithermal quartz veins. A reconnaissance study by the U.S. Bureau of Mines estimated that the mine generated approximately 640,000 tons of mill tailings, averaging 0.344 g/t Au and 15.2 g/t Ag. Seventy-four samples were collected and analyzed by the USGS using laboratory spectral reflectance methods spanning the < 1-mm wavelengths in the visible and near infrared (VNIR), > 2-mm wavelengths in the shortwave infrared (SWIR), and the 8- through 14-mm wavelength range also known as the thermal infrared (TIR). These samples were spread across 0.13 km² of exposed surface of the tailings piles. They include samples from the main alluvial channels directly upstream and downstream of the waste piles, as well as regolith and soil from older alluvial surfaces, not associated with previous mining activities.

In terms of the most dominant phyllosilicate minerals detected, the 2-mm SWIR results show that the tailings piles are not mineralogically distinct from any of the surrounding alluvial sediments. Most tailings contain the same variety of “low Al” muscovite, which retains much of the iron and magnesium not removed as a result of hydrothermal alteration or other fluid enrichment or depletion processes. The 1-mm VNIR results show greater variability in the types of iron-bearing minerals detected across different tailings samples. This includes evidence of (in decreasing abundances): chlorite-muscovite intimate mixture, goethite grain coatings, unidentified amorphous ferric-iron phases, a monoclinic amphibole type (cummingtonite?) and hematite. In contrast, the surrounding alluvial samples are mostly dominated by goethite grain coatings. The TIR results display the most lithologic contrast between the tailings piles, and the surrounding alluvial channel and older fan/terrace regolith samples. For example, with the exception of one outlying sample, the tailings pile samples were all spectrally matched to a mixture of fine-grained hydrothermal quartz and fine-grained carbonate minerals. Alternatively, the alluvial samples contained mostly coarse-grained non-hydrothermal quartz and feldspars. For future hyperspectral remote sensing studies of Comstock-type Au-Ag mine waste, the TIR wavelengths will provide the best data for separating the waste piles from surrounding geologic substrates. The 1-mm wavelengths will allow the mapping of compositional variability within the actual waste piles.
Layered double hydroxides supported by clay minerals as photocatalysts for visible light-driven degradation of organic pollutants

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Photocatalytic degradation is one of the most extensively studied methods of purifying water from organic pollutants. However, most of the designed and used photocatalysts, such as TiO₂, are not active in the visible region of light. Layered double hydroxides (LDH) are promising photocatalysts that can be used with visible light, yet their efficiency needs enhancement. The use of clays as support for LDH-photocatalysts may improve their performance, due to the increased LDH dispersion and the prevention of electron/hole recombination. Thus, the aim of this study was to obtain LDH-photocatalysts supported by smectite, kaolinite and halloysite and compare their photocatalytic performance.

The co-precipitation method was used to synthesize LDH materials (Zn/Cr, Ni/Cr, Cu/Cr and Co/Cr). The M\textsuperscript{II}:M\textsuperscript{III} ratio was set to 2:1. To obtain LDH-clay composites, the Zn/Cr LDH was co-precipitated in the presence of clays with different contents: 20%, 33% and 50% wt. Due to its stability in visible light, methylene blue (MB) was used as a model organic pollutant. The MB aqueous solutions containing photocatalysts were exposed to visible light (150 W LED lamp, light intensity: 145 000 Lx). Analogous experiments were conducted in the dark. The kinetics of MB degradation was studied by UV-Vis spectrophotometry.

The X-ray diffraction of all obtained phases confirmed the formation of layered structures. As shown by diffuse-reflectance UV-Vis spectroscopy, all materials showed strong absorption bands in the 300-750 nm region. This indicated their activity in visible light. For all LDH materials, the MB adsorption was negligible while the photodegradation reaction (after 1 h) reduced the MB concentration by: Cu/Cr – 9.30%, Ni/Cr – 14.67%, Co/Cr – 15.31% and Zn/Cr – 20.39%. Due to its effectiveness, the Zn/Cr material was used for further experiments. LDH supported on smectite (20% wt.) led to a 31.53% decrease of MB concentration (adsorption – 11.91%). Kaolinite and halloysite supports did not enhance the photocatalytic performance of LDH – the decrease of MB was less than 6%.

In conclusion, Zn/Cr LDH supported on smectite shows promising results and further studies of the composite are currently being carried out.

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Methane accessibility and densification in the Niobrara Formation at wet-gas thermal maturity conditions

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Wide Q-range total neutron scattering was used to evaluate methane (specifically perdeuterated methane, CD₄) accessibility and densification in a sample (C-marl equivalent) from the Late Cretaceous Niobrara Formation with the NIMROD instrument at the ISIS Neutron and Muon Source. The Niobrara is an active oil and gas producing formation within the Denver-Julesburg Basin. The sample contains organic matter (total organic carbon = 2.5 wt%) at the late oil/wet-gas thermal maturity stage (solid bitumen reflectance = 0.99%) with mineralogy dominated by calcite (~60 wt%), clays (~20 wt%), and quartz (~15 wt%). NIMROD allows for measurement of neutron scattering across Q-ranges from ~0.02 to 50 Å⁻¹ enabling simultaneous evaluation of confined fluid structure, pores with diameters from ~0.5 - 20 nm, and Bragg peaks from minerals. Furthermore, contrast matching experiments with pressurized CD₄ (up to 750 bar at 60°C using custom high-pressure sample cells) quantified the degree of open versus closed porosity (i.e., methane accessibility) in our sample.

Data show that the Niobrara Formation sample exhibits mass fractal scattering behavior similar to previously measured U.S. marine shales. With increasing CD₄ pressure, scattering intensities between Q = 0.02 – 0.1 Å⁻¹ decreased until 750 bar, and at that point 75% of pores with ~20 nm diameters were determined to be CD₄ accessible. In contrast, between Q = 0.1 – 1 Å⁻¹, scattering intensity initially increased at the lowest CD₄ pressure tested (200 bar) before decreasing with increasing pressure. These data are interpreted as evidence for the creation of fine organic porosity (i.e., pore diameters 0.5 – 5 nm) through partial solvation of bitumen by supercritical CD₄. No CD₄ adsorption into clay inner layers is resolvable, although the Bragg peak from swelling clays (e.g., smectite) is clear in the scattering signal. Additionally, there is strong evidence for densification of CD₄ within our sample as revealed by the shift in the CD₄ intermolecular scattering peak to higher Q-values compared to bulk CD₄. Our results provide insight into fluid properties within low permeability geologic matrices and are discussed with perspective toward pressure management of gas condensate wells.

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The Callovo-Oxfordian (COx) clayey formation has been selected as the host rock for geological radioactive waste disposal site in France. COx contains 25-55% of clay minerals. Clays exhibit unique properties, such as, low hydraulic conductivity, high sorption and retention capability for radionuclides and swelling/self sealing properties which make them excellent host rock candidates for radioactive waste disposal. Hydrogen gas (H\textsubscript{2}) can be formed in the waste repository under storage conditions through radiolysis of water due to the residual radioactivity or through anoxic corrosion of steel waste containers (3Fe+4H\textsubscript{2}O=Fe\textsubscript{3}O\textsubscript{4}+4H\textsubscript{2}(g)). The accumulation of H\textsubscript{2} presents a potential risk of overpressure and fracture of the surrounding host rocks within the repository. To prevent this, it is crucial that gases are either absorbed, diffused, or react with the constituent host rocks.

We apply the techniques of classical molecular dynamics (MD) and Monte Carlo (MC) simulations to quantitatively investigate the H\textsubscript{2} gas uptake in hydrated clay and improve the fundamental understanding of the physical and chemical processes governing the interactions between H\textsubscript{2} and H\textsubscript{2}O molecules in clay interlayers and interfaces. Grand Canonical MC simulations of H\textsubscript{2}/H\textsubscript{2}O binary mixture adsorption in Na- and Ca-montmorillonite interlayers at temperatures of 25, 50, and 90°C and pressures up to 120 bar show that the adsorption of H\textsubscript{2} gas exhibits a proportional increase with increasing pressure, while a decrease is observed with increasing temperature in accordance with the solubility of H\textsubscript{2} in water. However, the mole fraction of adsorbed H\textsubscript{2} in hydrated clay interlayers is higher in comparison to its solubility in water.

In addition, we performed MD simulations to quantitatively probe the local structural and energetic characteristics of H\textsubscript{2} adsorption in the interlayer, basal, and edge surfaces of montmorillonite through the use of enhanced MD technique. On the basal montmorillonite surfaces, H\textsubscript{2} molecules occupy the siloxane cavities, but this is limited by the Al/Si tetrahedral substitutions on the surface. The H\textsubscript{2} adsorption energetics of H\textsubscript{2} within the interlayers and on the edges of montmorillonite nanoparticles is strongly affected by the local hydration structure.
Structural hydrogen isotope alterations of clay minerals during chemical treatments: qualitative and attempted quantitative approaches

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Chemical pre-treatments are routinely used to remove impurities from clay-rich materials. This is done to ensure data quality is not impacted by impurities, however, exposure to reagents may alter the H-isotope composition of the hydroxyl hydrogen (H) in the clay mineral structure. This work investigates the impact of widely-used pre-treatments on clay mineral H-isotope compositions.

The extent of structural hydroxyl H-isotope alteration during chemical pre-treatment was investigated for nontronite (NAu-1), montmorillonite (SAz-1), saponite (SapCa-1), and kaolinite (KGa-2) reference materials obtained from the Clay Minerals Society Source Clay Repository. To trace alteration, aliquots of 200 and 70mg from each material, underwent pre-treatment in isotopically labelled water and reagents with \(\delta^2\text{H}\) values of ~ +200 and +570‰. Pre-treatments included: carbonate removal with 10% hydrochloric acid (HCl) and acetate buffer; organic matter removal using 30% peroxide (\(\text{H}_2\text{O}_2\)) and 6% sodium hypochlorite (\(\text{NaClO}\)); Fe-(oxy)hydroxide removal by Na-citrate-bicarbonate-dithionite solution (CBD). The H-isotope analysis was done by High Temperature Elemental Conversion coupled to an Isotope Ratio Mass Spectrometer.

The results showed that H-isotope ratios (\(\delta^2\text{H}/\delta^1\text{H}\)) for kaolinite were not altered by any treatment. The saponite \(\delta^2\text{H}/\delta^1\text{H}\) was altered by \(\text{NaClO}\), as ~5% of H-atoms were altered regardless of reagent \(\delta^2\text{H}\) value. This same effect was observed for montmorillonite reacted in \(\text{H}_2\text{O}_2\), whereby, the reacted fraction was ~10%. HCl resulted in >200‰ alterations for montmorillonite, which showed it to be an unsafe method, contrary to acetate buffer and CBD that did not show alteration. When 200mg of material was used, nontronite did not show significant \(\delta^2\text{H}/\delta^1\text{H}\) alteration with any treatment except for CBD. When the same treatments were done with only 70mg of material, nontronite \(\delta^2\text{H}/\delta^1\text{H}\) were significantly altered. This indicates that the structural \(\delta^2\text{H}/\delta^1\text{H}\) may be sensitive to the material-reagent ratio used during treatment. This effect was also seen for montmorillonite with three of the treatments, but was not as pronounced.

From this evidence it can be concluded that routine chemical pre-treatments can alter the \(\delta^2\text{H}\) value of various clay minerals differently and reaction conditions, such as, material-reagent ratios may contribute to alteration.

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Determining layer charge alterations of smectitic wettable surfaces in the Alternate Buffer Materials experiment (Äspö) with the new O-D spectroscopic method: Correlations with cation exchange capacity

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Properties critical to the desirable performance of a bentonite for safe nuclear waste storage are controlled by the layer charge (LC) of its smectitic component such as plasticity, expandability, and cation exchange capacity (CEC). The new, fast, and efficient spectroscopic method, “O-D method”, for LC determination of materials containing smectitic, wettable surfaces was used to identify subtle LC changes in ~175 thermally reacted samples and non-reacted reference materials from the Alternate Buffer Materials (ABM) 2 & 5 experimental bentonite disc packages from the Äspö Hardrock Laboratory, Sweden. A correlation was revealed when the new LC data was compared with previously obtained CEC results.

For LC analysis, a few mg of each sample, collected following a thermal gradient along each disc, was saturated with 99.9% D2O water and analyzed with the O-D method. The method employs Fourier Transform Infrared Reflectance spectroscopy and is based on a linear correlation between the sharp, high frequency O-D stretching band position of adsorbed D2O at 2685-2700 cm\(^{-1}\) and the LC of the bentonite smectitic component. It is highly sensitive, with reproducibility below 0.010 \(e^-\) per smectite formula unit. CEC was obtained for the same samples using the established Cu-trien method.

A trend was observed between the ABM5 LC and CEC results, whereby, both decreased correspondingly with an increase in temperature within the ABM5 package. This indicates that with a progressive increase in temperature, increased partial cation fixation occurs within the disc, which reduces the LC and hence the CEC. LC changes were between 0.020 and 0.089\(e^-\), in many ABM-reacted materials compared to their non-reacted references, being most pronounced for Febex, Ikosorb, Rokle, and Saponite. High temperatures up to 250°C were achieved in ABM5, which appeared to correspond with higher LC changes in comparison to ABM2 where the highest temperature reached ~140°C. Contrastingly, with respect to LC and CEC decreases in ABM5, some samples in ABM2, notably, Deponit, Ibeco, Rokle, and Ikosorb showed increases with increased temperature indicating possible crystal-chemical changes. Given the significantly longer reaction time of ABM2 versus ABM5, this suggests kinetics may be a factor in the long-term stability of certain bentonites.
Naturally Occurring Microbe-Clay mineral Interaction

Jin-wook Kim (Yonsei University, Seoul, Korea), Tae-hee Koo (Yonsei University, Seoul, Korea), and Hanbeom Park (Yonsei University, Seoul, Korea)

The naturally occurring microbial interaction with clay mineral is a consequence of a bacterial survival and growth strategy. Particularly, this reaction may control the smectite-to-illite transformation, source of bioavailable iron in the sediments, and evolution of microbial community in the deep biosphere. In the present study, role of microbial activity in the modification of clay minerals (e.g., mineral transformation and physico-chemical properties) in the extreme environments including cryospheric region contrast with a deep burial diagenetic setting will be presented.
Evidence for the biotic illitization at the high temperature and high pressure

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Previously undefined biogenic activity at high temperatures (80–140°C) and high pressure (55MPa) in the batch experiments have revealed that biogenic illitization occurred through microbial Fe-reduction. Collapsed smectite (K-smectite) and I/S mixed layer (2θ=9.84°) appeared in X-ray diffraction profiles and transmission electron microscopic (TEM) analysis (Al/Si=~0.4 with various interlayer K-contents) for both 80 and 140°C suggest that smectite-to-illite reaction has been progressed during the 4-month of batch experiment. However, the Fe(II)/FeTot in the bulk sediment was decreased in the lower temperature samples (80–110°C) whereas it slightly increased in the experimental and control set of 140°C condition. Furthermore, dissolved Fe in the supernatant was also only increased in the 80°C sample suggesting that reductive dissolution of structural Fe was activated only at 80°C. These geochemical results indicate that the illite formation occurred through the different pathways (biotic vs. abiotic) at two temperatures (80 and 140°C). This study will provide new evidence of biogenic illite in contrast to the illitization in the conventional diagenetic condition.
Synthesis and Evaluation of Novel Materials for Anionic Sorption

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One of the main functions of bentonite buffer and/or backfill in the engineered barrier system (EBS) is to capture and isolate cationic radionuclides in the near-field environment. Anionic radionuclides (e.g., I-129) have a significant role in Performance Assessment, as they are not sorbed/captured by the bentonite buffer. An EBS design that includes materials that provide some degree of sorption for anionic species has the potential to reduce the biosphere radionuclide release, where anionic species dominate the radionuclide dose release to the far-field [3]. This work presents a novel, low-cost anionic getter material that could potentially be incorporated into an EBS design. Glycol-exfoliated boehmite-“glycoboehmite” material has been previously synthesized and evaluated in Bell, et. al. (2021)[1]. Results show that this glycoboehmite precursor can be chemically modified with divalent cationic species, e.g. nickel, to create an effective sorbent for anionic species. We present the results of sorption studies that show the high sorption capacity of this novel class of getter materials. Arsenic as an anionic analogue to species of interest like I-129 and Tc-99 shows a 40-fold increase in sorption when glycoboehemite is modified with nickel (expressed as K_d (mL/g) solid: liquid partitioning coefficient). This work has also shown a 30-fold increase in iodide sorption with this modified material. We have also demonstrated that between two divalent metals added to the material, nickel shows higher iodide uptake than magnesium. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525 SAND2023-11977A

Characterization of pedogenic clay minerals with oxygen, hydrogen, and K-Ar isotope systems: In search of equilibrium

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Pedogenic clay minerals can store information about their formation conditions in oxygen and hydrogen isotope systems. In some cases, this information is difficult to retrieve, for instance in soils from alpine environments. The main aims of this study were 1) to verify the possibility of extracting the oxygen and hydrogen isotope compositions from the pedogenic clay minerals from alpine Podzols and 2) to determine if the obtained isotope compositions represent an equilibrium with the pedogenic environment.

Clay fractions (<0.2 μm) of Podzols from the Tatra Mountains, Poland, were investigated using: X-ray diffraction, chemical analysis, thermogravimetry and cation exchange capacity (CEC) measurements. Oxygen and hydrogen isotope compositions were measured on a CO₂ laser fluorination line and thermal conversion elemental analyzer, respectively, both connected to an isotope ratio mass spectrometer. Apparent ages of selected samples were determined using K-Ar dating.

Mineralogy of the clay samples was dominated by mixed-layer smectite (often with some degree of hydroxy-interlayering) dioctahedral mica, and kaolinite. In one profile, a small admixture of gibbsite was identified. K-Ar dating was used to check for potential contamination with aeolian micas. CEC was found to represent a good proxy of the intensity of mineral alterations and oxygen isotope composition. Assuming that smectite is the stable weathering product for investigated sites, it was possible to calculate the theoretical $\delta^{18}O$ value of the weathering product to be equal to + 27.7‰, which was higher than the expected range (+18-22‰). Hydrogen isotope compositions of investigated samples were positively correlated with mass loss >200°C. The most negative $\delta^2H$ values in the -100 - 105‰ range may represent isotopic equilibrium with the environment. Such a conclusion, however, should be treated with caution due to large uncertainties around the available phyllosilicate-water fractionation factors for hydrogen.

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Influences of particle size, shape, and crystal structure on the oriented attachment of nanoparticles.

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Oriented attachment (OA) is a recently identified pathway of crystal growth in which two primary particles, typically nanoparticles, attach and fuse to form a continuous single crystal. OA and OA-like processes can be especially important in the assembly of two-dimensional materials such as clays. This presentation will present new theoretical analysis on how the geometry of primary particles influences their probability of successfully achieving OA. First we consider how particle shape influences the probability of attaching on matched pairs of faces that will enable subsequent OA. When particles display many microfacets (as for spherically truncated particles), our analysis suggests that random collisions are highly unlikely to produce the matched pairs that are needed for OA without external bias or multiple attempts. However, Monte Carlo simulations of ballistic collisions between particles show that the platy geometries which typify many clay minerals are highly favorable for OA. Next, we consider how particles in face-to-face contact can rotate to obtain precise crystallographic alignment. Our analysis shows how Moiré-patterns of crystallographic registration between the faces can drive the emergence of complex rotational energy landscapes with deep primary minima and multiple local minima. Notably, the nature of the energy landscape varies with the size and shape of the contact area, with larger contact areas producing narrower primary minima and more numerous local minima that have the potential to trap particles in imperfect alignments. The implication our analyses is that perfect OA is easier to achieve for smaller particles with well-developed facets, and harder to achieve for larger particles and particles that display many microfacets.
Effect of incorporated carbonate on cation exchange of sodalite and cancrinite

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Sodalite and cancrinite are two feldspathoids commonly found under high alkaline condition such as at leaked nuclear waste site or in Bayer liquors in the aluminum refinery industry. Theoretically, these two minerals have high cation capacities (about 800 cmol/kg), which result from their unique structure. Three sodium ions with four water molecules or four sodium with one monovalent anion can typically occupy the β-cage in the sodalite structure, while only one sodium can reside in the ε-cage and all other ions locate in the 12-membered channel of cancrinite. The former sodalite is called hydrosodalite and its cation exchange with K, Li, Ca, and Mg has been reported. It is believed that incorporated anions in the sodalite and cancrinite could hinder the cation diffusion, deteriorating their cation exchange capacity. Several reports have pointed out that structural stacking disordering present in the sodalite and cancrinite when they form in the presence of carbonate. No research has been conducted to investigate the effect of the structural alteration on the cation exchange of sodalite and cancrinite. The objectives of this research are 1) to identify the sodalite and cancrinite formed in an alkaline solution with carbonate, 2) to explore the structural change and quantify their maximum holding capacity after exchanging with K, NH₄, Ca, and Mg.

Sodalite and cancrinite were synthesized by mixing kaolinite with NaOH and Na₂CO₃ for 20 hr at 100 and 230 °C, respectively. The mineral phases, chemical compositions, and cation exchange capacities of solid phase were analyzed by XRD, FTIR, SEM and ICP-OES. Preliminary results showed successful exchange of K, NH₄, Ca, and Mg at 80 °C on sodalite and cancrinite with the following lyotropic order: NH₄ ≈ K > Mg > Ca. Different XRD peaks and FTIR carbonate band shifts after exchange suggested the existence of multiple domains in the sodalite and cancrinite structures. Weak or almost absent carbonate bands and the decrease of cations to Al or Si ratio indicated carbonate ions may have been released from structure during cation exchange. However, this hypothesis needed to be further verified. Despite the structural carbonate blocking the exchange, some cations were still able to access those cation sites affected by the carbonate.
Small- and Ultrasmall-Angle Neutron Scattering as a Tool for Characterization of structure and porosity in Clay-Derived Rocks

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Small- and Ultrasmall-Angle Neutron Scattering, or (U)SANS is a powerful tool for the characterization of the structure and porosity of clay mineral derived rocks, providing complementary information to that available through BET, microscopy techniques, and related x-ray techniques. There are three key reasons to consider using neutron scattering methods: sensitivity to light elements, isotopic sensitivity, and the high penetration with low energy deposition of neutrons in most materials. Neutrons have a high scattering cross-section for hydrogen, with the two most common, non-radioactive isotopes—protium and deuterium—having scattering lengths with opposite sign, allowing for contrast variation studies using natural and deuterium-enriched fluids. The high penetration of neutrons in most materials means that neutrons can be used to study samples in complicated or bulky sample environments, such as furnaces, pressure cells, shear and compression, and reaction cells. Furthermore, the inelastic incoherent scattering of protium (the majority isotope of natural hydrogen) allows the changes in bulk hydrogen content of a sample to be quantitatively tracked during processing. The benefits and limitations of contrast-variation studies of fluid intrusion to probe pore networks and connectivity in clay-mineral derived rocks will be discussed, and applications of (U)SANS to probe modification to these rocks from in-situ and ex-situ processing will be presented.

A portion of this research used resources at the High Flux Isotope reactor and the Spallation Neutron Source, a DOE Office of Science User Facilities operated by the Oak Ridge National Laboratory. Access to the NIST SANS and USANS instruments was provided by the center for High Resolution Neutron Scattering, a partnership between the National Institute of Standards and Technology and the National Science Foundation under agreement No. DMR-1508249. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work.
Potassium isotope behavior during marine authigenic clay formation

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The study presented at the conference explores the sedimentary fluxes that impact the potassium (K) budget of oceans and the isotope composition of K ($\delta^{41}$K). The research focuses on modern sediments from continental margin settings and deep-sea environments. The findings suggest that sedimentary diagenesis associated with authigenic clay formation plays a significant role in altering the K elemental and isotopic budgets in sediment strata of various marine environments. Specifically, illite, glauconite, and feldspars are the primary hosts of K, and regional K-phase partitioning modulates the marine sedimentary K budget. The formation of glauconite in the sediments takes up isotopically light K from seawater and serves as an essential sink of seawater K during early diagenesis, especially on continental margins. The research provides insights into global K cycling and the poorly understood component of sedimentary diagenesis and authigenic clay formation in the oceans.
Stable hydrogen and oxygen isotope geochemistry of Fe$^{3+}$-rich, interstratified clay minerals from seafloor hydrothermal sites

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Cuadros et al. (2013) described the great complexity in crystal-chemistry of interstratified Fe- and Mg-rich clay minerals present at several submarine hydrothermal sites around the world. Here, we explore the stable hydrogen and oxygen isotope systematics of a subset of those samples, focusing on glauconite-nontronite, talc-nontronite, and talc-saponite. Stable isotope data from across this spectrum of Fe- to Mg-rich compositions provide an opportunity: (i) to assess further the conditions that favour formation of these phases, and (ii) to determine the relative importance of parameters such as temperature and crystal-chemistry, particularly Fe$^{3+}$ content, in controlling mineral-water hydrogen isotope fractionation.

For these samples, $\delta^{18}$O generally became less positive from nontronite through glauconite-nontronite and talc-nontronite to talc-saponite (Fig. 1). This pattern is consistent with progressively higher temperatures of clay mineral formation from seawater and seawater-derived hydrothermal fluids. Using available oxygen isotope geothermometers and brine isotopic compositions, formation temperatures ranged from ~40°C for nontronite to ~135-300°C for talc-saponite. Contrasting with this pattern, however, is the positive covariation between the $\delta^{2}$H and $\delta^{18}$O of talc-nontronite and glauconite-nontronite measured for samples from the Red Sea Atlantis II site (Fig. 1). Factors other than temperature have controlled clay mineral – water hydrogen isotope fractionation ($1000\ln \delta_{\text{clay-water}}$). The most obvious candidate is Fe$^{3+}$ content, as has been noted in earlier studies (e.g., Sheppard and Gilg, 1996). On a formula unit basis, samples examined in our study have tetrahedral Fe$^{3+}$ contents ranging from 0.00-0.66 and octahedral Fe$^{3+}$ contents ranging from 0.03-1.84. Octahedral Fe$^{2+}$ contents are much lower (0.00-0.29). Figure 2 illustrates the strong covariation ($R^2 = 0.83$) between $1000\ln \delta_{\text{clay-water}}$ and Fe$^{3+}$ content obtained for all samples. Why this covariation occurs remains unclear but may be linked to bonding configurations driven by Fe$^{3+}$ substitution in tetrahedral and octahedral sites.

Figure 1. $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ of submarine, hydrothermal, mixed-layer clay minerals and associated seawater and brines. G-N = glauconite-nontronite, N = nontronite, T-N = talc-nontronite, T-S = talc-saponite.

Figure 2. $1000\ln(\text{hy}_{\text{clay-water}})$ versus total Fe$^{3+}$ (expressed on a formula unit basis) for all samples. Dashed line illustrates linear best fit ($R^2 = 0.83$). G-N = glauconite-nontronite, N = nontronite, T-N = talc-nontronite, T-S = talc-saponite.
Towards understanding of illitization based on stable potassium (K) and magnesium (Mg) isotope systematics

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The transformation of smectite to illite (i.e., illitization) is a ubiquitous clay diagenetic process that has implications for thermal evolution of a sedimentary basin, hydrocarbon maturity, or preservation of environmental information in clay sediments. Because this mineralogical transition requires fixation of potassium (K) in the interlayer positions and release of structural magnesium (Mg), the stable isotope ratios of K ($^{41}\text{K}/^{39}\text{K}$) and Mg ($^{26}\text{Mg}/^{24}\text{Mg}$), in principle, could provide useful constraints on conditions under which this reaction occurs, such as external fluid sources or fluid–rock interactions. However, this potential utility has not been systematically explored or demonstrated.

Here, K and Mg isotope data were measured from two suites of well-characterized natural smectite-illite (I-S) samples from two sedimentary basins, namely, the Denver Basin and the Disturbed Belt of Montana. All I-S were separated from bentonites and dated previously by K-Ar geochronology, each sample suite covers wide extent of illitization. I-S from the Denver Basin exhibited a large spread of >1‰ in $\delta^{41}\text{K}$, whereas samples from the Disturbed Belt showed a distinctly smaller spread of ~0.2‰. Similarly, samples show a large spread of ~2‰ in $\delta^{26}\text{Mg}$ in the Denver Basin but only a ~0.6‰ spread in the Disturbed Belt. The marked contrast in K and Mg isotopes between the two basins reflected different modes of illitization in these two basins. In addition to this basinal contrast, a broad negative correlation was observed between K isotopes and Mg isotope data from both basins, likely resulted from fundamental crystal lattice controls on K and Mg isotope fractionation during illitization. Our results, the first of this kind, showed that the coupled use of K and Mg isotopes is a promising approach to reveal different history of smectite–illite transformation and the associated diagenetic conditions in sedimentary basins.
Thermo-Hydro-Mechanical Behavior of Compacted MX80 Bentonite at High Temperatures above 100°C

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The bentonite buffer in an engineered barrier system is intended to provide a tight seal around a waste package, ideally with a homogeneous distribution in density and hydraulic properties to limit hydraulic interaction between canister and host rock and minimize release of radionuclides or gas to the surrounding host rock in the case of canister failure. Accordingly, the hydration process of the bentonite buffer when exposed to high temperatures must be carefully predicted to ensure the adequate performance of the engineered barrier system. This study is formulated to aid in the simulation of engineered barrier systems for deep geological repositories that are high thermal limited (>200 °C), either due to closely spaced waste packages for cost savings or disposal of Dual Purpose Canisters. Repositories with high temperatures have drawn attention internationally recently, for example in the HotBENT project at the Grimsel Test Site in Switzerland (GTS 2020) that will test bentonite buffers at scale under in situ conditions with heater temperatures up to 200 °C. Although large scale experiments like those in the HotBENT project may collect important field data representative of actual repository conditions, a key challenge is that the thermo-hydro-mechanical material properties of unsaturated bentonite have not been well characterized under temperatures above 100 °C. The properties governing water retention, water transport in liquid and vapor forms, heat transfer, and volume change due to changes in water content (hydration) or temperature are highly coupled and are needed for predicting the long-term hydration process and development of swelling pressures. Due to the possibility to sustain relatively high air and water pressures within the bentonite both due to its low permeability and the high host rock pore water pressures greater than 1 MPa, it is expected that unsaturated conditions with liquid water and air can be present in the bentonite at temperatures above 100 °C. The coupled processes encountered in a bentonite buffer during heating and hydration are shown schematically in Figure 1. Simulation of these processes is complex as hydration from the host rock and heating from the waste will have competing effects on the soil properties which affect the rates of these coupled processes. A study underway at UCSD focuses on performing laboratory-scale tank tests to study the coupled processes in bentonite buffers and element-scale tests to collect data to validate new models for the thermo-hydro-mechanical properties of compacted bentonite at high temperatures, including the soil-water retention curve (SWRC) relating the degree of saturation and matric suction, the thermal conductivity function (TCF) relating the thermal conductivity and degree of saturation, and the hydraulic conductivity function (HCF) relating the hydraulic conductivity and...
matric suction. This study focuses on constrained conditions where the global volume does not change during heating or hydration.

One of the main goals of this study is to estimate the shapes of the TCF and HCF from the temperature-dependent SWRC. McCartney (2022) noted that many of the parameters of the SWRC model of Lu (2016) are temperature dependent. This SWRC model was adopted as it separately considers water retention by capillary and adsorption mechanisms. Key temperature-dependent parameters include the shape of the curve in the capillary regime \(a, n\) and \(b\), the cavitation suction \(y_c\) and maximum adsorption \(q_{a,max}\) (which together represent the transition from capillarity to adsorption mechanisms and are related to the cation exchange capacity), the adsorption strength \(m\), and the maximum suction \(y_{max}\). An example of the application of this SWRC is shown in Figure 2(a), and additional testing is underway to validate the temperature-dependency of the model at higher temperatures. Theoretical evaluation of the SWRC parameters indicates that water retention increases in some water content ranges and decreases in others up to approximately 100 °C, after which water retention decreases across the full range of water contents. Data from a tank-scale test performed by Lu and McCartney (2022) was used to define a nonisothermal HCF by Lu and McCartney (2023a), as shown in Figure 2(b), which indicates that the HCF depends primarily on the shape of the SWRC in the capillary regime. Lu and McCartney (2023b) proposed a new TCF for bentonite shown in Figure 2(c) that does not depend on temperature but whose parameters are also related to the shape of the SWRC in the capillary regime. Results from the tank-scale test of Lu and McCartney (2022) in Figure 2(d) indicate that central heating of bentonite leads to a wetting-drying process following a temperature-dependent hysteretic path, a complex phenomenon that must be considered in modeling long-term buffer response.
Figure 2: (a) Nonisothermal SWRC (McCartney 2022); (b) Nonisothermal HCF (Lu and McCartney 2023a); (c) TCF (Lu and McCartney 2023b); (d) Hysteretic SWRC (Lu and McCartney 2022)

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An approach to Li-clays in continental salars in the Mesa Central, between San Luis Potosí and Zacatecas, Mexico

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Lithium deposits in Mexico occurred as: 1) clay deposits in Sonora (Northern Mexico), in 2) continental salars with Lithium brines in the Mesa Central along the boundary between the states of San Luis Potosí and Zacatecas. The Mesa Central is arid to semiarid where meteoric solution dissolve and transport Li-K-B to closed basins where evaporation concentrates these brines.

The geology of the Mesa Central consists of Mesozoic metamorphic rocks, volcanic sedimentary, marine sedimentary and plutonic rocks, followed by Cenozoic, acid and intermediate volcanic and volcaniclastic, and intrusive rocks and later continental conglomerates. Younger lithologies consists of basalts, lacustrine sediments, evaporites, sinters, travertine, and alluvium. The mean goal of this study is the identification of Li-clays which may be contained in the continental salars selected from this region.

Seven continental salars with possible Lithium concentrations were selected from the Mesa Central. Clay minerals were identified using powder X-ray Diffraction (p-XRD). Two grain size fractions were analysed <180 µm (fifteen samples) and <75 µm (twenty samples). In both cases the samples were air-dried randomly oriented powder mounts and glycolated. The samples were scanned in the Polymethylmethacrylate (PPMA) holder between the angles of 2-65 °2θ, using steps size of 0.02, time/step=0.4 seg. for 20 min. For the <180 µm fraction the mineralogy identified include calcite, dolomite, quartz, orthoclase, anorthite, albite, muscovite, illite, analcime, clinoptilolite, heulandite, saponite, vesuvianite, lepidolite, eucryptite and petalite. For the <75 µm fraction calcite, dolomite, quartz, orthoclase, albite, muscovite, illite, montmorillonite, analcime, vesuvianite, kalsilite, almandine, clinoptilolite, heulandite, silinaite, lepidolite and hectorite. This identification indicates that hectorite clay is present in Salinas Hidalgo salar while silinaite in San Jose Saladillo, and Lepidolite in El Salitral and Cornejo. The subsequent analysis will be carried out are with ICP-OES+ICP-MS to know the amount of Li the samples of the studied area.
Green Magnetic Bentonite Composite for Efficient Removal of Cationic and Anionic Dye in Synthetic and Real Textile Wastewater.

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Textiles manufacturing is one of the key industries that create a significant economic growth in developing nations, especially in ASEAN countries. However, this industry suffers from huge environmental issues due to difficulty and expensive treatment of dye effluent. Tremendous effort has been devoted to finding an environmentally benign, inexpensive, robust, and high efficiencies material for treating this water pollutant.

This study aims to investigate the performance of magnetic bentonite clay to decolorize dye contaminated water. The novelty of this research lies in the different types of dye used (cationic e.g., methylene blue (MB), and anionic, e.g., methyl orange (MO)) and comparison with real textile effluent. The magnetic bentonite composite (MBC) was prepared using facile co-precipitation method and were characterized via state-of-the-art characterization techniques like Fourier-transform Infrared (FTIR) spectroscopy, Vibrating Sample Magnetometer (VSM), X-ray Diffraction (XRD) and X-ray Fluorescence (XRF), Scanning and Transmission Electron Microscopy with Energy Dispersive X-ray (SEM-EDX and TEM), pHzpc and N₂ adsorption-desorption isotherm. The dye removal efficiencies were evaluated through the adsorption isotherm and kinetic study conducted via batch method. Optimized experimental conditions were established earlier under specific pH, contact time, adsorbent loading, and initial dye concentration.

Preliminary findings show that the MBC has a better performance in removing the MB as compared to MO dye, implying the role of electrostatic interaction as an important removal mechanism. The maximum adsorption capacity achieved for MB and MO dyes were 99.5 and 34.8 mg/g, respectively, at an optimum pH 6 using 0.5 g/L adsorbent loading. The experimental data was best fitted to Langmuir isotherm ($R^2 = 0.998$) and in good agreement with the pseudo-second order ($R^2 = 0.999$). During regeneration, three consecutive cycles of MBC were successfully carried out. Research work for MBC’s performance in real textile wastewater is currently undergoing.

It is expected that the research outcomes could give new insight and fresh understanding on the capability of this magnetic clay in treating dye both in laboratory-prepared and real textile effluent. The findings are important to correctly forecast the practicality of magnetic clay as a new class of green, low cost and versatile adsorbent to overcome the continuing issues of water security.

Preliminary mineralogical investigations on clay minerals from Surtsey deposits (SW Iceland)

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Preliminary investigations on clay minerals in pyroclastic rocks from Surtsey (Iceland) are carried out in this work through a clay-phases separation technique.

Clay minerals, as well as zeolites, are among the most common authigenic minerals in volcaniclastic deposits (Chipera and Apps, 2001) and affected the very young volcanic island of Surtsey (SW Iceland) since its formation (1963-1967). Therefore, the island represents one of the most suitable sites to investigate the formation of these secondary mineralizations.

Surtsey volcaniclastic deposits consists in armoured lapilli tuffs in which fresh basaltic glass (i.e., sideromelane; Peacock, 1928) is likely to be the precursor of the newly-formed crystalline phases. It is well known that sideromelane (amorphous, clear, gel-like phase) experienced alteration to palagonite (a metastable alteration product; Prause et al., 2020 and references therein), which shows different textures (from cryptocrystalline, strongly birefringent, to dark, opaque and grainy palagonite; Prause et al., 2020) and mineralogy. Palagonite consists in a variety of amorphous/slightly-to-highly crystallized mineral products, the latter exhibiting characteristics of smectites with minor amounts, if any, of zeolites and oxides (Stroncik and Schmincke, 2002).

Clay minerals are very common in Surtsey deposits: they occur i) as a late maturation stage of palagonite, ii) as alteration rims around olivine and iii) as a complete pseudomorphic replacement of olivine crystals. Yet, very little information exists about them and this study represents the first attempt to characterize precisely the type of clay minerals by maximizing the preferred orientation of crystallites prior separation in aqueous suspension.


Engineering Electrically Conductive Clay-Like MXenes for Energy Storage

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MXenes constitute a large family (40+ phases) of two-dimensional transition metal carbides/nitrides with a composition of $M_{n+1}X_nT_x$ (M is an early transition metal, X is carbon or nitrogen, $n = 1-4$, and $T_x$ stands for surface terminations). Like clays, MXenes are hydrophilic, but the exhibit excellent electrical conductivity. Their capability to host ions make them ideal candidates as electrode materials for electrochemical energy storage. While intercalation plays an important role in the applications of MXenes since it is the mechanism for storing ions in it, less is known about the effect of pre-intercalation on the electrochemical performance of MXenes. We will discuss few examples where pre-intercalation introduced a significant change in the electrochemical performance of MXenes. First example, Na\(^+\), K\(^+\), and Mg\(^{2+}\) pre-intercalated multilayer Ti\(_3\)C\(_2\)T\(_x\) were explored as aqueous supercapacitor electrode with adjustable areal loadings (5-20 mg/cm\(^2\)). K-Ti\(_3\)C\(_2\)T\(_x\) exhibited the highest capacitances at different scan rates, achieving a gravimetric capacitance of up to 300 F/g, comparable to delaminated MXene but with an ultra-high areal capacitance of up to 5.7 F/cm\(^2\), which is manyfold higher than the 0.5 F/cm\(^2\) which can be achieved for delaminated MXene. The other example is using pre-intercalation of alkylammonium (AA) cations with different chain lengths to study the effect of interlayer spacing in MXene on their performance as electrodes for supercapacitor in room-temperature ionic liquids (RTIL) electrolytes that offer larger potential windows, leading to higher energy density. We found that pre-intercalated MXene with an interlayer spacing of $\approx 2.2$ nm can operate within a voltage window of $> 3$V in neat EMIMTFSI electrolyte and deliver a large specific capacitance of 257 F/g (1428 mF/cm\(^2\) and 492 F/cm\(^3\)) -an order of magnitude higher than pristine MXene-leading to high-energy density without compromising their high-power density. We will also report on using pre-intercalation to achieve new compositions with high alkali metal content (e.g., Ti\(_3\)C\(_2\)OFNa\(_2\)) that can be used as electrode materials for ion capacitor. Other atomic scale engineering strategies to achieve high electrochemical performance of MXene as both electrochemical energy storage and hydrogen evolution reaction.
Small-angle neutron scattering investigations of fluid behavior in shale nanopores

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Hydrocarbon production from unconventional shale formations currently suffers from low recovery rates, leading to US reliance on energy imports. Following primary recovery, which quickly depletes hydrocarbons stored in the shale fracture network, the majority of remaining hydrocarbons are stored within the nanoporous shale matrix. Enhanced oil recovery (EOR) has been proposed as one strategy to improve recovery by decreasing oil viscosity and facilitating oil movement to a production wellbore. However, implementation of EOR requires knowledge of fluid behavior in nano-sized pore spaces, which can be difficult to observe experimentally due to the small length scale. We address this challenge through the utilization of small-angle neutron scattering (SANS), a powerful tool for measuring porosity and pore size distribution at dynamic and elevated pressure conditions. Results shed new light on the links between pore mineralogy and pore accessibility to fluids, as well as quantification of hydrocarbon recovery during pressure cycling.
Evaluation of Coal Underclay from the Southern Appalachian Basin as a Potential Feedstock Material for Critical Minerals

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Previous research has shown that coal and its associated sediments are promising sources of critical minerals (CM). Underclays, also known as seatearths and root clays, are paleosol beds underlying coal seams. Underclay units in the Southern Appalachian Basin (SAB) have not previously been characterized for their CM contents. This study is aimed at examining the abundances and mode of occurrence of REE+Y+Sc (REE+) and Lithium (Li) in underclay units of the SAB to evaluate their potential as feedstock materials for these important elements. The mineralogy of 15 underclay samples collected from the Pennsylvanian Pottsville Formation was determined using X-ray diffraction (XRD) analysis and quantified by Rietveld refinement. Underclay REE+ and Li contents were determined by complete digestion, followed by ICP-MS analysis.

The mineralogy of SAB underclays is dominantly illite and kaolinite, averaging 41% and 17%, respectively, with minor muscovite, chlorite, microcline and vermiculite. Sample REE concentrations range from 150-178 ppm, averaging 218 ppm, and REE+ concentrations range from 187-334 ppm, averaging 266 ppm. Lithium concentrations range between 68-519 ppm, averaging 221 ppm. The Mary Lee Coal seam underclay in Tuscaloosa County, Alabama, has the highest REE+ and Li concentrations at 334 ppm and 519 ppm, respectively. The Newcastle coal seam underclay in Fayette and Jefferson Counties, Alabama, recorded the lowest REE+ and Li values at 187 and 68 ppm, respectively.

Statistical analysis of the dataset revealed that vermiculite abundance is strongly correlated ($r = 0.83, 0.79, 0.80, 0.75$) with light REE (La, Ce, Pr, Nd) concentrations, suggesting LREE enrichment through adsorption by this high CEC TOT clay. Phosphorus is strongly to very strongly correlated with the LREE and some of the MREE elements, indicating phosphate host(s) for these elements. Yttrium very strongly correlates with Dy, Ho, Er, Tm, Yb and Lu ($r = 0.92, 0.97, 0.98, 0.86$ and 0.92, respectively).

Underclay samples will next be subjected to micro-analysis using SEM-EDX and micro-XRF. Due to their low concentrations, trace minerals such as xenotime and monazite, which are possible host minerals for REEs, are typically undetectable by XRD. Micro-analysis will therefore assist in identifying underclay trace minerals and the host mineral/REE associations.
Kaolin uses in the traditional ceramic industry

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Kaolin ores are found in two types of deposits: primary and secondary. Primary deposits result from the weathering of granite-type rocks. The alteration of feldspars and micas result in the formation of kaolinite minerals (Fig. 1), which are mixed with micas, quartz, residual feldspars. A good example of this type of ore deposit is the Cornish kaolin in the UK (Fig 2.). Secondary deposits result from the sedimentation of fine particles derived from rock and soil alteration and lead to a higher content of kaolinite in the matrix compared to the primary deposit. A good example is the kaolin deposits in the Amazon River area of Brazil.

Fig. 1: The beauty of kaolinite minerals (Imerys).

Fig. 2: Kaolin from primary deposit: from the mine to the processing plant (Imerys, UK)

Depending on the origin of the kaolin deposits, the mineral processing is adapted to the targeted application. This paper presents an overview of the potential uses of kaolin in the traditional ceramic industry. It will illustrate it from the heavy-clay industry (roof tiles and brick), for which “red clays” are suitable, to the tableware industry, for which high whiteness and plasticity kaolin are used in the body formulation. Lastly, we will focus on the sanitaryware industry, for which the ceramic recipe is prepared in liquid form and casted into mold. It is thus needed to master the casting rate, i.e., the speed at which the particles are sedimenting and creating a wet cake, which means mastering the rheology of a high solid content suspension.

Even if traditional ceramics have a long history, there is still room to play for scientists, especially those with a background in clay mineralogy. Some old technical challenges are not solved but also new ones are arising: for example, around lightweighting while maintaining the good mechanical properties, or around valorizing some wastes, which will allow sparing kaolin for the forthcoming generations.
Efficient removal of methylene blue from aqueous solution using Charcoal functionated hybrid Mg/Fe LDH

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The increase of hazardous dyes in wastewater due to industrial growth has recently attracted much attention. Utilization of dyes in textile, cosmetic, food, paper, and pharmaceutical industries are the main sources of dye in aquatic reservoir. In this study, a hybrid Mg/Fe LDH with jute charcoal was prepared using co-precipitation method where the Mg/Fe molar ratio was 3:1. The efficiency of hybrid Mg/Fe LDH for the adsorption of methylene blue from the aqueous solution was investigated and compared with pristine Mg/Fe LDH. LDHs are promising materials in the anionic adsorption but it can take up the cationic pollutants too. To ensure high adsorption capacity of Mg/Fe LDH, jute charcoal was incorporated for functionalization which raises delocalized electron cloud and active sites. Here, hybrid Mg/Fe LDH was characterized by XRD, SEM, EDS and IR Spectroscopy method, which confirms the successful formation of the desired product, and the adsorption capability was investigated via adsorption isotherm, kinetic model and thermodynamic study. In case of adsorption model study, the Freundlich model exhibited better to describe the adsorption of methylene blue by pristine and hybrid Mg/Fe LDH comparing with the Langmuir model. According to the Freundlich model, the higher K value of hybrid Mg/Fe LDH (0.87) than Mg/Fe LDH (0.13) supported the larger adsorption capacity of hybrid Mg/Fe LDH. The pseudo-second order kinetic model was more appropriate than the first-order model to explain the adsorption of methylene blue onto pristine and hybrid Mg/Fe LDH. These results indicated that chemisorption is the rate-determining step. The amount of methylene blue removal at equilibrium was calculated 528 – 666 and 343 – 454 µmol/g at 10 °C to 60 °C and the activation energy was estimated 18.63 and 111.33 kJ/mol for hybrid Mg/Fe LDH and pristine Mg/Fe LDH respectively. Cationic dye methylene blue is assumed to be effectively removed from solution by hybrid Mg/Fe LDH through π–π interactions, cation–π interactions, H-bonding and electrostatic forces (Fig. 1). The thermodynamic study confirmed that the reaction of LDHs and methylene blue were exothermic, the negative value of ΔG and positive value of ΔS describes the feasible and spontaneous adsorption respectively.
Application of multifunctional hydrophobic graphite oxide assisted Mg2Al LDH hydrogel in adsorption of Pb and As from synthetic wastewater

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Due to the rapid development of industrialization, the increase in polluted water and the decrease in fresh water has become a concern for the whole world. Although the multifaceted role of the researchers in water purification is encouraging, there are still some limitations, such as the inability to remove various types of pollutants from wastewater using a particular material. Therefore, it becomes difficult for any one technology to be widely used on a worldwide scale. In this study, a hydrogel of Mg-Al layered double hydroxide combining with graphite oxide, [Alg(hGO/LDH)] has been developed through various modifications (Flow Chart 1) to create a particular material containing various active sites that capable of adsorbing contaminants of different character (e.g., cationic, anionic, hydrophobic, organic etc.) into the same material. Here, we only emphasis on the capabilities of [Alg(hGO/LDH)] in the adsorption of Pb (cationic) and As (anionic) from the wastewater. The successive development of the synthesized [Alg(hGO/LDH)] was characterized by XRD, FT-IR, SEM images and XPS analysis. The adsorption accomplishment was investigated through adsorption isotherm models, kinetics models and thermodynamic study. The [Alg(hGO/LDH)] was effective in adsorbing Pb and As from the aqueous solution, while the initial pH was maintained approximately 5 for Pb and 4 for As. The adsorption isotherms indicated that the [Alg(hGO/LDH)] fitted the Langmuir model toward Pb and As removal. It summarized that all the adsorbed Pb and As were in contact with the surface monolayer of the adsorbent. According to the Langmuir adsorption isotherm, the highest adsorption of Pb and As was 370.37 and 384.62 mg/g respectively by the adsorbent. At 10 – 60 °C temperature, a higher correlation (R² value) of pseudo 2nd order compared to 1st order was obtained which better describes the reaction kinetics with [Alg(hGO/LDH)]. The positive value of ΔS and negative value of ΔG represent the spontaneous and feasible adsorption of Pb and As respectively. The reaction in case of Pb adsorption was endothermic whereas an exothermic reaction was observed in As adsorption. This study provided a foundation for the industrial application in the adsorption of mixed pollutants from the aquatic environment.

Flow Chart 1: The reaction steps for the formation of alginate coated hydrophobic graphite oxide assisted Mg-Al LDH [Alg(hGO/LDH)]
Understanding Clay-Mineral Alteration of Silica-Undersaturated Mafic Volcanic Tuffs through Integration of XRD and SEM Analyses

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The Balcones Igneous Province (BIP) of central and south Texas is comprised primarily of mafic, silica-undersaturated, volcanic lapilli tuffs. These tuffs have been heavily altered by interaction with seawater, post-eruptive hydrothermal systems, and burial heating at shallow to medium depths. Clay minerals are the most common alteration and cementation product.

Where buried at shallow to moderate depths the tuffs have been a target for hydrocarbon exploration owing to their high porosities (up to 30%). Many of the pores are associated with clay minerals, making identification of the clays present more important. Attempts to identify the clays with energy dispersive spectroscopy alone are ineffective (e.g., dominant clay was erroneously thought to be chlorite).

A number of samples from different volcanic complexes in the BIP were chosen for X-ray diffraction (XRD) analysis. XRD showed that the dominant clay types in the samples were vermiculite or interlayered vermiculite/smectite, with lesser amounts of smectite, serpentine, and illite. One sample contained a minor amount of kaolinite.

Energy dispersive spectroscopy element maps helped to delineate various phases as to their location and diagenetic implications. Vermiculite and interlayered vermiculite/smectite replaced volcanic glass and some phenocrysts, as well as forming as cement in vesicles and interparticle pores. Smectite is seen as a common late phase cement partially filling vesicles and interparticle pores. Serpentine was found to occupy the centers of former olivine phenocrysts which had been wholly retrograded. Many nanopores associated with these rocks are in devitrified volcanic glass (now vermiculite and interlayered vermiculite/smectite) and appear to have been produced during devitrification.

The integration of XRD and SEM techniques allows for a better understanding of the distribution and physical characteristics of clays in these rocks.

Fig. 1. On the left is a secondary electron SEM image showing pores between vermiculite replacing a phenocryst in a grain in an altered tuff. On the right is an EDS element map showing the interior of an altered tuff grain. Reddish green is interlayered vermiculite/smectite, red is mostly serpentine, pink is Ca-Ti garnet, blue is phosphate, and bright green is spinel. Gray areas include pyrite and Ti oxide.
Effect of High Temperature on Swelling and Mineralogy of a Clay-Pellets Intended for Barrier Systems

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Deep geological repository is the most favorable option for the safe disposal of high-level nuclear waste (HLW) and spent nuclear fuel (SNF). The design of such a facility relies on the multi-barrier system, encompassing a cylindrical metallic container (encapsulating the HLW/SNF), an engineered barrier system (EBS, around the metallic container); and the host-rock (or natural barrier). The most preferred buffer material to construct the EBS is bentonite clays. They are being considered as potential buffer materials because of their high swelling capacity provides mechanical stability to the metallic canister containing the HLW/SNF; their good thermal conductivity assists to dissipate the heat released by the HLW/SNF; their low permeability delays the flow of water and gas through the system.

It is envisaged that EBS will be built using blocks of compacted bentonites or a combination of high-density clay-pellets mixtures and blocks of compacted bentonites (i.e., where the metallic container rests). Clay-pellets are also considered as possible seal materials to fill gaps that characteristics in this type of system, e.g., the gap between the EBS and the surrounding host-rock. Clay-pellets present several advantages, amongst others, they are very suitable for filling (small) technological voids, there is no need for additional in-situ compaction when they are used as a buffer/backfill material, and it is relatively easy to manufacture them.

Because of the nuclear waste radioactive decay, the clay barrier will be subjected to high temperatures. Most of the previous research in this area have considered a maximum temperature of 100°C. Recently, it has been an increasing interest in understanding the behavior of clayed materials at higher temperatures, up to 200°C. The main motivation is to optimize the repository footprint. However, the information in this area is scarce. This aim of this research is twofold, to gain a better understanding of the swelling behavior of clay-pellets mixtures at high temperatures and to investigate any possible changes on clay microstructure when subjected to hydration and heating at 200°C.
Sand in tropical and sub-tropical regolith: Clay minerals and textures in sand size aggregates and particles

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Critical Zone science has recognized the importance of interrelating human, physical, chemical, and biological factors for understanding regolith properties. This includes the nature of soil tilth, moisture capacity, nutrient availability, and the cycling of elements between the atmosphere above and the deep rock below. The sand fraction in intensely weathered regolith and soils are often assumed to be resistant primary minerals such as quartz, micas, and potassium feldspars. Size separation of the sand fraction regolith and soils from tropical and subtropical sites, both located on Precambrian crystalline basement, revealed abundant sand aggregates comprised of clay minerals and oxyhydroxides. X-ray diffraction and optical thin-section analysis showed the fine, medium, and coarse sand fractions all contained kaolinite and variable amounts of vermiculite, gibbsite, and/or goethite, with a trend of decreasing clay minerals in increasing size fraction. Coarse sand aggregates often displayed Liesegang-like rinds or rings concentrating Fe- and Al-rich phases, which suggests long-term diffusive nucleation and crystal growth process have operated and these grains are stable. Also, sand-sized micaceous minerals (biotite and phengite) transform to kaolinite, yet often retain their large plate-like habit. The processes that form sand-sized clay aggregates (so-called pseudo-sand) and particles in tropical and sub-tropical soils are not entirely understood, but it is posited that root growth compaction forces, infauna activity, and seasonal moisture cycles (i.e., redox and pH variations) play a role. The occurrence of clay-bearing sand particles and their persistence in soil suggests they can influence the cycling of moisture, gases, and nutrients in the Critical Zone. Surface properties of pseudo-sand particles and thus their ability to adsorb and desorb inorganic and organic compounds may be more heterogeneous than previously thought. Further mineral and textural study of these aggregates will help to disentangle our understanding of topical and sub-tropical biogeochemical cycles.
Having landed into marine or lacustrine environment, volcanic ash undergoes a rapid alteration which commonly leads to argillitization of its glassy component. Young ashes however offer an excellent opportunity to investigate the trace-element geochemistry of glass and authigenic smectite derived thereof to infer on REE mobility in the tuff alteration setting. The samples for this study sourced from Lower Miocene tephra deposits of the Dinaride Lake System in South-Eastern Europe are marked by similar volcanic provenance and may be found in a variety of depositional environments ranging from aquatic systems of the young Dinaridic orogen to the semi-arid peri-mountainous region to the northeast. Representative material – thin-section glass shards and clay fraction concentrates – was analyzed by laser ablation inductively coupled plasma mass spectrometry. The latter were additionally characterized by electron microscopy, X-ray diffractometry, Fourier transformed infra-red spectroscopy and N₂-physisorption experiments. Preliminary data showed that Y and HREE were likely mobilized from decomposing glass in the form of carbonate complexes and were consequently depleted in the studied clays. On the other hand, the Mg-rich smectite demonstrated an elevated adsorption potential of solvated LREE complexes. This may be explained through clay surface geochemistry controlled by Mg for Al octahedral substitution. Hairy morphology and smaller particle sizes of Mg-rich authigenic smectite, as evidenced by BSE imagery and comparatively greater BET surface areas, increased the density of edge/defect charges, which might have facilitated LREE adsorption. The occurrence of Mg-smectite in our study area is restricted to semi-arid paleolakes which demonstrates the importance of eogenetically-controlled clay mineral chemistry and morphology when studying REE retention in bentonite clays.
Dismantling of the bentonite buffer in the inner section of the Prototype Repository at the Äspö Hard Rock Laboratory

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The Prototype Repository is a full-scale test installed at the Äspö Hard Rock Laboratory in Sweden. Originally, the test consisted of six full scale deposition holes in a drift, at a depth of 450 metre. The inner section, with four deposition holes, has been operated since 2001. Each deposition hole was installed with bentonite buffer and a copper canister equipped with heaters to simulate residual heat from spent fuel. The overall objective of the Prototype Repository is to test and demonstrate the integrated function of subcomponents in a final repository for high level nuclear waste under realistic full-scale conditions.

The dismantling of the inner section started in January 2023 and will continue for two years. During the excavation of the test ~2000 tons of bentonite/crushed rock backfill, 100 tons of buffer bentonite and four copper canisters will be retrieved, sampled and examined.

The bentonite buffer was installed in the form of blocks around the canisters and in the form of pellets in the slot between the blocks and the rock. The state of the buffer in the deposition holes is expected to display a spatial variability, especially regarding the water uptake and the homogenisation and some extent also regarding the chemistry and mineralogy.

The position and the height of the bentonite rings will be measured to check for displacements. For each bentonite block, a coring scheme is specified according to which cores will be taken at certain intervals and in different directions (Figure 3). The cores will be analysed for: Basic geotechnical properties, Hydraulic conductivity and swelling pressure, Unconfined compression strength/shear strength, Aqueous leachates, elemental composition, Cation exchange capacity and exchangeable cations, mineralogical composition, iron redox conditions and a specific analysis of sulfur and carbon contents.

The data will be used to assess the performance of a bentonite buffer in the early evolution of a repository. A prediction of the state of the barrier has been performed prior to the excavation. This has been done both by qualitative reasoning and numerical modelling dependent on the process of interest. A comparison will be made between the prediction and the actual data.

Figure 3 Holes from cores taken from a buffer block
137 Cs (the bad) released into the natural environment due to nuclear weapons testing and nuclear plant accidents constitutes the main environmental concern because it is a strong gamma emitter having a half-life time of ~30 years. Recently, due to the Russian invasion of Ukraine, the potential risk of further release of 137-Cs into the environment dramatically increased. Taking those into consideration one should keep in mind that there is a clear need for an efficient and cheaply available adsorbent that could be used for the immobilization of Cs.

The present study aimed to investigate the Cs adsorption/immobilization potential of dioctahedral swelling clays from a smectite-vermiculite family.

Nearly 30 clay samples including the CMS standards, different bentonites, and natural soil clays were used in the study. Starting – (i.e. Na-pre-saturated clays) were first saturated with cesium (Cs) and split into two portions from which one was immediately (i.e. without drying) re-saturated with Na (CsNa-samples) while the second one was dried, re-dispersed and re-saturated with Na (CsdNa – samples). The fixation of Cs by the studied clays was evaluated using XRD, EDS, and ICP OES methods. The mean layer charges (LC) of studied samples were determined using OD – method.

All studied samples showed significant fixation of Cs under wet conditions (i.e. without drying of Cs-saturated samples). For most of the studied clays, no significant change in Cs-fixation was observed between CsNa and CsdNa samples. In most cases, the fixation of Cs caused a reduction in the mean absolute LC values. This indicated that the component having a nature of dioctahedral vermiculite was likely responsible for the fixation. Cs - fixation potential observed for high-charge smectites and vermiculites was high enough to consider the clays as promising materials for decontamination of radio cesium-contaminated waters.

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Clay-Fluid Interaction: Mechanisms and Rates of Hydrogen Exchange

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Hydrogen exchange in hydrous mineral-fluid systems has major implications within studies of paleoclimatology, radioactive waste storage, ore-forming fluids, and mantle-ocean interaction. While used extensively in these applications, little is known about the driving mechanisms and rates of hydrogen exchange, particularly in clay minerals. A physical chemical description of these mechanisms and their relative contributions to observed exchange is necessary for interpretive analysis of geological samples as well as accurate predictive simulations of associated processes. We present mechanistic and kinetic data for two fundamental clay minerals – kaolinite and montmorillonite – and their interaction with fluids, highlighting major differences between the two as well as implications within paleoenvironmental reconstructions.

We use results from mineral-water exchange experiments at elevated temperatures within a novel kinetic framework to extract information regarding mechanisms and rates of hydrogen exchange. CMS clay standards (KGa-1b and STx-1) were used in conjunction with deuterium-enriched purified water. Bulk mineral hydrogen isotopic compositions were measured using thermal conversion elemental analysis coupled with isotope ratio mass spectrometry (TCEA-IRMS).

Findings demonstrate minor hydrogen exchange occurs in montmorillonite-water and kaolinite-water systems at temperatures as low as 21 and 100°C, respectively, in as little as two months. Kinetic analysis strongly suggests that kaolinite exchange is primarily driven by surface-controlled reactions (i.e., Ostwald ripening), whereas volume diffusion dominates in montmorillonite systems (see Fig. 1). Furthermore, the new kinetic framework is used to more accurately model the rate behavior of exchange as well as extrapolations to geological timescales. Major geological implications are twofold: (1) results suggest that surface-controlled exchange ceases to dominate in kaolinite-water systems below 90°C and (2) although exchange can occur at low temperatures, post-depositional hydrogen exchange of montmorillonite is unlikely to cause reconstructive error in excess of ±1°C when used as a single crystal paleothermometer within most geological settings.

In conclusion, this work demonstrates the potential of clay mineral hydrogen isotopic compositions to record paleoenvironmental information, as well as requisite considerations when interpreting data from geological systems. It also outlines an in-depth analysis that should be applied to any mineral-fluid kinetic experiments, in addition to an improved framework to model the results.
Activated clay mineral-based beads for pharmaceuticals removal

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The growing amount of pharmaceuticals in wastewater meets the environmental issue. Due to their complexity and variety of chemical forms, there is a problem with the effective purification of wastewater containing pharmaceuticals in wastewater treatment plants. As a ramification, drugs infiltrate the environment posing a risk to aquatic organisms and human health. Therefore, effective purification methods are still searching. One of the promising method can be adsorption-based techniques with the application of granulated clay minerals mixed with organic-based materials: lignite, and fly ash with relatively high amount of unburned carbon. Modification by acid activation can be applied to improve sorption properties such as clay-organic mineral beads toward the uptake of pharmaceuticals.

Our work seeks to investigate two granulated clay mineral-based composites in proportion 20 wt.% bentonite to 80 wt.% lignite and 20 wt.% halloysite to 80 wt.% fly ash, activated by 0.5 M HCl. The obtained beads were characterized using Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). Their textural properties have been evaluated. Beads sorption ability to remove pharmaceuticals: ibuprofen (IB) and sulfamethoxazole (STX) have also been studied under dynamic states.

The results suggest that activating clay mineral-based composite beads could improve their sorption properties. Clay mineral-based composites possess significant amount of unburned coal and diverse functional groups lead to the immobilization of IB and STX. Nevertheless, after activation, porosity of beads was changed, which could affect the adsorption of pharmaceuticals from water.

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Effects of clay types on solid bitumen aromatization in pyrolysis experiments

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The generation of hydrocarbons from sedimentary organic matter (OM) is dominantly a thermal process. However, clays can also have a catalytic effect on OM aromatization and hydrocarbon cracking. Numerous studies have investigated the catalytic functions of clay minerals for hydrocarbon generation, both in natural systems and petroleum refining applications, but knowledge gaps persist. With the ongoing emphasis on shale oil and gas exploration and the ubiquity of clays in these self-sourcing reservoirs, research avenues still exist to explore clay-OM interactions in controlled pyrolysis experiments and apply findings to better understand natural OM maturation processes.

Data from laboratory pyrolysis residues of synthetic clay-OM mixtures provide a perspective on understanding OM maturity differences within the sample set as a function of clay type. Seven clays obtained from the Clay Minerals Society were used for this study, including a low-defect (KGa-1b) and high-defect (KGa-2) kaolinite, a trioctahedral smectite (SHCa-1), three dioctahedral smectites (STx-1b, SWy-3, NAu-2), and an illite (IMt-1). OM used in these experiments is a high-purity, natural solid bitumen at the late-oil maturity stage (solid bitumen reflectance = 0.85 ± 0.02%). Pyrolysis experiments were performed on clay + OM mixtures under hydrous and anhydrous conditions for 5 days at 300°C and Raman spectroscopy was used to measure OM maturity. For hydrous conditions, OM aromatization showed a negative linear correlation with cation exchange capacity (CEC) and specific surface area (SSA); i.e., aromatization was enhanced by clays with the lowest CEC and SSA (i.e., illite and kaolinite). In contrast, no trends between OM aromatization and CEC or SSA were noted in the anhydrous pyrolysis residues; however, OM from the mixtures with high-defect kaolinite (KGa-2) and two dioctahedral smectites (SWy-3, STx-1b) showed the largest degree of enhanced aromatization. These results highlight the complicated nature of OM-clay interactions in the presence and absence of water as well as the need for careful clay characterization in source-rock reservoirs to refine our understanding OM aromatization and in turn, improve sweet spot identification.
Nitrate elimination from aqueous solution by Fe(II) in electro-chemically reduced ferruginous smectite

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Nitrate in drinking water is a danger to human health, and causes other serious environmental problems. The goal of the present study was to develop a method to eliminate nitrate from water and to do it in a way that avoids the addition of other chemicals to the water. Nitrate can be reduced to nitrite, ammonium, or various N-gases by reaction with Fe(II), such as in reduced smectite. Smectite is a plentiful and inexpensive resource that could be used for this purpose, but two obstacles must first be overcome: (1) structural Fe in smectite usually is reduced with chemical reducing agents, such as Na-dithionite, which adds unwanted solutes to the water; and (2) the NO$_3^-$ anion is coulombically repelled by the negatively charged clay surfaces, thus precluding the redox reaction between them. This coulombic repulsion was overcome, however, by Su et al. (2013) and Pentrak et al. (2014) who introduced by cation exchange synthetic (polyallyldimethylammonium) and natural (chitosan) polymers, respectively, that reversed the negative charge of the smectite surfaces, rendering them attractive to NO$_3^-$. They succeeded in eliminating NO$_3^-$ from aqueous solution using batch reactors. In the present study, in order to avoid the addition of chemical agents to reduce the structural Fe, an electro-chemical (EV) method was devised. Two metal electrodes (Mo) were immersed into ferruginous smectite suspensions, one with and one without chitosan, and into 0.001 mol/L NaNO$_3$ solution. Five mL of 0.001 mol/L nitrate was added to each of the clay suspensions. The electrodes were then charged for 30 min at 100 mA and 100 V. The color of the smectite changed from yellow (Figure 1A) to blue green (Figure 1B) in both suspensions. Nitrate, nitrite, and ammonium were measured in the solutions using the method of Mulvaney et al. (1997), and confirmed that NO$_3^-$ was eliminated from all tested samples. Even no nitrite and only a trace of ammonium were detected. Further investigation of the influence of Fe-smectite, chitosan, and reduction parameters like voltage, current, and time on the EV reduction will provide more information about this promising technology for nitrate removal from contaminated water.

![Figure 1. Unreduced SWa-1-chitosan suspension (A), and after 30 min of the EV reduction (B).](image)

Microstructure of Individual Glauconite Pellets

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Glauconite, an authigenic, bluish-green, Fe-rich, dioctahedral mica with layer charges lying between muscovite and illite, typically forms in shallow marine environments under reducing conditions and appears visually as coarse-grained pellets or sands. They are among the least weathering-resistant minerals and, upon leaching of interlayer K⁺ cations via weathering, tend to partially transform to expandable nontronite. As such, interlayered glauconite-smectite phases can be readily found in these mica-like sediments. Recent offshore wind energy developments have encountered widespread, friable glauconite sands, which can change in coloration and consistency upon remolding (e.g., pile driving-induced shearing). For example, an initially brownish or black, cohesionless glauconite sand within the pile driving-disturbed zone can be converted to a green or dark green, soft, cohesive clay. Such a phenomenon has also been observed in geotechnical laboratory testing. To understand this abnormal phenomenological behavior, a micro/nano-scale investigation incorporating nano-scale X-ray (with an 8 keV energy) absorption-based computed tomography (CT) at a resolution of 30 nm, image analysis, and selective chemical dissolution (SCD) of Fe-oxides was conducted to uncover the nano/micro-scale structure of individual glauconite pellets. The resulting 32-bit CT images were processed to construct the three-dimensional (3D) models of the scanned individual pellets. Because the highly contrasting absorption coefficient of Fe-oxides, silica (e.g., quartz), and phyllosilicates (e.g., nontronite, glauconite), the 3D model images were used to quantify the surface coverage of the glauconite by Fe-oxides, typically ranging from 22% to 61%. The existence of a thin Fe-oxide layer covering the glauconite pellets was also qualitatively but definitively verified by the SCD technique, as the initially brownish pellets, upon the treatment, were completely dispersed and slacked into fine-grained suspension, accompanied with a conversion to a pure green color. Furthermore, intra-pellet pores are abundant in all three studied particles, and the internal porosity varies significantly, from 0.2 to 0.4. Within a single pellet, different mineral phases exist, including phyllosilicates such as glauconite and nontronite, silica and other silicates, and Fe-oxides. In particular, Fe-oxides may exist as a thin layer of coating wrapping a particle and hence masking the physico-chemical properties of the mineral phases inside the pellet. Moreover, the Fe-oxide coating layer is relatively strong and hence the pellets may not readily breakdown or slake under low pressure or small disturbance.
Adsorption of the antibiotic ciprofloxacin to montmorillonite - studied by MD simulations

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The continuous release into the environment has made pharmaceuticals pseudo-persistent a result of which, they are now classified as ‘emerging’ contaminants. However, natural and modified clay minerals are viable candidates for adsorbing and removing pharmaceuticals from the environment, due to their high specific surface area and modifiable surface properties.

In this study, we employed molecular dynamics (MD) simulations of ciprofloxacin (CIP) molecules at different protonation states, being either positive (CIP\(^+\)), neutral (CIP\(^{+/-}\)), or negative (CIP\(^-\)), to compute the adsorption free energies to sodium-montmorillonite (Na-MMT) using the umbrella sampling technique. Additional free energy perturbation (FEP) simulations were performed to obtain the hydration free energy and water/octanol partition coefficients of the molecules.

The biased umbrella sampling MD simulations revealed that despite having repulsive coulombic interactions with the MMT surface, CIP\(^-\) registered significant adsorption energy, although much lower than CIP\(^{+/-}\) and CIP\(^+\). Adsorption energies increased with different salt additions, with the CIP\(^-\) adsorption showing more improvement than CIP\(^{+/-}\) and CIP\(^+\). Overall, the salts’ performance improving CIP adsorption on the MMT basal plane was in the order of MgCl\(_2\) > KCl > CaCl\(_2\) > NaCl. However, no strong correlation between ionic strength and adsorption energy was observed. The FEP results showed that CIP\(^-\) has higher hydration energy than CIP\(^{+/-}\) and CIP\(^+\). Additionally, CIP\(^-\) is more hydrated in bulk water than when adsorbed, and the reverse behavior was observed for CIP\(^{+/-}\) and CIP\(^+\). Neither the addition of the salt nor the varying salt concentrations revealed a distinct trend with computed hydration energy. Moreover, FEP estimated water/octanol partition coefficients were compared with literature values.

In summary, we investigated the sensitivities of the hydration and adsorption free energy as a function of solution composition, ionic strength, and CIP molecule distance from the MMT surface. Accordingly, our results show the significant role ions play in increasing the adsorption of the less energetically favored molecules, and the effect of hydration for adsorption of molecules on MMT surface.

Figure 1. A schematic of CIP adsorbing on MMT basal plane
Cross heating of samples during IR-laser argon extraction

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IR laser heating allows to achieve relatively very high-power density and thus very large temperature gradients in a short time. It is one of the reasons why lasers are commonly used for heating of samples for K-Ar dating. This method allows to perform measurements with a low contribution of atmospheric argon. However, it is possible to cross heat neighboring samples, especially using a standard holder that is made of copper.

In order to address this issue, cross heating of samples in various types of holders was studied using non-contact optical pyrometer supported with K-Ar age dating tests on GLO standard. A total of six different holders were constructed, analysed and tested: standard copper, copper with cuts between sample holes, titanium, titanium with cuts, and two holders made of titanium rods with copper thermal shields at different distances between samples.

The experimental results show that the decrease of thermal conductivity of the holder (from 400 W/mK for copper to 22 W/mK for titanium) leads only to a small decrease of cross heating of neighboring samples. It indicates that temperature gradient is very large, conduction is the main mechanism of heat transfer between samples, and is practically not affected by the material of the holder. Additional cuts did not lead to a significant decrease of cross heating, either for copper and titanium holders. Therefore, thermal radiation is also an important contribution to heat transfer.

In order to minimize thermal conductivity and radiation between the samples, holders made of titanium rods with double thermal shields made of copper was constructed. Tests showed that this solution allowed to minimize thermal conductivity and radiation between the samples. Therefore, allowing to heat the samples at maximal optical power of 18 W for 5 minutes without release of radiogenic argon from neighboring GLO samples.

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Rapid transformation of biogenic silica to authigenic clay during reverse weathering

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Formation of authigenic clay minerals during early diagenesis of marine sediments (i.e., reverse weathering) is an important process for regulating ocean pH and atmospheric CO₂ over geologic time scales. This process is also considered the “missing sink” of the modern marine Si cycle. Although the importance of reverse weathering has been increasingly recognized, the rate and mechanisms of this process remain poorly constrained. The mechanisms, kinetics, and minerals derived from diatom biogenic silica, which is a common silica phase in marine sediments, are investigated in this study. Cleaned frustules of the diatom *Thalassiosira pseudonana* were incubated with Fe- and Al-containing minerals in anoxic, artificial seawater in the presence of dissolved Fe(II). After 40 days, a Fe(II)-containing aluminosilicate phase formed, which was identified as annite (Fe(II)-rich mica). The presence of dissolved Fe(II) and Al are identified as the critical triggers for authigenic clay formation. This work reveals a rapid dissolution-reprecipitation pathway in which the dissolved Al and Si (from dissolution of Al-containing phases and diatom-derived bSi) along with dissolved Fe(II) inputs are subsequently reprecipitated as authigenic aluminosilicate phases. These results will enhance our understanding of the geochemical triggers and precipitation mechanisms of authigenic clay formation in RW and serve as a fundamental basis for quantitative constraints and modeling of the global Si budget.
Unleashing the Transformative Power of Science Education at the Elementary Level, Through Engaging and Interactive Experiential Learning.

Taniece Thompson-Smith (Stafford Elementary School)

The building blocks of science begin at the elementary level in schools. In the Texas education system, 5th grade science scores lag behind reading and mathematics. Students learn best when facilitators of the learning experience spark curiosity or arouse interest. To challenge the proclivity of students not meeting 5th grade science expectations, we evaluated which geology topics consistently displayed scores falling below established expectations. We designed a day of experiential learning around those topics, that we called Geology Day. Geologists and other experts were invited to visit our school for the day. Our 5th grade cohort of approximately 80 students rotated through 7 stations equipped with hands-on experiences, real life examples and subject matter experts who facilitated experiences that targeted their multiple intelligences and higher order thinking. One of the concepts we included was soil; its properties, color, texture, capacity to retain water and the ability to support the growth of plants. To teach water retention with different soil types, students worked at a station facilitated by a geologist, who guided them through the scientific method in order to identify which soil was best for water retention. Students then discussed how soil retention was useful in the real world. Samples used for this experiment included kitty litter (non-swelling bentonite), quartz-rich sand, and gravel with clay. The data was then charted. Students later compared and contrasted the various soil samples, analyzed their data, discussed the margin of error and drew conclusions based on their findings. The results of this teaching approach were that students demonstrated a conceptual understanding of the topics reviewed, the corollary of that was improved benchmark scores. This data also confirmed our hypothesis that our science pedagogy determines if students become transformative intellectuals or if science continues to be a fugitive subject.
Electrostatic interactions at clay mineral surfaces: At the crossroads between mineralogy, geochemistry, and geophysics

Christophe Tournassat (ISTO, University of Orléans, France; EESA, Lawrence Berkeley National Laboratory, USA)

Clayey materials properties are key elements in several important subsurface energy-related applications, including the long-term disposal of nuclear wastes in geological repositories and the storage of CO₂ in subsurface geological formations. Clayey materials show a remarkable array of desirable macro-scale properties such as very low permeability, strong adsorption, semi-permeable membrane properties, and high swelling pressure, which lead to slow advection transport rates, contaminant retardation, limited diffusion for anions, and self-sealing of fractures. These properties arise from the interactions of charged mineral surfaces with water and solutes present in the nanopores of these materials, among which electrostatic interactions often play a dominant role.

The study of interactions between water molecules, ions, and individual clay mineral surfaces remains an intense field of research, which provides a basic understanding to build predictive models for the simulation of clayey material behavior as a function of physical and chemical forcing. The behavior of nanoporous clay environments is however complicated by the facts that the pore structure of clay materials, but also the surfaces and compositions of clay minerals, are heterogeneous, and that water and ions can be present in bulk water, incorporated within interlayer spaces, adsorbed to external surfaces, whether at basal or edge surfaces, or located within the electrical double layer. Mutual interactions between these system components lead to highly coupled processes and these couplings manifest themselves in macroscopic observations made up to geological formation scale, such as geologic ultrafiltration, i.e., the accumulation of solutes on the inflow side of clay-rich lithologies. To understand and predict the coupling phenomena, a preferred approach is usually built on the following sequence: i) to examine the physical processes at the molecular and pore scale, ii) to up-scale the physical laws toward the continuum scale, and iii) to compare continuum scale model predictions to geophysical and geochemical observables. My talk will address some of the challenges related to this type of up-scaling strategy, focusing on the role of electrostatic interactions on clay minerals properties.
Interpreting Diffusion Data with a Fast, Free, and User-friendly Reactive Transport Modeling Approach

Christophe Tournassat (ISTO, University of Orléans, France; EESA, Lawrence Berkeley National Laboratory, USA), Carl Steefel (EESA, Lawrence Berkeley National Laboratory, USA), Patricia Fox (EESA, Lawrence Berkeley National Laboratory, USA), Ruth Tinnacher (Department of Chemistry and Biochemistry, California State University East Bay, Hayward, CA, USA)

A freely available graphical user interface, CrunchEase, was created for the reactive transport code, CrunchClay. CrunchClay can be used to interpret through-diffusion data with a set of parameters, including the effective diffusion coefficient, clay porosity, and the radionuclide adsorption distribution coefficient \((D_e - \varepsilon - K_D)\). CrunchEase supports the user by automatizing the creation of input files, the running of simulations, and the extraction and comparison of data and simulation results. The coupling of CrunchEase with CrunchClay allows for a reactive transport approach that can accurately include and characterize the influence of unavoidable experimental biases on the estimation of diffusion parameters. These biases include the effects of filters holding the solid sample in place, the variations in the constant concentration gradient across the diffusion cell due to sampling events, the impact of tubing/dead volumes on the estimation of diffusive fluxes and sample porosity, and the effects of O-ring-filter setups on the delivery of solutions to the clay packing. Furthermore, the CrunchEase/CrunchClay package allows the user to simulate raw through-diffusion data, i.e., radionuclide concentrations and volumes in reservoirs, directly, without the need to convert experimental concentration data into diffusive flux values. This approach helps to minimize error propagation issues due to the experimental data interpretation. This direct modeling of raw data is also more accurate if tubing volumes and the time of reservoir sampling events are made available and specifically included. CrunchEase makes it also possible to transition more easily from a \((D_e - \varepsilon - K_D)\) modeling approach to a process-based understanding modeling approach. This is achieved by using the full capabilities of CrunchClay, which include surface complexation modeling and a multi-porosity description of the clay packing with charged diffuse layers. Overall, we believe that the development of the CrunchEase user interface will further facilitate the dialog between experimentalists and modelers on the most recent concepts applied to diffusion problems in clayey materials. This may ultimately lead to an improved decision-making process by radioactive waste agencies.
Molecular Simulations of Soil Organic Matter at Mineral Interfaces

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The global pool of organic matter (OM) in soils is roughly 1500 PgC, with a typical gross flux of approximately 60 PgC/yr. Back of the envelope calculations imply that the average turnover time of organic carbon in soils is on the order of 25 years. Carbon dating of OM, however, shows that certain forms of carbon become effectively removed from the global carbon cycle for many thousands of years. Clearly, this is an important phenomenon to understand if we wish to have a coherent and holistic picture of the carbon cycle, and if we wish to understand the feedback loops between carbon sources and sinks, anthropogenic carbon production, and climate change. An emerging conceptual view is that this recalcitrance may be related to the multilayer sorption of organic molecules on mineral surfaces.

In the present study, we use molecular modeling to understand the processes driving the adsorption and subsequent recalcitrance of soil OM upon the clay mineral surfaces of smectite and mica, as well as the iron-oxyhydroxide surface of goethite. Classical molecular dynamics simulations using the replica-exchange algorithm are used to understand the equilibrium fractionation of a representative set of soil organic matter (amino-acids, sugars, and lignin-like molecules) and its subsequent structural layering at the mineral-organic interface. Results are positively compared to the frequently cited Kleber model of soil OM-mineral interactions, in which certain soil OM molecules readily sorb directly to the mineral surface; certain soil OM molecules are bound to the surface mediated via complex OM-OM interactions; and the remaining soil OM is readily labile.

Using clustering techniques, we deconvolve the simulations to understand which key molecular features (important functional groups, aromaticity, charge, etc.) cause molecules to exist in each of these categories, Figure 1 (right). We discuss which types of molecules are likely bound to mineral surfaces (and through which mechanisms), and which soil OM molecules are more susceptible to desorption and subsequent bacterial degradation.

Figure 4: (Left) Soil OM sorption on the hydrated K-mica interface. (Right) The clustering of OM on the hydrated K-mica interface. Green tagged molecules are directly sorbed to the mineral, blue tagged OM are sorbed via OM-OM interactions, and yellow OM molecules are unbound.
Changes in U(VI) Sorption Behavior onto Montmorillonite with Temperature and Solution Chemistry

Ben Urick (California State University East Bay, Hayward, CA, USA); Christophe Tournassat (Université d’Orléans, Orléans, France; LBNL, Berkeley, USA); Ruth M. Tinnacher (California State University East Bay, Hayward, CA, USA)

Most future nuclear waste repositories will include engineered bentonite barriers to minimize the release of uranium (U) and other radioactive contaminants into the natural environment. Bentonite predominantly consists of montmorillonite clay besides small fractions of mineral impurities. Due to the initial thermal loading of waste packages and the continued release of decay heat over time, elevated temperatures have to be expected in future bentonite barriers. As a result, contaminant transport models for early-release scenarios will have to include potential effects of temperature on contaminant mobility, such as changes in mineral structure and surface characteristics, radionuclide adsorption behavior and diffusion coefficients. Furthermore, the predictions of any temperature-dependent radionuclide surface complexation or diffusion model will largely depend on an accurate representation of radionuclide solution speciation at elevated temperatures. Hence, the goal of this study is to gain a better understanding of potential changes in uranium(VI) solution speciation and adsorption processes onto montmorillonite as a function of temperature, based on model predictions.

All of our simulations were set up in PHREEQC (ThermoChimie 11a database) as a function of pH, partial pressures of CO₂ and temperature (25 or 80 °C). First, we evaluated a series of underlying parameters and processes that could cause apparent differences in U(VI) solution speciation at elevated temperatures. We found that temperature-induced changes in U(VI) solution complexation constants caused the largest shifts in U(VI) solution speciation. In a next step, we individually tested how U(VI) sorption behavior is affected by temperature-induced changes in U(VI) solution speciation, clay surface protonation constants, or U(VI) surface complexation reactions. Other temperature-induced changes in mineral structure and surface properties were excluded for simplicity at this point. The results for our U(VI) adsorption models at 80 °C suggest that the changes in U(VI) solution speciation alone would lead to a sharp decrease in U(VI) sorption. In contrast, temperature effects on clay surface protonation alone only cause a slight decrease in U(VI) adsorption; individual temperature effects on U(VI) surface complexation reactions a significant increase in U(VI) adsorption.

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Oriented attachment (OA) is a crystal growth pathway in which lattice-matched particles aggregate into larger crystal structures. Generally, OA occurs in two steps. First, two particles separating by a thin layer of solvent rotate and translate to align with one another. Then, the intervening solvent layer is removed, and the particles jump to contact. Although significant progress to understand the OA crystal growth process has been made, the effects of crystalline particle misalignment and the roles of solvent/particle and particle/particle interactions on the structure-energy relationships during OA remain elusive. In this study, we perform molecular dynamics (MD) simulations to calculate the potential of mean force (PMF) profile for the translation of a gibbsite (Al(OH)$_3$) particle on a gibbsite slab with one or two intervening water layers (1W or 2W). Our PMF results indicate that the changes in the surface-water and water-water hydrogen bond network during the translation are strongly coupled with the energetic changes in the 1W case. However, for 2W case, the particle/slab misalignment becomes the dominant factor controlling the energetic behavior of the system. Our results shed new light on the energy-structure relationships that define the oriented attachment of crystalline particles.

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Exchangeable potassium in fine, smectite-rich size separates: Implications for K-Ar dating

J. M. Wampler and W. Crawford Elliott (Georgia State University, Atlanta, GA USA)

On the plausible assumption that no radiogenic argon is associated with exchangeable K, removal of exchangeable K before K-Ar measurements (or correction based on later determination of exchangeable K) is essential for useful K-Ar dating of illite-smectite (I-S). Little attention has been paid to this issue, however, because illite-rich I-S has relatively little exchangeable K after treatment with Na-rich solutions during preparation of size separates (Aronson and Douthitt, 1986). Age values of smectite-rich I-S should be more strongly affected by the presence of exchangeable K than those of illite-rich I-S, however, because (1) larger cation exchange capacities provide more sites for exchangeable K and (2) a given amount of exchangeable K is a larger fraction of the total amount of K. The present study was undertaken to see if significant exchangeable K is present in various fine, smectite-rich size separates that had been prepared at various times and in various ways for K-Ar dating.

The smectite-rich fine-clay separates studied were from bentonites exposed in northeastern Turkey and at the western edge of the Denver Basin in Colorado and from clay-alteration zones deep within the Kiirunavaara mine at Kiruna, Sweden. The initial K contents ranged from 0.01 cg/g to 1.19 cg/g (cg/g = % by mass). The exchangeable K was displaced by successive batch extractions with 0.5 mol/kg NaCl solutions prepared from recrystallized NaCl, and the extracted K was measured by atomic absorption spectrophotometry. Various tests on duplicate portions were applied to confirm that essentially all of the extracted K had been exchangeable K, rather than fixed K released by mechanical or chemical action. The total amount of K extracted in successive batches, relative to the initial K content, ranged from about 10% to 74% (see figure).

Most of the studied separates had very small initial K contents—about 0.2 cg/g or less. All had been immersed more than once in Na-rich solutions during their preparation, but, for many, a large fraction of the K that remained was exchangeable. The exchangeable K, which would have been negligible for dating illite-rich I-S, was enough to make K-Ar age values far too small for some of these K-poor separates. Special effort to ensure removal of all exchangeable K will be required of those who would determine K-Ar age values for smectite-rich I-S or for smectite that has a trace amount of K.

Potassium and argon-isotope measurements of illitic clay: Unfinished work

J. M. Wampler (Georgia State University, Atlanta, GA USA)

The K-Ar dating method was first applied to illitic clay almost 65 years ago. Since then, the method has proved to be remarkably valuable toward understanding where, when, and how such clay has formed. The full scientific potential of K and Ar-isotope measurements of illitic clay has not yet been realized, however. A substantial increase in the accuracy of conventional K-Ar dating of clay, to be as accurate as ⁴⁰Ar/³⁹Ar total-gas age determination, will be an important step toward realizing that potential. In addition to the availability of highly sensitive noble gas mass spectrometers, the increase in accuracy will depend on use of a single test portion for both K and Ar-isotope measurement to eliminate weighing error, on careful attention to the accuracy of K measurement, and on new methods to reduce atmospheric-Ar contamination of smectite-rich illite-smectite (I-S). Use of single test portions will allow accurate calibration of age values against clay reference material such as the GL-O powder. Using single portions, the GL-O powder itself can be calibrated in age value against established K-Ar reference samples with no error from variable moisture content. Use of single portions allows work with very small amounts of clay, as the ⁴⁰Ar/³⁹Ar method now does. An aspect of improved accuracy that applies also to the ⁴⁰Ar/³⁹Ar method is the recent recognition that size fractions of smectite-rich I-S often have enough exchangeable K that K-Ar age values are far too small. Careful attention to removal of exchangeable K prior to K-Ar and ⁴⁰Ar/³⁹Ar measurements should produce more-accurate age values for illitic clay generally.

K-Ar dating has contributed widely to understanding of diagenetic and hydrothermal illite formation. Improved accuracy and the ability to work with very small test portions mean that the method still has much to contribute to such studies. There is great potential for expanded use of the K-Ar method in the study of soils and paleosols. The method is excellent for recognition of inherited illitic material in soil and can provide answers to important questions about provenance, including assessment of the contribution of aeolian material to soils. High accuracy conventional age determination on small test portions should be valuable in the still developing use of the K-Ar relationship to study the timing of fault-gouge formation.

Ar-isotope measurements can help answer questions about illitic clay that are not directly about the ages of the illitic materials present, such as questions about transport of alkali ions and radiogenic Ar at the periphery of illite crystallites. Is radiogenic Ar lost if it forms just inside the edge? Do some Cs⁺ ions selectively sorbed at the edge move into the interlayer? Can K⁺ ions just inside the edge be lost by exchange without loss of larger radiogenic Ar atoms from corresponding sites? Are some illitic components of sediments, soils, and gouges more susceptible than others to chemical processes that alter interlayer composition? Some such questions can be addressed by looking for differences in K-Ar age value after successive treatments to replace or remove materials that were near crystallite edges—more reliably so if age values are determined with high accuracy. Issues of this kind could be addressed more directly by measuring alkalis and Ar isotopes released during treatment instead of the K-Ar age value of the solid phase after treatment. Measuring Ar isotopes released during chemical processes is potentially a major aspect of future investigation of illitic clay. Finding a way to do that has begun but is unfinished.
Local structure of opal-CT: Multiscale modeling of stacking disorder in layered materials

Hsiu-Wen Wang, Katharine Page, Reinhard Neder, David L. Bish

The structure of opal has long fascinated scientists, occurring in a number of structural states, ranging from amorphous to exhibiting features of stacking disorder. Opal-CT represents the link in the length scales between amorphous and crystalline states, where C and T nomenclature signify cristobalite- and tridymite-like interstratification. However, details about local atomic (dis)order and arrangements extending to long-range stacking faults in opal polymorphs remain not entirely understood. Here, we report a multilevel modeling approach that considers stacking states in correlation with the abundance of C and T segments. Our approach optimized inter-tetrahedral bond lengths angle while preserving the regularity of the silicate tetrahedra. Structural disorder at the ~10-100 Å distance scale is evaluated using experimental pair distribution function and diffraction datasets, comparing peak intensities, widths, and asymmetry never obtained before. This work presents a complete multilevel structural description of natural opal-CT and explains many of the unusual features seen in X-ray powder diffraction patterns. This modeling approach can be adopted generally for analyzing layered materials and their assembly into 3D structures.
Smectite swelling hysteresis is driven by interfacial charge regulation

Yuntian Teng, Benjamin Gilbert, Michael L. Whittaker

Clays are found nearly anywhere minerals and water meet. The relative amounts of water and clay govern many macroscopic clay properties, such as water permeability and ion diffusivities, that must be known to predict the evolution of clay-based nuclear waste repository concepts over time. For swelling clays (smectites) such as bentonite, the variable water content between mineral layers is determined primarily by interlayer charge density, which strongly controls both water and ion fluxes under non-equilibrium conditions. However, no current clay swelling model captures the inherent history-dependent equilibrium water content that is observed in laboratory experiments on pure clay minerals, such as montmorillonite. Here, we show that charge regulation within the interlayer space, whereby ions change their average water- and mineral coordination numbers to balance hydration and electrostatic forces, is inherently hysteretic and controls the observed equilibrium water content of smectites. We observe interfacial ion binding configurations directly using cryogenic electron microscopy (cryoEM) and tomography (cryoET), and show that the Gibbs free energy for swelling exhibits two stable states over most values of relative humidity using hydration differential scanning calorimetry and thermogravimetry (h-DSC/TG). Combined, these observations indicate that the hydration free energy of the interlayer cation competes with electrostatic attraction to structural charge sites within the clay layers at similar energy and spatial scales, creating multiple stable binding configurations. Recent work has shown that layer size polydispersity attenuates this effect, suggesting that clay mineral heterogeneity acts to reduce the hysteresis observed in purified samples to produce a more monotonic response to the reservoir water activity.
Laboratory investigation of the impacts of clay on erosion and soil carbon sequestration

Judy Yang (Department of Civil, Environmental, and Geo-Engineering, Saint Anthony Falls Laboratory, University of Minnesota)

Clay minerals, such as smectite, play a critical role in the transport of sediment and the sequestration of carbon in soil. The electrochemically-active surfaces of clay make sediment cohesive, which reduces erosion by several orders of magnitude. In addition, clay adsorbs organic matter through surface interactions. The clay-stabilized carbon constitutes a significant carbon pool in soil. In this presentation, I will first discuss how my group at the Saint Anthony Falls Laboratory is designing flume experiments to study the impacts of clay on erosion. I will discuss how we directly visualize the transport a fluorescently-labeled smectite clay, laponite, using a laser and a digital camera. I will also describe how we image the microstructures of the clay using a Confocal Laser Scanning Microscope. Our study demonstrates how the microstructures of clay control the transport of smectite clay. Second, I will talk about how my group is designing “soil-on-a-chip,” a microfluidic device to study the sorption and desorption of carbon to clay. I will talk about how we place a transparent smectite clay into the simulated soil pore, inject fluorescently-labeled sugars into the soil pore, and quantify the sorption and desorption of sugars of different molecular weights to clay using a confocal microscope. Finally, I will discuss how our studies and methods will provide a theoretical foundation for future use of clay to reduce coastal and riverine erosion and to preserve carbon in soil.
The chemical effect on the swelling of the bentonite: laboratory tests and large scale modeling

Lianne Zheng, Wenming Dong, Jonny Rutqvist, Ayumi Koishi, Chenhui Zhu, Carl I. Steefel, Jens T. Birkholzer (Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.)

Bentonite has several beneficial barrier features such as a low permeability, high swelling and retardation capacity, to be used as a buffer material for the engineered barrier system (EBS) in a geological repository for high-level radioactive waste (HLW). In a repository, the bentonite buffer will undergo heating from the waste package and hydration from the host rock, which induces thermal, hydrological, mechanical and chemical (THMC) alterations and these changes also interacts with each. Among all these interactions, the effect of chemical changes on the mechanical alterations, mainly the swelling of bentonite, is probably the least understood and needs more studies. There are three potential chemical changes that could affect the swelling of bentonite: the abundance of smectite, porewater ionic strength and interlayer cations (or exchangeable cations). Although studies have been conducted to evaluate their effect, to quantify these effects and represent them in numerical models have been challenging. In this presentation, we first discuss the recent results from a series of microscopic test using μ-oedometer to measure time-resolved swelling force as a function of ionic strength (0.001M – 5M NaCl) and cation types (Na⁺ vs. K⁺), then present a method to consider chemical effect on swelling in a coupled THMC code and its application to a generic repository for HLW. The microscopic tests showed that clay interlayer basal spacing increases with decreasing ionic strength, and time-resolved swelling pressure increases with decreasing ionic strength, which agree with other publications. The swelling pressure continuously decreases with increasing K⁺/Na⁺ ratios under a constant ionic strength of 1M NaCl/KCl mixtures. In the THMC simulator, the chemical effect on swelling were implanted via extended linear swelling model and Barcelona Expansive Clay Model and demonstrated in a generic large-scale model. Model results showed that the change in the abundance of smectite dominates the effect of chemical change on swelling pressure in the long run.
Evolution of Bentonite Properties during Progressive Dehydration: A Molecular Dynamics Simulation Study

Xiaojin Zheng and Ian C. Bourg (Princeton University, Princeton, NJ USA)

Bentonites are fine-grained rocks composed of predominantly smectite clay minerals. Clay is one of the high-quality engineered barriers in the isolation of high-level radioactive waste (HLRW) because of its favorable properties including low permeability, sufficient thermal conductivity, and high ion exchange capacity. Coupled thermal-hydraulic-mechanical-chemical (THMC) processes, including the joint influence of thermal gradients, mechanical deformation, fluid transport, and geochemical reactions, may impact the performance of engineered clay barriers over a long timescale. The heat generated by radioactive decay brings particular challenges, as it requires the establishment of constitutive relations characterizing the material properties of bentonite, including thermal properties, as a function of temperature up to at least 100 °C and also, as it may trigger changes in bentonite dry density or saturation state. Consequently, monitoring the evolution of bentonite properties is crucial to prevent or minimize the possibility of radionuclide release from HLRW repositories.

In this work, we run large-scale molecular dynamics (MD) simulations of montmorillonite clay assemblages using the codes GROMACS and LAMMPS (Fig. 1). Simulations were initially equilibrated via the replica-exchange MD (REMD) technique within a wide range of temperatures up to 100 °C and then, progressive dehydration was carried out by randomly removing water molecules from the simulated system. The equilibrated clay-water mixtures in each dehydration step were analyzed to determine a series of bentonite material properties including hydraulic conductivity, water and ion self-diffusivity, thermal conductivity, heat capacity, thermal expansion, and swelling pressure as a function of temperature and dry bulk density. The results were then validated and refined by benchmarking against experimental results and previous MD simulation predictions. Our results highlight the key factors controlling the coupled properties of bentonite and generate new insight into the feasibility of upscaling from nanoscale assemblages of clay sheets to field-scale clay barriers. This work advances the understanding of the coupled THMC properties of bentonite and helps enable more accurate predictions of the performance of engineered clay barriers over long time scales.

Fig. 1. Snapshots of the simulated montmorillonite clay assemblage during progressive dehydration. The system contains 27 montmorillonite particles (in red/yellow) solvated with Na ions (in blue). Water molecules are not shown.
Experimental constraints on potassium isotope fractionation during cation exchange in clay minerals

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Stable potassium (K) isotopes (\(^{41}\text{K}/^{39}\text{K}\) or \(\delta^{41}\text{K}\)) have emerged as a novel tracer for the silicate cycle, including silicate weathering and clay formation, because K primarily resides in silicates, making its geochemical cycle more closely related to the silicate cycle than other major elements. Recent studies on K isotopes have shown, for the first time, that the \(\delta^{41}\text{K}\) value of seawater is \(~0.6\%\) higher than that of the bulk silicate Earth, but the exact cause for this contrast remains unknown. Cation exchange between solutions and clay minerals, a ubiquitous process in terrestrial and marine settings, may produce resolvable K isotope fractionation, thereby contributing to the observed isotopic contrast. However, field and laboratory studies yielded inconsistent results regarding direction and magnitude of K isotope fractionation associated with this process.

Here we report quantification of K isotope fractionation between aqueous K and three representative clay minerals (kaolinite, montmorillonite, and illite) through laboratory exchange experiments. Calcium- and Na-saturated clays were reacted with aqueous KCl solutions at circumneutral pH and room temperature, and evolution of K isotope compositions of aqueous and solid phases was tracked. Our results show that aqueous K exchange with either Na or Ca in the three clay minerals generally produced similar K isotope fractionation (\(\Delta^{41}\text{K}_{\text{aqueous-sorbed}}\)) of \(~0.15\%\), with sorbed K being isotopically light. Using a \(^{41}\text{K}\)-enriched tracer, we can demonstrate that only small fractions of non-exchangeable K ions in starting montmorillonite and illite participated in cation exchange processes. Our observed K isotope fractionation, therefore, reflects fractionation between aqueous K and K at exchangeable sites in most cases. The only exception is that K exchange with Na-saturated illite produced considerably larger K isotope fractionation of 0.4\%. Because Na can gain access to more non-exchangeable K relative to Ca in initial illite, the larger K isotope fractionation may reflect additional contributions from K isotope fractionation between aqueous K and K in non-exchangeable sites. Our results imply that cation exchange is insufficient to explain the heavy K isotope signature of seawater, whereas locking of K in non-exchangeable sites during clay formation (such as illitization) may play an important, but currently under constrained role.
Crushed Rock Analysis with Fluid Loss Quantification via Combined Open & Closed Retort

J. Alex Zumberge (GeoMark Research, Houston, TX USA), and Jadranka Milovac (GeoMark Research, Houston, TX USA)

To overcome the shortcomings of certain crushed rock analytical methods related to characterizing tight unconventional reservoirs and to address the challenges related to core measurements in organic rich mudstones, a technique was developed that incorporates data collected from multiple sources and in turn, provides more accurate partitioning of the pore space. The proposed method uses NMR to quantify fluid loss due to crushing the rock, which for certain samples can be significant. It further combines both open and closed retort to benefit from a tandem approach. Open retort provides insight into free and bound water components, while the closed system ensures fluid preservation during retorting (thermal extraction). Thermally extracted fluids are quantified volumetrically (BVW and BVO), while the recovered retort oil can be further geochemically analyzed for its composition and potentially compared to produced fluid for hydrocarbon allocation work, etc. This technique provides direct measurement of the volume of oil in the sample, to the contrary of some other methods that rather compute it based on an assumed density. Lastly, the procedure is followed by a chemical extraction. Each step incorporates internal cross-checks, and detailed geochemical analysis which include TOC and programmed pyrolysis.

In this talk we will be presenting details of the methodology, including the steps which make it unique. Furthermore, we illustrate the workflow in a case study from the Niobrara formation, Powder River Basin. We will also briefly discuss the workflow differences among GRI, TRA, and this method (TruSat) from the perspective of implications on measured properties (porosity and saturation) in organic rich rocks.
ABSTRACTS
Poster Session
Clay Mineralogy of Per- and Polyfluoroalkyl Substances (PFAS) Contaminated Soils from Agricultural Fields in Society Hill, South Carolina

Adeyemi Oluwaseun and Schroeder A. Paul (University of Georgia, Department of Geology, Athens, USA)

Per-and polyfluoroalkyl substances (PFAS) is an acronym for a family of anthropogenic compounds. PFAS are also known as ‘forever chemicals’ due to their chemical stability related to strong carbon-to-fluorine bonds. PFAS are used in fire-retardant foams, textiles, and food containers. PFAS are pervasive environmental pollutants found from metropolitan runoff to the extreme reaches of the Arctic. PFAS are toxins to human health. Agricultural fields treated with wastewater biosolids as soil supplements with a high PFAS content occur throughout the United States. Recent studies suggest a connection between clay minerals (e.g., kaolinite, hydroxy-interlayer vermiculite, and illite), oxyhydroxides (e.g., goethite and gibbsite), and PFAS. These clays and oxyhydroxides contain adsorbed hydrated cations with pore-mineral surfaces likely influenced by solution ionic strength, pH, and redox conditions and thus have the potential to adsorb/desorb PFAS.

We examined 89 samples from 2 drill sites (~18 m) in spray application fields where biosolids from a textile factory were applied. This study determined the: 1) degree of contamination of PFAS performed by the U.S. Environmental Protection Agency (EPA), 2) Clay mineralogy (using X-ray diffraction) of a PFAS-contaminated sample subset (16), and 3) the relationship between specific clay minerals sorption potential to pH using published zero point of charges for identified minerals.

Results reveal high PFAS contamination in the top 3 meters. The clay minerals include kaolinite, vermiculite, gibbsite, goethite, and illite. Since most PFAS have negative charges, minerals that have positively charged surfaces are potential sorption substrates for PFAS. These minerals bear a positive surface charge at pHs less than goethite and gibbsite zero charge points, ~8 and ~9, respectively. Our study’s soils have a pH of < 8, so, thus suggesting these minerals are good candidates to sorb PFAS.
Smectite is a common clay mineral in sedimentary basins whose transition into illite coupled with a loss of structural water may adversely affect hydrocarbon production. Therefore, the illitization is a crucial process that affects reservoir quality and consequently the hydrocarbon potential of the basin. The illitization of smectite has been extensively studied discretely in sandstone and mudstone. Our knowledge however, on how the process progresses in an interbedding of the two lithologies is not as rich as the former. This study aims to explore the illitization of smectite in the alternating sandstones and mudstones of the Pennsylvanian strata in the Anadarko basin, with a particular focus on the precipitation of siderite to the illitization process. We hypothesize an eogenetic siderite precipitation in the Missourian aged strata affected the dynamics of illitization in the basin. We postulate that, the siderite cemented areas prevented pore fluid interaction in and out of the engulfed areas, preferentially inducing a higher rate of illitization in the surrounding sediments and a halt to smectite illitization in the siderite impregnated host rock. This study will implore a combination of X-ray Diffraction, Scanning Electron Microscopy, and Fourier Transform Infrared Spectroscopy to analyze the mineralogy, chemistry and texture in and out of the siderite cemented areas in all 38 selected siderite cemented samples to corroborate our hypothesis or not on whether siderite precipitation hinders smectite illitization. The goal of this research is to provide new insights into factors that control the rate of smectite illitization in sedimentary basins, and also contribute to the knowledge of the diagenetic evolution of clay minerals in the prolific Anadarko basin, which may have significant implications for petroleum exploration and production.
Understanding chemical weathering in an euxinic environment using bulk sediment and clay-preserved proxies

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Much of ancient Earth history is recorded in and interpreted from sediments deposited from euxinic (sulfide-rich) waters. However, modern euxinic environments are useful proxies for early earth. Therefore, we sought to understand the morphological and chemical proxies preserved in sediment impacted by a modern euxinic spring as compared to adjacent non-euxinic stream-bank-sediment (unimpacted). We used X-ray diffraction (XRD) to analyze the mineralogy of the bulk sediment and isolated clay fraction. We further examined clay nanoparticles using Scanning/Transmission Electron Microscopy (S/TEM) and Energy-Dispersive X-ray spectroscopy (EDX) to study the clay morphology and chemistry. The bulk mineralogy of the impacted sediment includes pyrite and barite in addition to albite, quartz, illite, calcite and K-feldspar, which were present in the unimpacted sediment. However, dolomite was present in the unimpacted sediment but absent in the impacted sediment. While the sediments currently in contact with the euxinic water are much darker and appear to have a texture indicating they are richer in clays compared to the unimpacted sediments, the XRD results of clay-oriented mounts show the impacted and the unimpacted clay fractions are both comprised of smectite, chlorite, kaolinite, illite, smectite/chlorite and illite/smectite mixed layer clays. We chose to focus additional analyses on smectite clay nanoparticles because of their elevated abundance in the impacted layer and known potential for redox reactivity; TEM images of these smectites reveal platy and cornflake textured smectites in both impacted and unimpacted samples. However, EDX results reveal differences between the smectites in the impacted and unimpacted samples; the unimpacted smectites have higher concentrations of silica, aluminum, and iron, whereas impacted smectites have elevated titanium. Additionally, the unimpacted smectites contain calcium and potassium as interlayer cations while calcium, potassium, and sodium, with traces of barium, strontium, and nickel are seen in the impacted smectites. Furthermore, STEM EDX shows evidence of nanoscale barite and fluorite precipitation on the impacted smectites. These nanoprecipitates were also supplied by the euxinic spring. Ultimately, this study demonstrates that smectite nanoparticles primarily respond to euxinic conditions by immobilizing trace elements by adsorption or cation exchange rather than significantly changing their octahedral sheet cation composition.
Lacustrine sediments are used as indicators of paleoclimates and paleoenvironments, given that the geochemistry of lake water is sensitive to climate change related processes, such as evaporation and weathering \(^1\). Silicates and clay minerals represent a significant portion of lacustrine sediments. Authigenic clays are often found in alkaline lakes, frequently reported as magnesium silicate phases such as kerolite, smectites, sepiolite, and palygorskite \(^2,3,4\). The formation of these minerals in lakes plays a crucial role in solution chemistry, as they readily precipitate directly from supersaturated waters at ambient temperatures and pressures \(^1\). Yet, some biogeochemical processes may favor Mg-silicate formation, possibly obscuring the relationships between the identity and presence/absence of Mg-silicates and the lake water chemistry \(^4\). For instance, metabolic activity of cyanobacteria can modify the saturation states of solutions with respect to authigenic clay (mineral) phases since these microorganisms can, for instance, accumulate ions within extracellular polymeric substances leading the surrounding solutions to become supersaturated \(^5\).

The purpose of the present study is to investigate the mineralogical and geochemical characteristics of the clay (mineral) phases in lacustrine carbonate sediments found on the Cariboo Plateau in British Columbia, Canada, and their relationships with environmental conditions. We collected lake water samples, grab samples of lake sediments, and samples of microbial mats present in the lakes, with the purpose of comparing their mineralogy. Mineralogy and microstructure of the sediments was analyzed using SEM, powder XRD, and FTIR. The water geochemistry was determined using ICP-MS/MS and alkalinity obtained by colorimetry. Results of this study give a greater understanding of conditions in which low-temperature authigenic clays form. Given their widespread abundance and unique chemical behaviour, it is important to study how these phases form and respond to their environment to better interpret the paleoenvironmental messages carried by the sedimentary record.

Detailed mineralogical characterization and nanoporosity evaluation of USGS Shale Geochemical Reference Materials

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Geochemical reference materials (GRMs) are used to address the quality control and assurance needs of analytical geochemists, mineralogists, and others involved in the study of geologic samples. In addition to providing laboratory references materials for calibrations or checks on analytical methods, the availability of GRMs can provide consistent, readily available materials for experimental research into a variety of geologic processes. Over the last 10 years, the U.S. Geological Survey (USGS) has been developing a series of organic-rich mudstone or “shale” GRMs for use in petroleum systems research and other studies of sedimentary basins including evaluation of paleoenvironmental conditions and ancient climate. As high-resolution chemostratigraphic characterization of mudstone sequences have become more common in order to support the development of unconventional petroleum systems, the availability of relevant GRMs to ensure data quality in these studies has become more important.

Initial work has been completed to determine major and trace element concentrations, organic geochemical properties, and bulk mineralogy for a set of six USGS shale GRMs representing a range of organic carbon contents (2 – 8 wt. %), lithologies, and thermal maturities (immature to oil window). These GRMs were collected from the following formations and locations: Middle Devonian Marcellus Shale (Oatka Creek Member) in LeRoy, New York; Upper Devonian-Lower Mississippian Woodford Shale near Ardmore, Oklahoma; Upper Cretaceous Mancos Shale near Delta, Colorado; Upper Cretaceous Boquillas Formation (Eagle Ford Shale-equivalent) near Del Rio, Texas; Upper Cretaceous Niobrara Formation (C-marl) near Lyons, Colorado; and Eocene Green River Formation (Mahogany zone oil shale) near Rifle, Colorado. Additional characterization studies have been or are being undertaken to expand the utility of these GRMs, focusing on clay mineralogy, nanoporosity, and surface properties. Datasets have been collected using N₂ gas adsorption before and after organic removal to evaluate GRM porosity and surface area, with emphasis on the roles organic matter and mineralogy, specifically clay minerals, play in controlling those characteristics. Scanning electron microscopy work has also been conducted to visually document pore character. The Boquillas GRM (ShBOQ-1) is currently available, and the remaining GRMs will be released if there is sufficient interest from potential users.
Fine Fraction Material from Dumps: Opportunities for Environmental Engineering in the Future

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Waste and its dumping are a global problem since historical times. Society’s efforts towards the zero-waste concept are supported by the biobased and circular economy. Open questions are, how to use rejected material from sorted waste lines and where the inert material from former landfills can be applied. Processing of inert waste is possible by landfill mining resulting in biocover material (Figure 1) applicable to cap, e.g., dumped waste [1]. Thus, the mass of dumped waste is reduced, and part of waste turns into a valuable secondary resource.

Figure 1. Schematic cross-section of biocover application.

Humic substances are constituents of soil organic matter; due to their complex structure, they act in combination with clay minerals as sorbents [2] with the potential to be incorporated into low-cost composite materials. Though, the composition of such materials depends on climatic conditions and inert material structure and properties. For methane degradation function, admixtures should be added to maintain the functionality of microorganisms. The tests implemented at laboratory and field scales reveal successful direction in creating biocovers using a fine fraction of waste in a mixture with organic materials such as compost, beach wrack or digestate. Clay minerals and humic substances act synergetically with high sorption capacities providing microorganisms with necessary nutrients. Because about 18% of global methane is released from dumps and landfills, such biocover significantly applies as innovative technology to reduce greenhouse gas emissions. The study aimed to provide specific and simple solution for landfill closure approved by theoretical considerations for environmental engineering, chemistry and waste management.

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Understanding Rare Earth Element Distribution in Low/Medium Grade Hydrothermal Chlorite

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This study provides new insights into the distribution of rare earth elements (REE) in a range of chlorite from hydrothermally altered mafic rocks from the Dinarides. Low-medium grade metamorphic conditions to include zeolite, prehnite-pumpellyite, and greenschist facies assemblages reveal unique geochemical signatures of chlorite, thus reflecting the interaction between hydrothermal fluids and host rock lithologies. A diverse set of chlorite have been identified and may comply with characteristic rare earth element signatures that can be categorized and defined by specific geochemical and textural parameters. Fe-rich chlorite may contain significant enrichments in REE in contrast to Mg-rich members, particularly with the LREE. Additionally, numerous textural varieties such as amygdales and pseudomorphic chlorite have been identified and may also reflect their own distinct trace element signatures. This research will (a) use stable isotope geothermometric methods to constrain the formation conditions of a variety of chlorite, (b) make estimates on redox state using the enrichment/depletion of Ce and Eu, and (c) make inferences concerning the sources of REE which provide the initial rare earth element budget of the fluids, all to provide further support for the rare earth elemental codependency on the conditions in which they themselves and the fluid have been subjected to.
Geology and mineralogy of the S’Aliderru bentonite deposit (Sardinia, Italy): preliminary data

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S’Aliderru bentonite deposit is located in the northern Sardinia bentonite (Tertiary) basin (Italy). The deposit derives from the alteration of calcalkaline pyroclastic rocks of Oligo-Miocene age, which fill a structural depression occurring in the Mesozoic carbonate basement. The present work has the aim to define geological and mineralogical features of the S’Aliderru deposit and define its genesis.

S’Aliderru deposit extends for 0,8 km N-S, 0,4 km E-W, with an average thickness of 50 m. The orebody consists of multiple bentonite lenses of variable colour, interbedded with moderately to strongly altered pyroclastic rocks, travertine bodies and sandy-to-conglomeratic lenses, and is locally dislocated by faults. Mineralogical analysis (XRPD) allowed to determine that S’Aliderru bentonites are essentially montmorillonitic, with subordinate calcite, quartz, cristobalite, feldspars and muscovite. Three bentonite types were recognized: the first type includes bentonites mainly formed by montmorillonite, plagioclase and cristobalite; the second type includes bentonites composed exclusively of montmorillonite; the third type includes bentonites composed of montmorillonite and kaolinite. The volcanic source rocks are characterized by plagioclase with subordinate feldspar phenocrysts in a glass matrix. Petrographic study also allowed identification of marine organism fossils in the bentonite and in the conglomerates, suggesting a partly submarine depositional environment. The EDS chemical compositions of the clay minerals report discrete magnesium amounts and are comprised in the range montmorillonite-beidellite, with some exceptions related to anomalous Fe contents. As accessory phases it was possible to recognize Fe- and Mn-oxides, barite, hollandite, probably associated with late hydrothermal fluid circulation.

Preliminary data evidenced the complexity of the S’Aliderru bentonite deposit, which probably formed in a marine environment and was subsequently subjected to tectonics and hydrothermal alteration. The extraordinary thickness of the mineralized horizons makes S’Aliderru a crucial deposit to produce bentonite for a high number of technological applications of this material.
NMR investigation of the phosphorus mineralization affected by the calcite-water interfacial chemistry

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With the depletion of rock phosphate and increasing demand for P fertilization, alternative approaches like the mineralization of phytic acid, one of the predominant organic P species in many soils could be an important source to supply phosphate in soils. However, due to the active interaction between phytase and clay minerals, phytic acid and minerals, phytic acid mineralization is generally suppressed in soils. Clay minerals have been found to mostly inhibit phytase activity, yet the effects of calcite haven’t been studied. The objective of this study is therefore to investigate the influence of calcite on phytase activity and the mechanisms. The phytase kinetics followed the Michaelis-Menten kinetics model at pH6. Increased $K_m$ and decreased $V_{max}$ indicated that calcite acted as a mixed inhibitor. Although the overall phytase activity decreased at pH8, calcite was found to enhance the phytase activity.
The siliciclastic Cutler Group comprises predominantly red bed strata that accumulated across large regions of the Colorado Plateau. The proximal Cutler records Pennsylvanian uplift followed by Permian subsidence along the Uncompaghre Front and has a complex geologic and hydrologic history now reflected in a variegated pattern of red, green, drab, and bleached zones. The adjacent Paradox Basin to the southwest hosts hydrocarbons and salt diapirs, as well as uranium, vanadium and copper deposits near the Uncompahgre front, and is intruded by the Oligocene age La Sal laccolith. Permian Cutler strata onlap fractured and faulted Precambrian basement at the Uncompahgre Front, including a paleo-embayment proximally that leads towards a poorly constrained hydrologic system within Precambrian-hosted Unaweep Canyon. To better understand the origin and significance of color variegations in the proximal Cutler, we investigated the chemistry, mineralogy, and texture of their clay minerals and accessory phases. Field samples were categorized by their representative colors, and the clay fraction and accessory phases extracted for analysis, in addition to sending selected whole-rock samples for thin sections and chemistry. Analyses included x-ray diffraction (XRD) and scanning and transmission electron microscopy (SEM; S/TEM) with energy dispersive x-ray spectroscopy (EDX). Alteration of abundant biotite produced many authigenic clays, including smectite, chlorite, and mixed-layer chlorite/smectite. In contrast to previous models predicting Mg-clays, we found abundant Al-clays, including tosudite. Further, we integrate the clay morphology and chemistry with low temperature thermochronology, cathodoluminescence imaging, and geochronology of accessory phases (apatite, zircon, monazite) to constrain the temperature and relative timing of alteration in the system, enabling a more robust reconstruction of the formation history of the authigenic clay minerals. Our study contributes to the current interest in Permian climate of equatorial Pangea, the evolution of the regional fluid dynamics in the post-Permian Cutler system, and the potential for new uranium deposit occurrences of economic interest.
Clay Mineral Control on Organic Matter Distribution in Mudrocks from the Permian Basin, USA

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The preservation of organic matter (OM) within mudrocks can lead to commercially significant unconventional hydrocarbon reservoirs. Mechanisms that conserve OM generally involve clay mineral characteristics such as sorption, encapsulation by clay minerals, and/or intercalation as organo-mineral nanocomposites.

Samples were collected from Late Paleozoic mudrocks within the Midland Basin to determine clay mineralogy and organic matter types and geochemistry. Discrete illite and randomly to highly ordered illite-smectite and chlorite were documented while the abundances of total organic carbon (TOC) were up to 11 wt. %. An additional, subset of samples was separated into smaller grain size fractions (> 1 µm, >0.6 µm, and >0.2 µm) to examine clay mineralogy and organic matter contents through XRD, FTIR, and TOC analysis. From preliminary results, a decrease in grain size shows increased smectite components in all samples. This increase in smectite components also shows a relative increase in TOC wt.% with each additional decrease in grain size. All samples show an increase of TOC wt.% when compared to the >2 µm. FTIR measurements show similar trends with both relative increases in smectitic components and organic matter presence as grain size decreases. Understanding this general trend of increased TOC with increased smectitic components through decrease grain size, suggest most TOC resides below the >2 µm and that organo-clay composites may exist, and further investigation is needed.

In brief, we call for smectitic component to be the main agent controlling the distribution of the large portion of organic matter likely in the form of organo-clay complexes. As such these complexes may affect the dynamics of smectite to illite burial transformation as well as OM maturation which in turn ultimately influence the basin modelling interpretations.
Effect of $\gamma$-irradiation on the redox state of the structural iron in Montmorillonite

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Radiolysis of the clay pore water in nuclear waste repositories involving clay barriers is unavoidable due to the ionizing radiation from the canisters holding the nuclear waste. Iron is the major redox-active element in most planned clay buffers, and hence the structural Fe(II)/Fe$_{Tot}$ ratio and the overall redox conditions of the clay or solutes adjacent the waste canisters may change due to transient oxidizing and reducing species formed by radiolysis. This research is focused on the effects of $\gamma$-radiation on the structural Fe(II)/Fe$_{Tot}$ from dilute montmorillonite suspensions as well as saturated compacted montmorillonite under different oxic/anoxic conditions.

Ionizing radiation can cause several different effects in clay minerals and their surrounding chemical environment [1]. In the Swedish KBS-3 repository, the Bentonite clay barrier will be exposed to 40-200kGy of ionizing radiation (mainly $\gamma$-radiation from $^{137}$Cs, $t_{1/2}$ ~30y), where approx. 50% of the emitted $\gamma$-radiation energy would be deposited in the first 4 cm adjacent the copper canister holding the spent nuclear fuel. Interestingly, and often overlooked, this dose can be comparable to the dose acquired in typical XANES/EXAFS investigations used to characterize the structural Fe in clay minerals, which may explain the discrepancy between reports from synchrotron and traditional wet-chemistry methods about structural Fe(II)/Fe(III) ratios.

Experiments with dilute clay suspensions revealed that exposure to $\gamma$-radiation can  

i) enhance the colloidal stability of montmorillonite suspensions [2],  

ii) alter the sorption capacity for certain radionuclides [3,4], as well as change the  

iii) radio-chemically reduce montmorillonite, causing an increase in the structural Fe(II)/Fe$_{Tot}$ from $\leq$3% to 25-30% [5]. From saturated and compacted montmorillonite similar Fe(II)/Fe$_{Tot}$ ratios were also found, albeit with higher experimental uncertainty, possibly demonstrating the effect of present oxygen on the structural Fe(II)-Fe(III) redox state.

Atomistic simulations of smectite interlayer entry of anions and the relevance for nuclear waste applications

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This research used atomistic molecular dynamics (MD) simulations to study anion- and size exclusion of different common anions (halides, sulfur- and (bi)carbonate anions), and repository groundwater relevant carbonate- and hydroxyl uranyl complexes in smectite interlayer nanopores. This is accomplished by computing the free energy penalty associated with solute diffusion across the clay particle mesopore-nanopores, at different hydration states of smectite clay particles.

The study is motivated by the fact that smectite-rich Bentonite clay barriers and argillaceous clay-rocks are currently being evaluated as transport barriers in different concepts for geologic disposal of high-level nuclear waste in many countries. Several prior studies have recognized that molecular scale properties obtained per MD simulations from smectite clay systems are sensitive to several types of model and methodological choices.

Using a range of halides (F-, Cl-, Br-, I-), this study scrutinizes prior results from MD simulation studies on “anion exclusion” effects of Cl- in the two- and three-layer hydrates of Na-smectites [1,2], using atomistic simulations with the MD package Gromacs and the Clayff forcefield and SPC/E water model [3,4]. Analogously, we further investigate the free energy penalty for several larger anions (HS-/SO4²-, HCO3-/CO3²-) and several Ca²+-carbonate uranyl complexes. This is because the complexity of the smectite clay microstructure renders the prediction of U adsorption and diffusion difficult. In the presence of water, CaCO₃(s) impurities are expected to lead to milli-molar concentrations of dissolved Ca²+ over a wide range of pH conditions. In addition, ternary U(VI)-Ca-carbonate solution species (CaUO₂(CO₃)₃²⁻ and Ca₂UO₂(CO₃)₃) will largely replace U(VI)-carbonate species (UO₂(CO₃)₃⁴⁻ and UO₂(CO₃)₂²⁻) at alkaline pH. These larger, but lower-charged U(VI) species, may show different sorption and diffusion characteristics, e.g. if their access to negatively-charged clay interlayer spaces is different from binary U(VI)-carbonate complexes.

Statistical method to understand the sediment provenance in the Amundsen Sea, West Antarctica

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Clay mineral assemblages, illite chemical index and crystallinity in marine sediments have been widely used to investigate sediment provenance and marine sedimentary environment. However, there is a limitation of using conventional method of using variations in mineralogy to understand sediment provenance from multi-sources. It is, therefore, inevitable to use clustering analysis to compromise the various controls that could affect the sediment properties linked to the multiple sources. This hypothesis was applied to the clay mineral assemblages, illite chemical index, and illite crystallinity of surface sediments from Amundsen Sea, previously well characterized by elemental composition of smectite for the glacial-interglacial periods. The advantage of the statistical approach for the interpretation of provenance changes in sediment supplied from multiple sources will be discussed.
Rapid Changes in the Diagenesis Degree of the Triassic Rocks as the Main Reason for Drilling Problems, an Example from the Polish Permian Basin

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The Polish Permian Basin, a part of the Southern Permian Basin in Western and Central Europe, is a main target for hydrocarbon exploration in Poland. Serious drilling problems related to hole instability occur in many wells in that region during the drilling through the Triassic strata, which is considered as an overburden of the hydrocarbon fields. The main issues include a tight hole, over-pull, caving, pack-off, stuck pipe, excessive torque, and drag. The significant washouts are visible in the interval of the Upper Triassic strata.

To identify the causes of the above-mentioned drilling problems, a detailed analysis of the mineralogy of the Triassic rocks was conducted. The chemostratigraphic and lithological profiles of the Triassic strata for two boreholes G-1 and P-5H were drawn up based on the pXRF and XRD measurements on the drill cuttings. Very similar quantities of clay minerals were found in both the Upper and Lower Triassic sediments. The reasons for the drilling problems remain unknown.

The answer brought the analysis of the paleothermical data, which allowed us to recognize the evident differences in the diagenesis degree between the individual Triassic horizons. The clearly visible, abrupt changes in the thermal maturity within the Triassic strata were recognized on the diagenetic profiles (based on the illite-smectite paleothermometer) constructed for five different boreholes: Objezierze IG-1, Września IG-1, Zakrzyń IG-1, Kalisz IG-1, and Marcinki IG-1. It was stated that in the boreholes Zakrzyń IG-1, Kalisz-IG1, and Marcinki-IG1 thermal maturity of the Upper Triassic rocks is much lower than for the Lower Triassic rocks. The content of the smectite swelling layers in illite-smectite remains respectively 10-20% for the Lower and Middle Triassic, and 50-64% for the Upper Triassic.

It seems that most of the drilling problems occurring in the Upper Triassic interval could be connected with a low degree of diagenesis of the rocks, which also translates into the big differences in the geomechanical properties of analyzed rocks. The reason for the observed diversity in the diagenetic maturity is most probably the drop of the paleothermal gradient in that region connected with declining volcanic activity at the beginning of the Triassic.
Illite is a ubiquitous clay mineral on the Earth with a great potential for various industries. Dongchang (DC) illite deposits associated with hydrothermal alteration of mica schist in Yeongdong (YD) area, South Korea is one of the biggest illite deposit. The estimated amount of illite in YD area is about a half billion tons of illite, which might be a good candidate of new potential source clay. Size fraction (bulk, >2 µm, 0.5-2 µm, 0.2-0.5 µm and <0.2 µm) for DC illite deposit has been performed to measure the mineral and chemical properties including illite crystallinity, packet size, and chemical composition by X-ray diffraction and transmission electron microscope-energy dispersive spectroscopy analysis. DC illite is composed of illite with minor contents of quartz for the bulk, and quartz disappeared for the less than 0.2 µm of size fraction. DC illite is 2M1 polytype of illite with high Al/Si ratio (0.6059) and K (1.15 wt%) contents contrast with Yongkoong (YK) illite, other illite deposit (2M1 or 1M, Al/Si = 0.5327, K content = 0.71 wt%) in YD area, suggesting variation in the hydrothermal alteration for two illite deposits. In addition, illite size analysis, estimation of impurity in illite for various size fractions using Fourier-transform infrared spectroscopy (FTIR) will be measured to characterize the DC illite.
The effect of synthesis conditions on formation and properties of kaolinite-based nanotubes

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Kaolinite with its simple 1:1 layered structure was regarded as a non-swelling mineral. Currently the knowledge on its intercalation and grafting chemistry has greatly expanded. The appropriate kaolinite tuning allows to obtain halloysite-like nanotubes [1]. The nanoscrolls attract much attention due to several potential applications e.g.: selective adsorption, (photo)catalysis and drug delivery. Therefore, in this study selected factors affecting nanotubes formation were investigated.

For the synthesis a kaolinite-rich sample from Maria III deposit (Poland) was selected (M). The synthesis involved two steps: (i) DMSO intercalation (MDS) and (ii) simultaneous formation of methoxy-kaolinite and HDTMA-Br intercalation. In particular we have focused on optimization of the (ii) step with the help of XRD, FTIR, SEM/TEM and N2 adsorption/desorption methods.

The methoxy-kaolinite synthesis is necessary for HDTMA intercalation (d$_{001}$ ~45 Å) which subsequently leads to nanoscrolls formation. The results indicated that 1.0 M/L AlCl$_3$ catalyst is crucial for fast synthesis (30 min) of methoxy-kaolinite in agreement with earlier report [2]. Lower AlCl$_3$ concentration (0.1 and 0.5 M/L) is not sufficient. The AlCl$_3$ enables simultaneous HDTMA intercalation (1.0 M/L methanol solution). Again, at lower HDTMA concentration (0.1 and 0.5 M/L) the intercalation is less efficient. The most effective route for nanotubes production is via direct MDS reaction with 1.0 M AlCl$_3$/1.0 M HDTMA for a 1-20 g/100 ml suspension density at room temperature. Methanol washing involving ultrasonification is necessary to remove excess substrates. The repeated intercalation as well as calcination (600°C, 3 h) do not lead to significant changes of the materials’ S$_{BET}$ (~65-75 m$^2$/g) and pore size distribution. The 15-40 nm mesopores dominate and correspond to internal diameter of nanotubes observed by SEM/TEM.

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Preparations, characterization and use of a Chitosan-clay biocomposite in glyphosate removal

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In recent years, the dependence of the agricultural sector on herbicides has been an environmental and public health issue with a difficult solution. Due to population growth and the need to produce more and more food products, herbicide use has been found to be the fastest and cheapest solution.

Glyphosate is an herbicide that is worldly used in agriculture to destroy plants. It can contaminate water sources through runoff from fields where it is used, leaching into groundwater, or accidental spills. When present in water at high levels, glyphosate can be harmful to human health. [1]

The International Agency for Research on Cancer classified glyphosate as a "probable human carcinogen, as well as negative effects on the reproductive and developmental systems. [2]

It is important to monitor levels of glyphosate in water and take steps to reduce contamination, one of the best materials use it to adsorb and remove this contamination is clay materials, it has the ability to adsorb various molecules and ions, which makes it useful in various fields such as water treatment, agriculture and environmental remediation.

This study aimed to preparation of an eco-friendly material with minimal toxicity, biocompatibility, biodegradability, and high availability in nature, for this we synthesize a biocomposite (Chitosan-clay), for a removal of glyphosate from water.

To understand the mechanism of adsorption the composite material was characterized by: FTIR, XRD and \( \text{pH}_{\text{PZC}} \).

The optimization of adsorption parameter was also evaluated under various experimental conditions: the effect of pH, contact time, the mass of adsorbent temperature and concentration. The results showed that the material developed during this work has proven its effectiveness, it can be used in the elimination of glyphosate from water.

Sorano (Tuscany - Italy) zeolitized tuffs mining waste, a resource for countless technological applications: preliminary results

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As is now widely known, any industrial activity produces waste and they represent a logistic and environmental problem since they require precise regulations and treatments for disposal/storage. Anyway, materials deriving from these wastes can be regarded as by-products for different technological applications. Waste from mining operations, although they may be in some way, contaminated by the processing itself or by the wear and tear of industrial tools, retain all the mineralogical and compositional characteristics of the original material. For this reason, a waste from Sorano (Tuscany - Italy) zeolitized tuffs mining operation (figure 1) with a high zeolite content (Cappelletti et al. 1999) can be seen as a by-product useful for industrial applications in a variety of sectors.

This research presents preliminary results of the characterization of this waste, propaedeutic for its re-use in several technological applications: lightweight aggregate production (de Gennaro et al 2009), flux for ceramic tile manufacturing (de Gennaro et al 2007), pharmaceutical carrier (Mercurio et al 2018), pozzolanic addition in cement (Montesano et al 2022). Experimental research, started from waste characterization, was performed by using techniques accrued in the above-mentioned experiences and then describing the obtained products according to European Uni Standards recommendations. The experimental procedures, used in this research with Sorano zeolitized tuff waste, can be safely extended to other similar materials, representing a circular alternative to landfill-disposal.

Figure 1 - Zeolitized tuff quarry in Sorano (a) and waste produced by block cutting operations (b)
Cappelletti et al. 1999 - Mineralogical and technical features of zeolite deposits from northern Latium - Per. Mineral., 68, 2, 127-144


Mercurio et al. 2018 - Surface-modified phillipsite-rich tuff from the Campania region (southern Italy) as a promising drug carrier: An ibuprofen sodium salt trial - American Mineralogist, 103, 700–710.

Montesano et al. 2022 - Mineralogical and Technological Characterization of Zeolites from Basin and Range as Pozzolanic Addition of Cement – Materials 2022, 15, 2684
Swelling pressure of a compacted Ca-bentonite with different pore fluid

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Compacted clay is being considered as a potential material for the construction of engineered barrier systems (EBS) and seals in the context of deep geological disposals envisaged for the isolation of high-level nuclear waste (HLW) and spent nuclear fuel (SNF). Such a facility contemplates placing the HLW/SNF encapsulated in a metallic container in horizontal drifts or vertical boreholes excavated in deep and good-quality rocks (i.e., the natural barrier). The EBS will be subjected to complex multiphysics processes triggered by the heat released by the HLW/SNF, the hydration of the clay (triggered by the water coming from surrounding rock), and increments in stresses induced by the progressive wetting and swelling of the compacted bentonite under highly confined conditions.

Two main swelling mechanisms control the expansion of compacted clays, namely, crystalline swelling, and osmotic (or double layer) swelling. Crystalline swelling of smectite is driven by adsorption of water molecules in the interlayer of smectite that occurs at inter-layer separations of 10–22 Å, whereas diffuse double layer swelling occurs at inter-layer separations of 2.2 nm and greater [1].

This study focuses on the swelling pressure (SP) of a Ca-bentonite with different pore fluids. To gain a better understanding of this complex problem, the experimental study is combined with molecular dynamics (MD) simulations. The SP tests are conducted in a high-capacity swelling pressure cell that ensures confined conditions. The MD model systems correspond to dry densities of the Ca-smectites used in the experimental investigations. Models of bulk hydrated smectites and expanded interlayers correspond to the crystalline and osmotic, swelling regimes, respectively. The simulation methodology is based on recent studies to estimate the SP of clays combining MD simulations and electrical double layer theory [2].


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Molecular modeling to predict the optimal mineralogy of smectites as binders of aflatoxin

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Laboratory experiments have verified that smectites can adsorb aflatoxin B₁ (AfB₁) effectively and the efficiency of this process depends on the chemical, physical, and mineralogical characteristics of the smectites. Several relationships between these characteristics and AfB₁ sorption have been determined experimentally, but the molecular mechanisms underlying these were not investigated. In the current study the effects of charge density, type of exchange cation, and charge origin (octahedral vs. tetrahedral) on AfB₁ sorption on smectites were analyzed by a series of molecular simulations.

The calculations confirmed the formation of water bridges between carbonyl groups of AfB₁ molecules and interlayer cations. In all of the AfB₁–smectite complexes studied, substantial amounts of organic molecules tended to be lying flat on the clay surface. With larger amounts of adsorbed AfB₁ molecules in the structures and/or depending on water content, self-association of two AfB₁ molecules bound by π–π interaction and with each of the molecules lying flat on the clay surface was thermodynamically favorable.

The thermodynamics of AfB₁ sorption depends heavily on the water content in the structure, being optimal for basal distances corresponding to two layers of water, but the adsorbed AfB₁ molecules affected only slightly the thermodynamics of water adsorption. A clear preference for sorption of AfB₁ on smectites with bivalent cations (Ba²⁺, Ca²⁺) and an octahedral origin of its layer charge was confirmed and this was explained as steric hindrance between hydrated ions and AfB₁ molecules, which tend to lie flat on smectite surfaces devoid of ions. Ba-montmorillonite with a charge of 0.4 per half unit cell was shown to have the smallest and thus the best potential energy of adsorption compared to the other layer charges.
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The 61st Annual Meeting of The Clay Minerals Society and the 5th Asian Clay Conference
Location: Honolulu, Hawaii
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