CMS2020
Clays on the Columbia: Bridging Scales and Disciplines
57th Annual Meeting of the Clay Minerals Society
October 18–23, 2020
MEETING PROGRAM
www.clays.org
Thanks to Our Sponsors!

Platinum Sponsor

Environmental Molecular Sciences Division
Earth Systems Science Division
Earth and Biological Sciences Directorate
Physical and Computational Sciences Directorate
Center for Remediation of Complex Sites (RemPlex)

Silver Sponsors

Thiele Kaolin Company

International Center for Diffraction Data

The Virginia Tech National Center for Earth and Environmental Nanotechnology Infrastructure
Table of Contents

Table of Contents.......................................................................................................................... ii
MIXER AND PLENARY SESSIONS................................................................................................ 1
   Sunday, October 18, 2020 ................................................................................................ 1
   Monday, October 19, 2020 .............................................................................................. 1
   Tuesday, October 20, 2020 ............................................................................................. 1
   Wednesday, October 21, 2020 ....................................................................................... 1
   Thursday, October 22, 2020 ......................................................................................... 1
LOCAL ORGANIZING COMMITTEE ....................................................................................... 2
THE CLAY MINERALS SOCIETY ADMINISTRATION ......................................................... 2
   Executive Committee ............................................................................................ 2
   Council 2 .................................................................................................................. 2
PAST PRESIDENTS ..................................................................................................................... 3
SUSTAINING CONTRIBUTORS OF THE SOCIETY ................................................................. 3
SPONSORS OF THE CMS2020 INTERNATIONAL MEETING ................................................... 3
AWARDS ...................................................................................................................................... 4
   Marilyn and Sturges W. Bailey Award ......................................................................... 4
   Marion L. And Chrystie M. Jackson Mid-Career Clay Scientist Award ....................... 5
   George W. Brindley Lecture Award ............................................................................. 6
   Pioneer in Clay Science Lecture ................................................................................ 7
EDITORS OF CLAYS AND CLAY MINERALS ..................................................................... 8
GUIDELINES FOR THE CMS2020 VIRTUAL MEETING ..................................................... 9
CLAY MINERALS SOCIETY 2020 AWARDS AND LECTURES ............................................ 10
   Marilyn and Sturges W. Bailey Award Lecture ............................................................. 10
      Monday, October 19, 2020, 8:15 – 9:15 am ................................................................. 10
   Marion L. and Chrystie M. Jackson Mid-Career Clay Scientist Award Lecture .......... 11
      Tuesday, October 20, 2020, 8:15 – 9:15 am ................................................................. 11
   Pioneer in Clay Science Lecture ................................................................................ 12
      Thursday, October 22, 2020, 8:15 – 9:15 am ................................................................. 12
DESCRIPTION OF THE TECHNICAL SESSIONS ............................................................ 13
   Theme 1: Clays: Oil/Gas Interactions ......................................................................... 13
      Oil Sands Tailings Clay Challenge ........................................................................... 13
      Fundamental Shale Research at the DOE National Laboratories focusing on Fossil
      Energy (Department of Energy, Office of Fossil Energy) ........................................ 13
      Advancements in the Application and Characterization of Clay Minerals in
      Petroleum Industry Organizer: Hasmukh A. Patel (Aramco Services Company: Aramco
      Research Center – Houston, Texas, USA) ................................................................. 14
The Evolution of Micro- and Nanoporosity in Black Shales ........................................ 14
Theme II: Clays Role in Waste Affected Environments: Remediation and
Contaminant Fate and Transport .................................................................................. 14
Impacts of In Situ Remediation and Waste Disposal on Local Mineralogy .............. 14
Role of Minerals in Concentrating Radionuclides at the Molecular and
Landscape Scales ........................................................................................................ 15
Advances in Understanding Clay-Based Barrier System for Deep
Geological Repositories ............................................................................................. 15
Colloid Mobilization and Colloid-Facilitated Contaminant Transport in the
Subsurface .................................................................................................................. 16
Clays and Layered Double Hydroxides in Extreme Environments – An
IDREAM EFRC Session ............................................................................................ 16
Redox Reactions of Clays and Clay Minerals in Natural and Engineered
Systems ....................................................................................................................... 16
Theme III: Clay Water Interfacial Structure and Interactions................................. 17
Visualizing Solution Structure at the Mineral Aqueous Interface ............................... 17
Mineral Clay Nucleation, Crystallization, and Aggregation ..................................... 17
Clay Swelling and Aggregation: Modeling and experiments .................................... 18
Nanomechanical Properties of Layered Materials: Towards hierarchical
theories of bulk properties .................................................................................. 18
Advances in Probing the Clay/Clay Mineral-Water Interface ..................................... 18
Experimental and Computational Advances for Studying the Structure
and Reactivity of Nanoscale Metal Oxides in Geochemical
Environments ........................................................................................................... 19
Theme IV: Clays and Climate Change ....................................................................... 19
Impact of Clays on the Earth’s Climate ..................................................................... 19
Stability of Mineral-Organic Matter Interactions under Varying
Biogeochemical Conditions ...................................................................................... 19
Theme V: Special Topics and General Session ........................................................... 20
Clays and Rare-Earth Elements Cycling ....................................................................... 20
Quantitative Analysis of Clay-Bearing Samples: Putting numbers on clay
mineral analyses, approaches, and applications across ocean, earth, and extra-terrestrial sciences ................................................................. 20
Incipient Weathering of Primary Minerals to Clay Minerals: Biological and
physical factors ........................................................................................................... 21
Aqueous Processes in the Solar System: Evidence from phyllosilicates ................. 21
Extraterrestrial Clays: Insight from Earth-based studies ............................................ 21
Clays for Antibacterial/Medicinal Applications ........................................................... 22
General Session .......................................................................................................... 22
WORKSHOPS ............................................................................................................... 22
CMS Workshop: Emerging Methods in Clay Science - Thursday 10/22 and Friday
10/23 ............................................................................................................................ 22
PNNL Workshop: A Hanford Perspective on Environmental Remediation - Wednesday, October 21 ................................................................. 23
ICDD Workshop: X-ray Diffraction Applications: JADE Software - Friday, October 23 ........................................................................................................................ 23
ABBREVIATIONS OF THE THEMES AND SESSIONS OF THE MEETING .............................................................................................................. 24
PROGRAM AT A GLANCE .................................................................................................................................................................................. 25
THE TECHNICAL SESSIONS MEETING PROGRAM ........................................................................................................................................... 27

Monday, October 19, 2020 Morning Sessions ........................................................................................................... 27
Theme II, Session 6 [Zoom Room 1] ........................................................................................................ 27
Theme III, Session 2 [Zoom Room 2] ........................................................................................................ 28
Theme III, Session 5 [Zoom Room 3] ........................................................................................................ 29
Theme IV, Session 2 [Zoom Room 4] ........................................................................................................ 30
Theme V, Session 4 [Zoom Room 5] ........................................................................................................ 31

Monday, October 19, 2020 Afternoon Sessions ....................................................................................................... 32
Theme II, Session 5 [Zoom Room 1] ........................................................................................................ 32
Theme III, Session 2 [Zoom Room 2] ........................................................................................................ 33
Theme V, Session 7 [Zoom Room 2] ........................................................................................................ 33
Theme III, Session 6 [Zoom Room 3] ........................................................................................................ 34
Theme IV, Session 2 [Zoom Room 4] ........................................................................................................ 35
Theme V, Session 5 [Zoom Room 5] ........................................................................................................ 36

Tuesday, October 20, 2020 Morning Sessions ........................................................................................................ 37
Theme I, Session 2 [Zoom Room 1] ........................................................................................................ 37
Theme II, Session 6 [Zoom Room 2] ........................................................................................................ 38
Theme II, Session 1 [Zoom Room 3] ........................................................................................................ 39
Theme III, Session 3 [Zoom Room 4] ........................................................................................................ 40
Theme V, Session 1 [Zoom Room 5] ........................................................................................................ 40

Tuesday, October 20, 2020 Afternoon Sessions ........................................................................................................ 41
Theme I, Session 3 [Zoom Room 1] ........................................................................................................ 41
Theme II, Session 4 [Zoom Room 2] ........................................................................................................ 42
Theme II, Session 2 [Zoom Room 3] ........................................................................................................ 43
Theme III, Session 3 [Zoom Room 4] ........................................................................................................ 44
Theme V, Session 7 [Zoom Room 4] ........................................................................................................ 45
Theme V, Session 6 [Zoom Room 5] ........................................................................................................ 46

Wednesday, October 21, 2020 ................................................................................................................................. 47
Plenary Morning Session ................................................................................................................................. 47

Wednesday, October 21, 2020 Morning and Afternoon Session ......................................................................................... 48
Workshop and Panel Discussion ......................................................................................................................... 48

Thursday, October 22, 2020 Morning Sessions ........................................................................................................... 49
Theme II, Session 3 [Zoom Room 1] ........................................................................................................ 49
Theme III, Session 1 [Zoom Room 2] ................................................................. 50
Theme III, Session 4 [Zoom Room 3] ................................................................. 50
Theme IV, Session 1 [Zoom Room 4] ................................................................. 51
Theme V, Session 2 [Zoom Room 5] ................................................................. 52
Theme V, Session 3 [Zoom Room 5] ................................................................. 52
Thursday, October 22, 2020 Afternoon Sessions ........................................ 53
  Theme I, Session 1 [Zoom Room 1] ................................................................. 53
  Theme III, Session 1 [Zoom Room 2] ............................................................. 53
  Theme I, Session 4 [Zoom Room 4] ................................................................. 53
Thursday, October 22, 2020 Afternoon Sessions ........................................ 54
  CMS Workshop .............................................................................................. 54
Friday, October 23, 2020 Morning Sessions .................................................. 55
  CMS Workshop .............................................................................................. 55
  ICDD Workshop .............................................................................................. 55
Friday, October 23, 2020 Afternoon Session .................................................. 56
  Virtual Geology Field Trip ............................................................................... 56
ABSTRACTS (IN ALPHABETICAL ORDER BY FIRST AUTHOR) ......................... 57
MIXER AND PLENARY SESSIONS

Sunday, October 18, 2020

13:00-15:00  Virtual welcoming session and mixer

Monday, October 19, 2020

Plenary Session 7:30 – 8:15 am (USA Pacific Time: UTC -8)

Welcoming message and a summary of the meeting program. Dr. Nikolla P. Qafoku, General Chair, 57th Annual Meeting of the Clay Minerals Society

Welcoming message. Dr. Steve Ashby, Director, Pacific Northwest National Laboratory

Guidelines for the virtual meeting. Dr. James E. Amonette, Deputy General Chair, 57th Annual Meeting of the Clay Minerals Society

Tuesday, October 20, 2020

Plenary Session 7:30 – 8:15 am

Guidelines for the virtual meeting. Drs. Nikolla P. Qafoku and James E. Amonette

Clay Mineral Society presidential address. Prof. Bruno Lanson, 2020 CMS President

Wednesday, October 21, 2020

Plenary Morning Session 7:30 – 9:30 am

The Clay Minerals Society reception and award presentations

Reynolds Cup award winners

Clay Minerals Society business meeting

Thursday, October 22, 2020

Plenary Session 7:30 – 8:15 am

Guidelines for the virtual meeting. Drs. Nikolla P. Qafoku and James E. Amonette
LOCAL ORGANIZING COMMITTEE

General Chair: Nik Qafoku  
Deputy Chair: Jim Amonette  
Website and Meeting Coordinator: Blake Wright  
Information Technology Support: Sarah Heilman  
Workshop Organizers: Eugene Ilton, Ravi Kukkadapu  
Virtual Fieldtrip Organizer: Bruce Bjornstad  
Technical Program: Nik Qafoku, Jim Amonette, Hilary Emerson, Kirsten Hofmockel, Eugene Ilton, Ravi Kukkadapu, Carolyn Pearce, Quin Miller, Katherine Muller, Todd Schaeff, Fred Zhang

THE CLAY MINERALS SOCIETY ADMINISTRATION

3635 Concorde Pkwy, Suite 500  
Chantilly, VA 20151-1110, USA  
Mary Gray, Manager

Executive Committee
President: Bruno Lanson  
Vice President: Jeffrey A. Greathouse  
Past President: Andrey G. Kalinichev  
Vice President Elect: Stephen Hillier  
Secretary: Warren Huff  
Treasurer: Paul A. Schroeder  
Editor-in-Chief: Joseph W. Stucki

Council
Janice Bishop ‘21  
Anke Neumann ‘21  
Nikolla Qafoku ‘21  
Erwan Paineau ‘21  
Heather Kaminsky ‘22  
Sang Soo Lee ‘22  
Quin R. S. Miller ‘22  
Rebecca Stokes ‘22  
Christopher Greenwell ‘23  
Toshihiro Kogure ‘23  
Tanya Peretyazhko ‘23  
Patrick Sellin ‘23
PAST PRESIDENTS

Chairs of the Interdivisional Committee on Clay Minerals of the National Academy of Sciences—National Research Council
1952–1956 Ralph E. Grim
1957–1959 Walter D. Keller
1960–1962 A. F. Frederickson
1963 Richards A. Rowland

Presidents
1963–1964 Richards A. Rowland
1964–1965 James W. Earley
1965–1966 Haydn H. Murray
1966–1967 Marion L. Jackson
1967–1968 Charles E. Weaver
1968–1969 Paul G. Nahin
1969–1970 George W. Brindley, Katherine Mathes
1971–1972 Sturges W. Bailey
1974–1975 John C. Hathaway
1975–1976 Stanley B. McCaleb
1977–1978 John B. Hayes
1978–1979 Max M. Mortland
1979–1980 Finis Turner
1983–1984 Wayne Hower
1984–1985 Wayne M. Bundy
1985–1986 Marion G. Reed
1986–1987 Sam H. Patterson
1987–1988 Necip Guven
1989–1990 Brij L. Sawhney
1993–1994 Dennis D. Eberl
1996–1997 Stephen Guggenheim
1998–1999 David L. Bish
1999–2000 Patricia M. Costanzo
2000–2001 Darrell G. Schultze
2001–2002 Blair F. Jones
2002–2003 Jessica Elzea Kogel
2003–2004 Kathryn L. Nagy
2004–2005 Duane M. Moore
2005–2006 Cliff T. Johnston
2006–2007 Richard K. Brown
2008–2009 Andrew R. Thomas
2009–2010 Derek C. Bain
2010–2011 Paul A. Schroeder
2011–2012 David A. Laird
2012–2013 Peter Komadel
2013–2014 Michael A. Velbel
2014–2015 W. Crawford Elliott
2015–2016 Prakash B. Malla
2016–2017 Jan Srodon
2017–2018 Douglas K. McCarty
2018–2019 Lynda B. Williams
2019–2020 Andrey G. Kalinichev

SUSTAINING CONTRIBUTORS OF THE SOCIETY

John D. Bloch
Richard K. Brown
Randall T. Cygan
Michael Charles Dix

Dennis D. Eberl
Stephen Guggenheim
Marc A. Herpfer
Lynda B. Williams

Paul A. Schroeder
Michael A. Velbel

SPONSORS OF THE CMS2020 INTERNATIONAL MEETING

Pacific Northwest National Laboratory
- Environmental Molecular Sciences Division
- Earth Systems Science Division
- Earth and Biological Sciences Directorate
- Energy and Environment Directorate
- Physical and Computational Sciences Directorate
- Center for Remediation of Complex Sites (RemPlex)

Thiele Kaolin Company

International Centre for Diffraction Data

The Virginia Tech National Center for Earth and Environmental Nanotechnology Infrastructure
AWARDS

Marilyn and Sturges W. Bailey Award

The Marilyn and Sturges W. Bailey Award, the highest honor of The Clay Minerals Society, is awarded solely for scientific eminence in clay mineralogy (in its broadest sense) as evidenced by the publication of outstanding original scientific research and by the impact of this research on the clay sciences. This award replaces the Society’s Distinguished Member Award and is not restricted to members of the Society.

Distinguished Members
1968 Ralph E. Grim
1969 Clarence S. Ross
1970 Paul F. Kerr
1971 Walter D. Keller
1972 George W. Brindley
1975 Sturges W. Bailey
1975 William F. Bradley
1975 José J. Fripiat
1977 Marion 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 William D. Johns
1996 Victor A. Drits
1997 Udo Schwertmann
1998 Brij L. Sawhney

Bailey Awardees
2000 Boris Zvyagin
2001 Keith Norrish
2002 Gerhard Lagaly
2004 Benny K. G. Theng
2005 M. Jeff Wilson
2006 Frederick J. Wicksvi
2008 Norber Clauer
2009 Joseph W. Stucki
2010 José M. Serratosa
2011 Sridhar Komarneni
2012 Akahiko Yamagishi
2013 Stephen Guggenheim
2015 R. James Kirkpatrick
2016 Lisa Heller-Kallai
2018 Gordon “Jock” Churchman
2019 Dennis “Denny” Eberl
Marion L. And Chrystie M. Jackson Mid-Career Clay Scientist Award

The Marion L. and Chrystie M. Jackson Mid-Career Clay Scientist Award recognizes a mid-career scientist for excellence in the contribution of new knowledge to clay minerals science through original and scholarly research. The honoree must be within the ages of 39 and 60.

Jackson Awardees
1992 Joseph W. Stucki
1993 Jan S´rodon´
1994 Stephen Guggenheim
1995 David L. Bish
1996 Darrell G. Schulze
1997 Jerry M. Bigham
1998 Murray McBride
1999 Stephen Boyd
2000 Jillian Banfield
2001 Cliff T. Johnston
2002 Sridhar Komarneni
2003 Peter Komadel
2004 Fred J. Longstaffe
2005 Samuel J. Traina
2006 J. Theo Kloprogge
2007 Paul A. Schroeder
2008 Hailiang Dong
2009 Lynda B. Williams
2010 Toshihiro Kogure
2011 Douglas K. McCarty
2012 Jeffrey E. Post
2013 George E. Christidis
2014 Will P. Gates
2015 Balwant Singh
2016 Janice L. Bishop
2018 Stephen J. Hillier
2019 Colleen M. Hansel
George W. Brindley Lecture Award

The George W. Brindley Lecture Award recognizes an outstanding clay scientist, someone who is both a dynamic speaker and involved in innovative research, and charges the recipient to deliver a lecture that will infuse The Clay Minerals Society with new ideas. The speaker is challenged to deliver a lecture that Brindley himself would applaud.

Brindley Lecturers
1984 Walter D. Keller
1985 José J. Fripiat
1986 Ralph E. Grim
1987 Sturges W. Bailey
1988 Marion L. Jackson
1989 William D. Johns
1990 Alain Baronnet
1991 Thomas J. Pinnavaia
1992 Philip F. Low
1993 Dennis D. Eberl
1995 Gerhard Lagaly
1996 Samuel M. Savin
1997 Paul H. Nadeau
1998 Bruce Velde
1999 Richard Eggleton
2000 Duane M. Moore
2001 Robert Schoonheydt
2002 David L. Bish
2003 Alain Manceau
2005 Maria F. Brigatti
2008 Robert J. Gilkes
2009 Michael F. Hochella, Jr.
2010 Randall T. Cygan
2013 Andrey G. Kalinicchev
2017 Sridhar Komarneni
2018 Cliff T. Johnston
2019 Bruno Lanson
Pioneer in Clay Science Lecture

The lecture award recognizes research contributions that have led to important new directions in clay mineral science and technology. The recipient is responsible for delivering a plenary lecture supporting symposia organized for the national meeting.

Pioneer in Clay Science Lecturers

1987 Marion L. Jackson  
1988 R. M. Barrer  
1989 H. van Olphen  
1990 John W. Jordan  
1991 Charles E. Weaver  
1992 Udo Schwertmann  
1993 Linus Pauling  
1994 Joe L. White  
1995 Rustum Roy  
1996 Max M. Mortland  
1997 Koji Wada  
1998 Robert C. Reynolds  
1999 V. Colin Farmer  
2000 William F. Moll  
2001 Don Scafe  
2002 Victor Drits  
2003 Vernon J. Hurst  
2004 Hideomi Kodama  
2005 Jillian Banfield  
2006 Jean-Maurice Cases  
2007 Spencer G. Lucas  
2008 Emilio Galan  
2009 Haydn H. Murray  
2011 Glenn A. Waychunas  
2013 Thomas J. Pinnavaia  
2014 Douglas W. Ming  
2015 Reinhard Kleeberg  
2016 Donald L. Sparks  
2017 Fred J. Longstaffe  
2018 Jan Środoń  
2019 Laurent J. Michot

Citation of Special Recognition

1984 Richards A. Rowland  
1984 Ada Swineford  
1991 Frederick A. Mumpton  
1994 Kenneth M. Towe  
1996 Don Scafe  
2003 William D. Johns  
2013 Haydn H. Murray  
2014 Warren D. Huff  
2015 Stephen J. Hillier  
2016 J. Reed Glasmann  
2018 Duane M. Moore  
2019 Bruno Lanson
<table>
<thead>
<tr>
<th>Year</th>
<th>Editors</th>
</tr>
</thead>
<tbody>
<tr>
<td>1952</td>
<td>J. A. Pash and M. D. Turner</td>
</tr>
<tr>
<td>1953</td>
<td>Ada Swineford and Norman Plummer</td>
</tr>
<tr>
<td>1954</td>
<td>W. O. Milligan</td>
</tr>
<tr>
<td>1955-1961</td>
<td>Ada Swineford</td>
</tr>
<tr>
<td>1962-1964</td>
<td>William F. Bradley</td>
</tr>
<tr>
<td>1964-1969</td>
<td>Sturges W. Bailey</td>
</tr>
<tr>
<td>1970-1972</td>
<td>Max M. Mortland</td>
</tr>
<tr>
<td>1975–1978</td>
<td>Richards A. Rowland</td>
</tr>
<tr>
<td>1979–1990</td>
<td>Frederick A. Mumpton</td>
</tr>
<tr>
<td>1999–2000</td>
<td>Stephen Guggenheim</td>
</tr>
<tr>
<td>2000–2007</td>
<td>Derek C. Bain</td>
</tr>
<tr>
<td>2008–Present</td>
<td>Joseph W. Stucki</td>
</tr>
</tbody>
</table>
GUIDELINES FOR THE CMS2020 VIRTUAL MEETING

The format of the sessions will be live presentation via Zoom followed by Q&A. Presenters may also choose to submit a prerecorded presentation that will be deleted after the session. This will allow for real-time interactions via the chat windows, along with a 5–10 minute discussion at the end of the session. Presenters will broadcast their slides by sharing their screen in PowerPoint or PDF presentation mode.

Attendees are strongly encouraged to test their slideshows, screen sharing, and audio prior to their presentation by joining 30 minutes prior to the start of their session. We recommend testing with the exact peripheral and external monitor configuration that will be used during the presentation.

Zoom Etiquette and Logistics

1. Each session will use one of the five Zoom Rooms. For transparency and to facilitate networking, list your full name, affiliation, and email when you log into Zoom. A strength of the virtual meeting format is that it de-anonymizes the room, increasing transparency and accessibility of the participants and session chairs.

2. Attendees are encouraged to reach out to presenters, session chairs, and other attendees via email during and after the conference. This new frontier of interacting at virtual conferences requires both a boldness in initiating networking and an openness to new correspondence.

3. Attendees and session chairs will keep their webcams turned off and microphones muted during presentations.

4. Do not record any of the presentations or capture screenshots, as some presenters may have unpublished results and/or do not want to be recorded without their consent.

5. During the presentation, use the chat box to ask brief questions. Presenters will not be monitoring the chat during their presentation. At the end of the presentation, the session chairs will ask the questions, with further clarification from the attendee if required. After the question and discussion time is complete, the presenter may use the chat window to reply to other questions and go into more detail if required. This format will encourage an ongoing dialogue via text and audiovisual that spans the sessions, including short breaks.

6. Participants are also encouraged to use “hand clap” and other emoji reactions to encourage and thank the speakers.

Poster Presentations

After the oral presentations are complete, there will be time allotted for poster presentations. These short presentations will be 5–7 minutes and then the Q&A will continue in breakout sessions, one for each poster. This venue will be used to highlight session presentations or standalone posters for the wider CMS audience. At the end of the poster presentations, each poster presenter will be allotted a breakout room so others may join and continue the discussions, simulating a poster hall.
CLAY MINERALS SOCIETY 2020 AWARDS AND LECTURES

Marilyn and Sturges W. Bailey Award Lecture

Monday, October 19, 2020, 8:15 – 9:15 am

CLAY-BASED BIONANOCOMPOSITES FOR HEALTH AND ENVIRONMENTAL APPLICATIONS

Prof. Eduardo Ruiz-Hitzky
Materials Science Institute of Madrid, CSIC, c/ Sor Juana Inés de la Cruz 3, E-28049 Madrid, Spain

It is widely known the ability of clay minerals to interact at the nanometric scale with organic matter coming from living beings, resulting in highly functionalized hybrid materials whose properties derive from the synergy between the two types of components, acting in certain cases as bioinspired or biomimetic systems. When the organic component is a biopolymer, the products of these assemblies were called bionanocomposites (1) because of their relationship with the well-known polymer-clay nanocomposites, though in the present case comprising a component of biological origin (2). Smectites are commonly employed to produce bionanocomposites though other types of clays, such as vermiculite, halloysite, and especially fibrous clays (sepiolite and palygorskite), can be also advantageous nanofillers for the production of those biohybrid materials. This lecture aims to introduce recent contributions on that topic developed by our research group at the ICMM-CSIC, highlighting the wide diversity of materials that can be prepared for application in the fields of Sustainability, Biomedical Engineering and Healthcare. Examples range from the removal of water pollutants to virus-clay systems for more efficient vaccines, incorporating polysaccharides, proteins and nucleic acids (3,4). More recently, nanocellulose-clay bionanocomposites including sepiolite and palygorskite leads to hetero-nanofibrous hybrid films named as hybrid nanopaper (5). Clay-based bionanocomposites come along as a trending topic that incorporates the abovementioned sustainable, ecofriendly and low-cost components. It should be expected it grows-up rapidly by producing materials with complementary functionalities, such as electrical conductivity, magnetic response, or specific bioactivity. These characteristics may deserve improving applications, e.g. in the removal of toxic pollutants (heavy and radioactive metals, dyes, pharmaceuticals, dioxins, polyaromatic molecules, etc) and microplastics in marine environment, carriers and adjuvants of drugs and vaccines, respectively, as well as tissue engineering (bioactive dental materials, bone replacements, etc.) or clinical bandages, among others.

Iron (Fe) bearing oxide, sulfide, and silicate minerals are important components of natural soils, sediments, and aquifers, i.e. the subsurface realm of the critical zone. Such phases engage in redox reactions with inorganic and organic compounds that impact a wide variety of geological and environmental process, such as sediment diagenesis, chemical weathering, and the mobility and fate of organic and inorganic contaminants. Because Fe-bearing minerals are typically highly insoluble in circumneutral pH, near-surface environments, their redox transformation takes place by way of chemical reactions at the mineral-water interface. Microorganisms can contribute in a dramatic way to both reductive and oxidative transformations of solid-phase Fe-bearing minerals, through mechanisms referred to collectively as “extracellular electron transfer” (EET) that take place external to the cell surface. Reductive EET pathways have been studied extensively in the context of microorganisms that couple heterotrophic metabolism to dissimilatory reduction of Fe(III)-oxide and Fe(III)-phyllosilicate minerals. Less is known about oxidative EET metabolism, particularly in relation to weathering of insoluble Fe(II)-bearing sulfide and silicate phases. This presentation will summarize (1) previous and ongoing experimental information on kinetic and thermodynamic controls on the microbial reduction of Fe(III)-oxides and Fe(III)-phyllosilicates; and (2) new experimental studies (combination of in situ geochemistry, microbiological experimentation, and genomic sequencing) that reveal previously unrecognized pathways whereby microorganisms may accelerate oxidative weathering of insoluble Fe(II)-bearing mineral phases.
Pioneer in Clay Science Lecture

Thursday, October 22, 2020, 8:15 – 9:15 am

ORGANIC-MINERAL INTERACTIONS AT THE MOLECULAR LEVEL: IMPACTS AND RESEARCH NEEDS

Prof. James D. Kubicki, Dept. of Geological Sciences, The University of Texas at El Paso (jdkubicki@utep.edu)

Interactions of natural organic matter with mineral and mineraloid surfaces are critical in the environment. Global processes such as C cycling and climate change are heavily impacted by this chemistry. Soil stability and quality depend upon bonding of organic compounds to inorganic substrates which is a major factor in agricultural productivity. Furthermore, the health impacts of mineral aerosols are functions of the surface chemistry of the inhaled particulate matter.

When considering C cycling and climate change, one needs to consider that soil organic matter and biota contain approximately four time the C as found in land plants globally. The loss of this organic matter and conversion to CO₂ adds to the atmospheric concentration, and more importantly, depletes soils of organic matter critical to water retention and soil health. Thus, as temperatures and droughts increase, many soils are simultaneously losing their resiliency to support plants in the new climatic conditions. The seminal paper of Torn et al. (1997) demonstrated that mineraloids in soils are particularly useful for slowing the organic C turnover rate, so understanding this organic-inorganic interface is imperative.

Another relationship to understanding climate change is the role that aerosols play in the Earth’s radiation balance and precipitation. Minerals with surficial layers of organic matter may have dramatically different optical properties with respect to reflecting and absorbing visible light and/or retaining IR radiation. Because aerosols act as cloud condensation nuclei, the surficial properties for water adsorption onto these particles are central to predicting precipitation patterns. Certainly whether a mineral is hydrophilic or hydrophobic will be affected by the presence of adsorbed organic matter. Given that aerosol effects and precipitation prediction are two of the largest uncertainties in current climate models, increasing our understanding and decreasing the uncertainties is desirable.

The human health impacts of aerosols is of increasing concern. Mineral dusts are a significant component of the overall global aerosol burden, especially in arid regions such as the U.S. Southwest, the Sahel, the Middle East and China. The direct impacts of particular matter on lung health have been studied for decades, but the role of organic coatings has not been a major focus. Additionally, new research is demonstrating indirect health impacts such as the role of Pb in obesity. Because ingested minerals can be a source of elements such as Pb, As and Hg, the organic coatings on these minerals may impact the bioavailability and risk associated with this environmental stressor.

This talk will discuss these issues and research employing spectroscopic methods combined with computational chemistry to determine the mechanisms organic compound adsorption onto several minerals. These results can be used to model rates of desorption/degradation as well as optical properties. Research needs for the coming decade will be addressed as we move to model and predict natural processes accounting for their complexity, varying spatial and temporal scales and wide variety of environmental factors.

DESCRIPTION OF THE TECHNICAL SESSIONS

Theme 1: Clays: Oil/Gas Interactions

Oil Sands Tailings Clay Challenge
Organizer: Heather Kaminsky (Centre for Oil Sands Sustainability, Edmonton, Canada)

Oil Sands tailings are a mixture of clay, sand, water and residual hydrocarbons. The clays in this mixture are characterized by a high degree of disorder, small particle sizes and a high degree of asymmetry. In addition, the clay surfaces are frequently covered to varying degrees with bitumen and bacterial residue. These characteristics make them form extremely stable suspensions and trap water. Dewatering the clay mixture beyond the liquid limit is difficult requires a change in the properties of the clays themselves. This challenge has contributed to the accumulation of more than 1.2 billion cubic meters of fluid tailings in the oil sands region. Canada’s Oil Sands Innovation Alliance (COSIA) is actively seeking solutions to help dewater these tailings and convert them to a trafficable, geotechnically and geochemically stable landscape. Although COSIA members are currently pursuing potential opportunities, there is value in looking to work with institutes with deep experience in clays or other materials of similar characteristics or behavior. The objective of this symposium is to provide more information about the problem and to identify, and potentially advance, more solutions.

In addition to a collection of invited speakers on this topic we welcome the relevant presentations on any of the following topics:

- Characterization of oil sands clays
- On-line characterization of clay slurries
- Methods for analysis of clay slurries that explain dewatering and transport characteristics
- Treatment technologies to modify behavior of clay suspensions and surfaces to reduce their water holding capacity
- Methods and models for understanding consolidation behavior of clay dominated slurries.

Fundamental Shale Research at the DOE National Laboratories focusing on Fossil Energy (Department of Energy, Office of Fossil Energy)

Organizers: Cristina Lopano and Dustin Crandall (NETL)

There are a number of uncertainties associated with the behavior of hydrocarbon producing shales, from how geomechanical alteration under engineered subsurface stresses impacts reservoir permeability to how geochemical interaction with drilling fluids changes the ability to effectively produce from fractured formations. The Department of Energy’s (DOE) Office of Fossil Energy has brought together resources across the DOE National Laboratory system to examine fundamental interactions that impact production from shales. A selection of recent discoveries and examinations in progress are presented in this session.
Advancements in the Application and Characterization of Clay Minerals in Petroleum Industry
Organizer: Hasmukh A. Patel (Aramco Services Company: Aramco Research Center – Houston, Texas, USA)
Co-organizer: Roland J.-M. Pellenq (Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139)

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.

The Evolution of Micro- and Nanoporosity in Black Shales
Organizers: Lawrence M. Anovitz (Oak Ridge National Laboratory), W. Crawford Elliot (Georgia State University), and R. Douglas Elmore (University of Oklahoma)

The availability of neutron and X-ray scattering techniques has stimulated a number of studies describing the occurrences, sizes and shapes of pores in shales. This session explores the relation between the presence and size distribution of micro- and nanoporosity in argillaceous rocks such as black shales, diagenetically formed illite in their clay fractions, and the extent of thermal maturation. An understanding of the fractions and size distributions of the various kinds of micro and nanoporosity in such rocks will lead to improved knowledge of their physical characteristics including permeability, the presence of microfractures, and the delineation of porosity forming mechanisms in shales.

Theme II: Clays Role in Waste Affected Environments: Remediation and Contaminant Fate and Transport

Impacts of In Situ Remediation and Waste Disposal on Local Mineralogy
Organizers: Hilary Emerson and Katherine Muller (Earth Systems Science Division, PNNL), Amy Hixon (University of Notre Dame), Ashleigh Kirstin Sockwell (Florida International University), Timothy Dittrich (Wayne State University), Lindsay Shuller-Nickles (Clemson University)

The focus of this session is on understanding of the changes in local mineralogy due to alterations induced by in situ remediation applications or waste disposal operations. This includes research on radionuclide incorporation into natural and synthesized mineral phases for long-term removal of contaminants from the biosphere. The alterations induced by unintended reactions with waste may have long-term physical and biogeochemical effects on the subsurface. Identification of the controlling processes and mechanisms may inform on the long-term impacts of historic releases as well as the potential challenges for impacts to future sites. Mineral transformations may include dissolution, precipitation, and sorption processes caused by biogeochemical changes as well as physical (e.g. porosity changes) alterations induced by remediation injections. For example, in situ remediation via injection of reactive gases like ammonia or hydrogen sulfide, secondary reactions from in situ degradation of cementitious waste forms. This may include both experimental and computational research ranging in spatial...
and temporal scale from atomistic scale modeling of interfacial reactions to field scale evaluation of natural analogue alteration.

Role of Minerals in Concentrating Radionuclides at the Molecular and Landscape Scales

Organizers: Daniel I. Kaplan (Savannah River National Laboratory); John C. Seaman (University of Georgia – Athens); Yuji Arai (University of Illinois at Urbana-Champaign)

Radionuclides entering the environment often concentrate in unpredicted hotspots. Such hotspots have been attributed to a growing number of hydrobiogeochemical gradients existing at scales ranging from molecular to landscape. For example, at the landscape scale, several radionuclides have been shown to concentrate in wetlands, estuaries, and vadose zone that have steep hydrological, biological, chemical, and mineralogic gradients. Similarly, radionuclides have been shown to concentrate in particle-depositional environments in low-energy reaches of a rivers (e.g., upgradient of dams) and where rivers mix with saline marine systems and at the interface of vadose zone sediments and aquifer. At a smaller scale, several radionuclides have been shown to concentrate in: the rhizosphere, root plaques, plants, and subsurface clayey facies created by microbial, organic matter, and/or hydrological gradients. Understanding hydrobiogeochemical gradients at the molecular scale has provided important insight for interpreting and predicting the occurrence of hotspots in nature. For example, groundwater radionuclides have been shown to reconcentrate in: the natural organic matter and iron-(oxy)hydroxide mineral coatings of mineral particles, wedge-sites in 2:1 clays, Ti-substituted oxides, and microbial extracellular polymeric substances and cell surfaces. Topics of interest in this session will include: 1) laboratory, field, or modeling examples of radionuclide hotspots in the landscape and molecular scales, 2) hydrological, biological, or geochemical processes responsible for the formation of non-uniform distribution of radionuclides in terrestrial, aquatic, and marine system, and 3) dynamic processes, including hydrological, redox, and speciation transformational, that influence radionuclide distributions.

Advances in Understanding Clay-Based Barrier System for Deep Geological Repositories

Organizers: Sarah Saslow, Mark Nutt and Matt Asmussen (PNNL), Carlos Jove-Colon (Sandia National Laboratory) and Stephan Kaufhold (BGR, Germany)

Clay minerals remain one of the favored natural barrier systems in the design of deep geological repositories for nuclear waste storage. Due to their low hydraulic conductivity, high sorption capacity, and homogeneity, clays effectively reduce the mobility of gas, water, and dissolved species and slow radionuclide transport into the biosphere over the course of the one-million-year life-cycle of the repository. Amongst all clay minerals, smectites are most interesting with respect to the barrier performance because of their swelling potential. The swelling of smectites in simple systems, e.g. under laboratory-controlled conditions, is more or less understood. The understanding of the effect of varying conditions (concentrated solutions, temperature, pressure) and of different relative arrangement of minerals in the clays (microstructure) on swelling and sealing, however, needs further research. This session is intended to bring together experts to (i) provide a deeper insight into parameters determining the barrier properties; (ii) discuss advancements in our understanding of radionuclide interactions with these clay barriers from the micro- to field-scale; and (iii) explore properties of candidate backfill materials from a range of repository designs to assess system commonalities and areas of development required to ensure sustainable performance in the repositories. Modeling, experimental, and up-scaling studies focused on interfacial interactions, physiochemical
processes, transport kinetics, mineralogical transformation, biogeochemical reactions, and other processes related to the performance of clay barriers are encouraged.

**Colloid Mobilization and Colloid-Facilitated Contaminant Transport in the Subsurface**

*Organizers: Fred Zhang (PNNL), Jianying Shang (China Agricultural University), Kenton Rod (PNNL)*

Many environmentally contaminants sorb strongly to subsurface minerals. Sometimes, these contaminants have migrated further than predicted. In some cases, colloids seem to have caused the unexpected high rates of contaminant migration. Groundwater studies have repeatedly shown colloid-facilitated contaminant transport. This session welcomes all the experimental studies and computer simulations on colloid mobilization, colloid-facilitated contaminant transport, the transport of colloid-sized artificial and natural particles, and relevant applications and field observation.

**Clays and Layered Double Hydroxides in Extreme Environments – An IDREAM EFRC Session**

*Organizer: Trent R. Graham and Carolyn Pearce (PNNL), Youjun Deng (Texas A&M)*

Clay-like hydrotalcite materials are commonly known as layered double hydroxides (LDHs). Widely used in ion separations, drug delivery, corrosion inhibition, chemical separations and catalysis, the variable composition of LDHs presents opportunities to tailor their material properties. Their structure is composed of brucite like, two-dimensional metal hydroxide layers. Univalent (Li+), divalent and/or trivalent elements can be arranged in the metal hydroxide layers. The layers are typically bound together by charge balancing, interlayer anions that are often hydrated. LDHs are extensively used for contaminant uptake. However, the mechanisms of intercalation remain incompletely characterized, particularly in extreme environments. In an exemplary case of complex caustic solutions, the phase transformation and stability of LDHs in representative high-level radioactive waste typical of Department of Energy Sites, such as the Hanford Site in WA, are not readily predictable. In this session, we welcome both experimental and computational contributions on synthesis of LDH and other nanometer sized clay particles, characterization of LDH/clay reaction mechanisms, and their application in extreme environment remediation, such as highly-alkaline, high temperature radioactive wastes, highly acidic, alkaline, or saline mine tailings and reclamation areas. Topics related to mineralogical transformations, characterization of solid and solution species, and interactions of clay/LDH with heavy metals, nutrients, and organic contaminants under far-from-equilibrium conditions are welcome.

**Redox Reactions of Clays and Clay Minerals in Natural and Engineered Systems**

*Organizers: Anke Neumann (Newcastle University, UK) and Keith D Morrison (LLNL)*

Clays and clay minerals are ubiquitously present in soils and sediments and contain redox active elements such as Fe, S, or Mn. Both biological and abiotic processes can lead to redox reactions of these clay-bound elements, which in turn can affect other sediment and soil components such as contaminant, nutrients or metals. Building upon observations of these redox reactions and redox cycles of clays and clay minerals in natural systems in Earth’s critical zone, these reactions have been utilized in engineered systems, for example for (enhanced/stimulated) natural attenuation of contaminants, but may also negatively impact on
engineered systems’ performance, e.g. the containment of radioactive waste. This session welcomes contributions ranging from fundamental mechanistic (laboratory) studies of redox process at the nano- to microscale of clay materials, over observations in the field, to applications of clay and clay mineral redox reactions in full-scale engineered systems. We invite studies concerned with biotic and/or abiotic processes, exploring reduction and/or oxidation/oxygenation of clays and clay minerals as well as evaluating the consequences of clay and clay mineral redox processes on element, nutrient, and metal cycling and contaminant fate.

**Theme III: Clay Water Interfacial Structure and Interactions**

**Visualizing Solution Structure at the Mineral Aqueous Interface**

**Organizers: Elias Nakouzi (PNNL) and Joanne Stubbs (University of Chicago)**

Solution structure at mineral-aqueous interfaces creates ion distributions, inter-particle forces, and chemical potential gradients that influence particle stability, attachment, and aggregation. However, our understanding of interfacial solution structure remains very limited. Recent advances in synchrotron capabilities, surface spectroscopy techniques, and computational methods, as well as emerging techniques such as 3D atomic force microscopy promise access to a new class of experimental and theoretical data—particularly at the molecular scale—and ultimately a predictive understanding of geochemical interfaces. This session will explore relevant topics including:

- Water distribution at mineral surfaces such as clays, oxides, carbonates, and other materials
- Ion adsorption dynamics and mechanisms
- Influence of solution structure on reactivity and geochemical outcomes
- Role of hydration forces in outcomes such as particle stability and aggregation
- Recent capability developments that enable investigating these problems.

**Mineral Clay Nucleation, Crystallization, and Aggregation**

**Organizers: Guomin Zhu and Benjamin Legg (PNNL)**

Mineral nucleation, crystallization, and aggregation are critical processes in natural and synthetic systems. These processes are often coupled together to create complex pathways of mineralization, dissolution, and phase transformation that have wide-ranging importance to biogeochemical cycles. This symposium will explore the mechanisms by which nucleation, growth, and aggregation occur in complex, environmentally-relevant solutions, and the ways that inorganic and organic impurities/additives can modify these phenomena. Topics that would be covered in the session include, but are not limited to:

- Classical and nonclassical nucleation pathways.
- Crystal growth and dissolution mechanisms.
- Mineral phase transformations.
- Particle aggregation phenomena.
- Influences of organic and inorganic additives.
Clay Swelling and Aggregation: Modeling and experiments
Organizers: Louise Criscenti (Sandia National Laboratory) and Laura Lammers (Lawrence Berkeley National Laboratory).
Invited speakers: Roland Pellenq, MIT and Tom Underwood, Princeton

Clay swelling and aggregation are important processes in both engineered and natural systems, as clay-rich materials provide critical subsurface sealing capabilities for byproducts of energy production. While the phenomenology of clay swelling has been studied for many decades, it is still not possible to predict the evolution of clay permeability and mass transport in response to chemical and mechanical perturbations. In shales and engineered barriers, clay swelling properties depend on mineral interactions with different fluid types including brine, natural gas and oil. Clay aggregation and compaction affect the overall permeability of both shales and engineered barriers, including pore size and shape distributions and interconnectivity. In this symposium we welcome presentations on both experiments and models that shed light on clay swelling and aggregation phenomena and the impact these phenomena have on reactivity and transport from the nanoscale to the macroscale.

Nanomechanical Properties of Layered Materials: Towards hierarchical theories of bulk properties
Organizers: Michael Whittaker and Benjamin Gilbert (Lawrence Berkeley National Laboratory)

The development of robust predictive models for the mechanical properties of clay-rich rocks and geological engineering materials is essential for their safe and sustainable use in energy and water applications. Chemical and mechanical interactions between layered aluminosilicate particles control the properties of these materials, which are typically nanoscale in at least one dimension, morphologically and mechanically anisotropic, compositionally heterogenous and defective over a range of length scales. The development of continuum-scale constitutive models based on fine-scale mineralogy, structure, fluid chemistry and the properties of constituent clay mineral particles represents a significant challenge in fundamental geoscience, but these materials have much in common with synthetic layered materials such as graphene, MXenes, transition metal dichalcogenides, and more. We welcome contributions that develop experimental, theoretical and simulation methods to address the molecular-scale forces between layered materials, the mechanical properties of individual layers and the properties of large-scale materials comprising layered constituents, particularly under relevant temperature, pressure and stress conditions.

Advances in Probing the Clay/Clay Mineral-Water Interface
Organizer: Omar Harvey (Texas Christian University)

The session invites oral and poster presentations focused on recent advances in probing the surface-water interface of clays and clay minerals. Submissions may be based on experimental or modeling data at the atomic-, molecular- or particle-scale and include, but not limited to, microscopic, spectroscopic and calorimetric studies focus on elucidating; the structure of water at the mineral surface, interactions of charged and uncharged species, organic-mineral interactions, microbe-mineral interactions, nanoscale dynamics of mineral behavior, as well as spatiotemporal evolution of the interface under different conditions.
Experimental and Computational Advances for Studying the Structure and Reactivity of Nanoscale Metal Oxides in Geochemical Environments

Organizers: Owen Duckworth (North Carolina State University), Nadine Kabengi (Georgia State University), Marc Michel (Virginia Tech)

Metal oxides are ubiquitous in nature, existing as relatively pure minerals and as amorphous phases that bind and coat other soil components. Because of their relatively high specific surface areas and their tendency to undergo chemisorption reactions, metal oxides are one of the most important soil components controlling solubility and mobility of pollutants in the environment. A host of experimental and computational techniques, separately and in combination, have been utilized to probe nanoscale metal oxides in geochemical environments. Over the next decade, developments in molecular-level experimental, computational and theoretical approaches will usher in a new era of studying metal oxides and give rise to challenging questions. This session seeks to highlight how recent advances in experimental and computational methods have shaped our current understanding of the role of nanoscale metal oxides and how future advances will affect this field. The topics to be covered in this session include, but are not limited to:

- New experimental/computational approaches
- Structure and reactivity of mineral surfaces
- Adsorption/desorption rates and mechanisms
- Surface mediated redox reactions
- Interactions of metal oxides with contaminants and microorganisms

Theme IV: Clays and Climate Change

Impact of Clays on the Earth’s Climate

Organizers: Jim Amonette, Nancy Hess, and Ravi K. Kukkadapu (PNNL)

This symposium will explore the impact of clay minerals, including layer silicates, oxides, and oxyhydroxides, on the Earth's climate system, and the potential uses of these minerals to help sequester carbon and manage solar radiation levels. Examples of topics considered include the role of clay aerosols in atmospheric chemistry, the impact of clay dust particles on oceanic biogeochemistry and marine carbon sequestration, and the various ways by which clay aerosols and dust particles affect planetary albedo.

Stability of Mineral-Organic Matter Interactions under Varying Biogeochemical Conditions

Organizers: Ravi Kukkadapu, Qian Zhao and Nancy Hess (EMSL, PNNL) and Nik Qafoku (PNNL). Confirmed Invited Speakers: Thomas Borch (Colorado State University), Aaron Thompson (University of Georgia), Tyler Sowers (Don Spark’s Graduate student – now at EPA), Steven Hall (Iowa State University), Jennifer Willemsen (Ian Bourg’s Graduate student – Department of Civil and Environmental Engineering, Princeton, NY), Ludmilla Aristilde (Department of Civil and Environmental Engineering, Northwestern University), Mohammad Afsar (Yan Lin’s Postdoc – Department of Plant and Soil Sciences, University of Delaware, Newark, DE), Mike Rowley (University of Lausanne, Switzerland)
This session will explore the multifaceted interactions between soil organic matter and mineral surfaces and these interactions respond to environmental change. While the attachment of soil organic matter to mineral surfaces is generally considered to result in greater persistence of those compounds in the environment, recent research has shown that this is not always the case. These interactions can be highly dynamic and are subject to varying biogeochemical conditions. These recent results, from both experimental and modeling approaches, suggest that specific types of organic molecules are more likely to form associations with oxy-hydroxide and clay mineral surfaces. Additionally, certain mineral surfaces are more reactive, increasing stability of organic molecules, leading to their accelerated oxidation and decomposition, or impacting their transport through the environment. We welcome submissions that contribute to this rapidly evolving understanding through novel experiment and/or modeling approaches and challenge our existing conceptual models of soil organic matter and mineral surface interactions. A series of papers from this session will be published in a special issue of the Soil Science Society of America Journal.

**Theme V: Special Topics and General Session**

**Clays and Rare-Earth Elements Cycling**

**Organizers: Chris Brown and Eirik Krogstad (PNNL)**

Rare earth elements (REEs) are receiving increased attention due to concerns about the lack of a stable domestic supply to support critical material manufacturing needs (e.g., batteries, electronics, and magnets). This has spurred research funded via multiple sectors that is focused on recovering REEs from nonconventional sources, such as geothermal brines, coproduced fluids from hydrocarbon recovery efforts, and waste products from coal fly ash. However, it has long been known that REEs bind strongly to clay minerals, making clay-rich deposits potentially attractive targets for solution mining activities. This session offers a venue to share new insights into the mechanisms controlling REE distributions in natural systems, with a particular focus on sorption mechanisms to clays.

**Quantitative Analysis of Clay-Bearing Samples: Putting numbers on clay mineral analyses, approaches, and applications across ocean, earth, and extra-terrestrial sciences**

**Organizers: Stephen Hillier (the James Hutton Institute, Aberdeen, UK and Department of Soil and Environment, SLU, Uppsala, Sweden), Mark Raven (CSIRO Land and Water, Adelaide, South Australia), Kristian Ufer (Federal Institute for Geosciences and Natural Resources, Hannover, Germany)**

Many research and applied studies across the earth and extra-terrestrial sciences, as well as the various extractive and containment industries, require quantitative analysis of clay bearing rocks, sediments, or soils. Analysis of these clay bearing materials may range from attempts to provide fully quantitative analyses, through those that are described as ‘semi quantitative’ to others that simply require some form of ‘quantitative representation’ in order to compare large numbers of samples and assess trends. Depending on the application the range of approaches include the use of sophisticated X-ray diffraction Rietveld and full pattern fitting methods, 1D modelling of 00l diffraction patterns, through analysis of spectroscopic and indirect chemical or microscopy data-based approaches, to simple XRD peak ratio measurements of clay peaks in separated clay-size fractions prepared as oriented specimens. Applications range from those requiring detailed assessment of absolute bulk compositions that include all non-clay minerals...
as well as amorphous components, to those focused on detailed modelling of clay fractions to understand changes in mixed-layering, to simple relative abundances used, for example, as proxies for climate or provenance change. Interest in quantitative clay mineral analyses of one sort or another has continued to increase. This session aims to bring together all those interested in ‘putting numbers’ on clay mineral analyses, to share experience and discuss the various common challenges and issues that quantitative analyses of clay minerals and clay materials still present. The session will conclude with a presentation to announce the winners and top finishers of the 10th Reynolds Cup.

**Incipient Weathering of Primary Minerals to Clay Minerals: Biological and physical factors**

**Organizers:** Paul Schroeder (UGA), David D’Amore, Ashlee Dere, Rebecca Lybrand, Raquel Portes, Diogo Spinola, Tom Trainor

Primary minerals, such as feldspars and micas, are thermodynamically unstable under low-temperature, moist, biologically active earth surface conditions. Evidence indicates that hydrolysis and oxidation processes occur both deep (~100 meters) below the Earth’s surface, in addition to primary mineral weathering at the near surface. This session explores the processes by which biological interactions, in concert with physical interactions, take place within the deep and shallow critical zone to further understand the mechanisms and transformation rates of primary minerals to clay minerals. Studies based on novel experimental methods and new observations at all scales from nanometers to watersheds are welcomed contributions.

**Aqueous Processes in the Solar System: Evidence from phyllosilicates**

**Organizers:** Elizabeth B. Rampe (NASA JSC), Patrick J. Gasda (LANL), Valerie Fox (Caltech) and Sean Czarnecki (Arizona State University)

Phyllosilicates are an important mineral group for characterizing aqueous processes on planetary bodies, including meteorites, asteroids, and Mars. Phyllosilicates and other hydrated minerals have been recognized from remote infrared measurements of asteroids Ryugu and Bennu, from which the missions Hayabusa2 and OSIRIS-REx will return samples in the next few years. Clay minerals are found in ancient terrains on the surface of Mars from orbital infrared measurements and from in-situ analyses by rovers, including the on-going Glen Torridon campaign by the Mars Science Laboratory Curiosity rover. The goal of this session is to highlight the diversity of phyllosilicates identified in bodies throughout the Solar System and to discuss their implications for the aqueous history of meteorites, asteroids, and Mars. We welcome abstracts that focus on constraining phyllosilicate mineralogy of planetary materials through spacecraft measurements specifically. We also welcome abstracts that discuss curation practices and future analyses of phyllosilicate-bearing extraterrestrial samples.

**Extraterrestrial Clays: Insight from Earth-based studies**

**Organizers:** Rebecca Lybrand (OSU), Tanya Peretyazhko (Jacobs, NASA-JSC) and Brad Sutter (Jacobs, NASA-JSC)

The nature of clay minerals on celestial bodies beyond the Earth is an emerging area of interest. Extraterrestrial clay minerals have been identified by sample-based studies in meteorites, by remote sensing of the surface of Mars and asteroid Ceres, by direct X-ray diffraction observations by MSL Curiosity rover, and through terrestrial analog studies on Earth. The Earth-based studies allow for more detailed interpretations of the geologic history of clay-bearing
bodies in the Solar System. Identification and characterization of clay minerals hold valuable clues into the evolution of celestial bodies such as aqueous alteration and processes that may allow life to develop. Clay minerals can serve as geochemical indicators of potential habitable environments and paleoclimate markers. We welcome meteorite, laboratory-based, field-analogue, and theoretical studies aimed to understand clay minerals on diverse Solar System bodies. We hope that this session will promote discussion and broaden perspectives on origin, genesis, and distribution of clay minerals and their role in biosignature preservation.

Clays for Antibacterial/Medicinal Applications
Organizers: Youjun Deng (University of Texas A&M) and Jakub Matusik (AGH Krakow, Poland)

Toxins produced by microbes such as fungi, bacteria, and algae are threats to food security, human and animal health, and environmental safety. Clays and similar materials having layered structure have been explored, and in some cases successfully used, to kill the microbes, or to detoxify these compounds by adsorption, degradation, or the combination of the two mechanisms. This session invites researchers, industrial representatives, and regulative agencies to share their findings and stories of applying clays and similar materials in detoxification of the biological toxins and microbial control. Research topics will range from molecular modeling, bench top experiments, cytotoxicity study, to animal and human clinical trials. Updates on regulations, guidance, and statistics on the uses of clays for this purposes are also welcome.

General Session
Organizers: Amanda Lawter (PNNL), Nik Qafoku (PNNL), Jim Amonette (PNNL)

WORKSHOPS
CMS Workshop: Emerging Methods in Clay Science - Thursday 10/22 and Friday 10/23
Organizers: Eugene S. Ilton (PNNL) and Ravi K. Kukkadapu (PNNL)

This workshop highlights powerful novel technologies and theoretical approaches that can tackle tough problems over a range of scales and conditions. Some of these methods may still be immature but full of promise. One theme is using state-of-the-art theoretical approaches to extract unprecedented rich information from both X-ray scattering methods and electronic spectroscopies. Another theme is the development of new experimental methods for characterizing soil organic material as well as organic-mineral interactions down to the single molecule level. How such information can be used to benchmark large scale simulations designed to predict organic-mineral interactions will be discussed. Additional topics include breakthrough techniques for exploring mineral surface and interfacial solvent structures that should increase our abilities to predict, for example, adsorption and mineral growth kinetics. Finally, we show how closely integrating well established independent techniques can yield surprising new and powerful insights into supercritical fluid-clay interactions with implications for geologic carbon storage.
PNNL Workshop: A Hanford Perspective on Environmental Remediation- Wednesday, October 21

Organizers: Debra S. Barnett (PNNL) and Frances N. Smith (PNNL)

Earth Systems Science Division of the Pacific Northwest National Laboratory (PNNL) is organizing a newly developed interactive workshop on the topic of: “A Hanford Perspective on Environmental Remediation” that will be presented during the 57th Annual International Meeting of the Clay Minerals Society to be held on October 18-23, 2020 in Richland, WA. The workshop is open to all meeting attendees and will compliment a series of sessions organized under the second theme of the meeting: “Clays Role in Waste Affected Environments: Remediation and contaminant fate and transport”. Content addresses environmental remediation challenges faced by many sites using the Hanford Site as an example. The workshop’s eight topics start with a high-level overview that will lead participants through Hanford’s legacy to modern-day environmental cleanup challenges and solutions. Presentations will focus on historical perspective, remediation accomplishments, remaining challenges, and remediation approaches applicable to other sites. Importantly, presenters will be early- and mid-career staff (mentees) who will co-develop presentations on these topic areas under the guidance of senior staff members (mentors).

ICDD Workshop: X-ray Diffraction Applications: JADE Software - Friday, October 23

Organizers: Steffen Weber (ICDD/Materials Data Inc.) and Maj Randi (ICDD/Materials Data Inc.)

This free 3-hour workshop, hosted by the International Center for Diffraction Data (ICDD), will provide training in the use of JADE Software for analysis of X-ray diffraction data. Topics covered include general software overview, data import, user PDF card creation for clays, phase identification, and quantitative analysis. Depending on participant interest and available time, more advanced methods such as reference intensity ratios, individual profile fitting, instrument curve creation, crystallite size and strain, cluster analysis, and custom crystal structure databases will be addressed.
ABBREVIATIONS OF THE THEMES AND SESSIONS OF THE MEETING

**Theme I: Clays: Oil/Gas Interactions**
- I/1 Oil sands tailings clay challenge
- I/2 Fundamental shale research at the DOE National Laboratories
- I/3 Advanc. appl. and characterization of clays in petroleum industry
- I/4 The evolution of micro and nanoporosity in black shales

**Theme II: Clays Role in Waste Affected Environments**
- II/1 Impacts of in-situ remediation and waste disposal on mineralogy
- II/2 Role of minerals in concentrating radionuclides at different scales
- II/3 Advanc. in understanding clay-based barrier system in geo rep.
- II/4 Colloid mobilization and colloid-facilitated contaminant transport
- II/5 Clays and layered double hydroxides in extreme environments
- II/6 Redox reactions of clays and clay minerals in nat/engine systems

**Theme III: Clay: Water Interfacial Structure and Interactions**
- III/1 Visualizing solution structure at the mineral aqueous interface
- III/2 Mineral clay nucleation, crystallization and aggregation
- III/3 Clay swelling and aggregation: Modeling and Experiments
- III/4 Nanomechanical properties of layered materials
- III/5 Advances in probing clay/clay mineral - water interface
- III/6 Exp/comput advances for studying structure and reactivity

**Theme IV: Clays and Climate Change**
- IV/1 Impact of clays on the Earth’s climate
- IV/2 Stability of mineral-organic matter interactions

**Theme V: Special Topics and General Session**
- V/1 Clays and rare-Earth element cycling
- V/2 Quantitative analysis of clay-bearing samples
- V/3 Incipient weathering of primary minerals to clay minerals
- V/4 Aqueous processes in the solar system: Evidence phyllosilicates
- V/5 Extraterrestrial clays: Insights from Earth-based studies
- V/6 Clays for antibacterial/medical applications
- V/7 General session

**I Clays: Oil/Gas Interactions**
- I/1 Oil sands tailings
- I/2 Shale research at DOE labs
- I/3 Clays in petroleum
- I/4 Porosity in black shales

**II Clays in Waste Environments**
- II/1 Remediation and disposal
- II/2 Minerals and radionuclides
- II/3 Clays in repositories
- II/4 Colloid transport
- II/5 Clays in extreme environments
- II/6 Redox of clays

**III Clay: Water Interface**
- III/1 Solution structure
- III/2 Nucleation aggregation
- III/3 Swelling and aggregation
- III/4 Nanomechanical properties
- III/5 Probing clay: water
- III/6 Nano metal oxides

**IV Clays and Climate Change**
- IV/1 Clay impact on climate
- IV/2 Mineral:organic interactions

**V Special & General**
- V/1 Clays and rare-earth elements
- V/2 Quantitative analysis
- V/3 Weathering
- V/4 Solar system processes
- V/5 Extraterrestrial clays
- V/6 Medicinal applications
- V/7 General
## Program at a Glance

<table>
<thead>
<tr>
<th>Start Time</th>
<th>Day 1</th>
<th>Day 2</th>
<th>Day 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>7:30</td>
<td>Zoom Room 1 - Theme I: Clays in Petroleum Environments</td>
<td>Zoom Room 2 - Theme III: Clays in Waste Environments</td>
<td>Plenary Session (Webinar)</td>
</tr>
<tr>
<td>8:15</td>
<td>Zoom Room 1 - Theme I: Clays in Petroleum Environments</td>
<td>Zoom Room 2 - Theme III: Clay:Water Interface</td>
<td>Marilyn and Sturgis W. Bailey Award Lecture (Webinar)</td>
</tr>
<tr>
<td>9:15</td>
<td>Zoom Room 3 - Theme III: Clay:Water Interface</td>
<td>Zoom Room 4 - Theme IV: Clays &amp; Climate Change</td>
<td>Marlon L. and Chrystie M. Jackson Mid-Career Clay Scientist Award Lecture (Webinar)</td>
</tr>
<tr>
<td>9:30</td>
<td>Zoom Room 5 - Theme V: Special &amp; General</td>
<td>Zoom Room 5 - Theme V: Special &amp; General</td>
<td>technical sessions</td>
</tr>
<tr>
<td>10:50</td>
<td>Break</td>
<td>Break</td>
<td>Technical Sessions</td>
</tr>
<tr>
<td>11:00</td>
<td>Zoom Room 1 - Theme I: Clays in Petroleum Environments</td>
<td>Zoom Room 2 - Theme III: Clay:Water Interface</td>
<td>Technical Sessions</td>
</tr>
<tr>
<td>12:20</td>
<td>Zoom Room 3 - Theme III: Clay:Water Interface</td>
<td>Zoom Room 4 - Theme IV: Clays &amp; Climate Change</td>
<td>technical sessions</td>
</tr>
<tr>
<td>13:00</td>
<td>Zoom Room 5 - Theme V: Special &amp; General</td>
<td>Zoom Room 5 - Theme V: Special &amp; General</td>
<td>Break</td>
</tr>
<tr>
<td>14:20</td>
<td>Break</td>
<td>Break</td>
<td>Break</td>
</tr>
<tr>
<td>14:30</td>
<td>Welcome Mixer (Zoom Room 3)</td>
<td>Lunch Break</td>
<td>Break</td>
</tr>
<tr>
<td>15:50</td>
<td>Break</td>
<td>Break</td>
<td>Break</td>
</tr>
<tr>
<td>16:00</td>
<td>Zoom Room 1 - Theme I: Clays in Petroleum Environments</td>
<td>Zoom Room 2 - Theme III: Clay:Water Interface</td>
<td>Lunch Break</td>
</tr>
<tr>
<td>16:30</td>
<td>Zoom Room 3 - Theme III: Clay:Water Interface</td>
<td>Zoom Room 4 - Theme IV: Clays &amp; Climate Change</td>
<td>Break</td>
</tr>
<tr>
<td>18:00</td>
<td>Zoom Room 5 - Theme V: Special &amp; General</td>
<td>Zoom Room 5 - Theme V: Special &amp; General</td>
<td>Break</td>
</tr>
<tr>
<td>21:30</td>
<td>Break</td>
<td>Break</td>
<td>Break</td>
</tr>
<tr>
<td>Start Time</td>
<td>Day 4</td>
<td>Day 5</td>
<td>Day 6</td>
</tr>
<tr>
<td>------------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>(USA Pacific: UTC -8)</td>
<td>Wednesday</td>
<td>Thursday</td>
<td>Friday</td>
</tr>
<tr>
<td>7:30</td>
<td>CMS Reception and Award Presentations (Webinar)</td>
<td>Plenary Session (Webinar)</td>
<td>Zoom Room 1: CMS WORKSHOP: EMERGING METHODS IN CLAY SCIENCE</td>
</tr>
<tr>
<td>8:15</td>
<td>CMS Business Meeting (Zoom Room 1)</td>
<td>Pioneer in Clay Science Lecture (Webinar)</td>
<td>Break</td>
</tr>
<tr>
<td>9:15</td>
<td>Break</td>
<td>Technical Sessions</td>
<td>Break</td>
</tr>
<tr>
<td>9:30</td>
<td>Zoom Room 1: Themes I and II</td>
<td>Break</td>
<td>Break</td>
</tr>
<tr>
<td>10:50</td>
<td>Break</td>
<td>I/3: Clays in repositories</td>
<td>Break</td>
</tr>
<tr>
<td>11:00</td>
<td>Break</td>
<td>II/3: Clay:Water Interface</td>
<td>Break</td>
</tr>
<tr>
<td>12:20</td>
<td>Lunch Break</td>
<td>III/1: Solution structure</td>
<td>Break</td>
</tr>
<tr>
<td>13:00</td>
<td>Break</td>
<td>III/4: Nanomechanical properties</td>
<td>Break</td>
</tr>
<tr>
<td>14:20</td>
<td>Break</td>
<td>IV/1: Clay impact on climate</td>
<td>Break</td>
</tr>
<tr>
<td>14:30</td>
<td>Break</td>
<td>V/2: Quantitative analysis</td>
<td>Break</td>
</tr>
<tr>
<td>15:50</td>
<td>Break</td>
<td>V/3: Weathering</td>
<td>Break</td>
</tr>
<tr>
<td>16:00</td>
<td>Break</td>
<td>Zoom Room 1: ICDD WORKSHOP: JADE DIFFRACTION SOFTWARE</td>
<td>Break</td>
</tr>
<tr>
<td>16:30</td>
<td>Break</td>
<td>Zoom Room 1: VIRTUAL FIELD TRIP: Ice Age Floodscapes of the Pacific Northwest</td>
<td>Break</td>
</tr>
<tr>
<td>18:00</td>
<td>Break</td>
<td>Zoom Room 1: CMS WORKSHOP: EMERGING METHODS IN CLAY SCIENCE</td>
<td>Break</td>
</tr>
<tr>
<td>21:30</td>
<td>Break</td>
<td>Zoom Room 1: CMS WORKSHOP: EMERGING METHODS IN CLAY SCIENCE</td>
<td>Break</td>
</tr>
</tbody>
</table>
THE TECHNICAL SESSIONS MEETING PROGRAM
(all times are USA Pacific Time: UTC -8)

Monday, October 19, 2020
Morning Sessions

Theme II, Session 6 [Zoom Room 1]

Redox Reactions of Clays and Clay Minerals in Natural and Engineered Systems

Organizers: Anke Neumann and Keith D. Morrison

9:30–10:00 Invited: Samapti Kundu, Na’ama Korin, and Adi Radian*: Novel Sorbent-Catalysts Based on Fe-Montmorillonite-Cyclodextrin Composites for the Adsorption and Surface Oxidation of Micropollutants

10:00–10:20 Amal K Deb*, Bhabananda Biswas, Ravi Naidu, and Mohammad M Rahman: Environmentally Benign CUNPS@HNT Composite and its Catalytic Performance


10:40–11:00 Break


Poster Presentation
11:40–12:40 Jordan Stanberry*, Ilana Szlamkowicz, Lauren Purdy, and Vasileios Anagnostopoulos: Oxidative Dissolution of TcO2 by Synthetic Birnessite Under Anaerobic Conditions

Jim E. Szecsody*, Hilary P. Emerson, Adam R. Mangel, and Jon N Thomle: Use of Spectral Induced Polarization to Characterize Clay Redox Reactivity

Ilana Szlamkowicz*, Luke Longen, Andrew Grabe, and Vasileios Anagnostopoulos: Geochemical Controls of Mn(III) Minerals Over Iodide Environmental Fate
**Theme III, Session 2 [Zoom Room 2]**

**Mineral Clay Nucleation, Crystallization, and Aggregation**

*Organizers: Guomin Zhu and Benjamin Legg*

<table>
<thead>
<tr>
<th>Time</th>
<th>Presentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:30–10:00</td>
<td>Michael Hochella: <em>Nucleation, Growth, and Implications of Nano-Manganese Oxides via Nano-Iron Oxide Catalysis</em></td>
</tr>
<tr>
<td>10:00–10:30</td>
<td>Presentation withdrawn</td>
</tr>
<tr>
<td>10:30–10:50</td>
<td>Seokju Hong and Wooyong Um: <em>Hydrothermal Synthesis of Pollucite Below 100ºC for Cs Immobilization</em></td>
</tr>
<tr>
<td>10:50–11:00</td>
<td>Break</td>
</tr>
<tr>
<td>11:00–11:20</td>
<td>Sebastien N Kerisit, Shawn L Riechers, Sebastian T Mergelsberg, Trenton R Graham, Odeta Qafoku, Micah P Prange, Eugene S Ilton, Nabajit Lahiri, Yingge Du, Libor Kovarik, Tamas Varga, and Bruce W Arey: <em>Molecular-Scale Controls on Heterogeneous Nucleation and Growth at Mineral-Water Interfaces</em></td>
</tr>
<tr>
<td>11:20–11:40</td>
<td>Maria L Sushko, Guomin Zhu, Lili Liu, Elias Nakouzi, Kevin M Rosso, and James J De Yoreo: <em>Role of Interfacial Structure and Dynamics in Crystallization Pathway Selection</em></td>
</tr>
<tr>
<td>11:40–12:00</td>
<td>Marc Michel*, McNeill Bauer, and Clément Levard: <em>Factors Regulating the Formation of Synthetic Imogolite Nanoparticles</em></td>
</tr>
<tr>
<td>12:00–12:20</td>
<td>Miao Song, Jaewon Lee, Jaehun Chun, Dongdong Xiao, Gang Zhou, Ning Lu, Elias Nakouzi, and Dongsheng Li*: <em>Non-Classical Crystal Growth Pathway: Oriented Attachments Direct Crystal Morphologies and Structures</em></td>
</tr>
<tr>
<td>12:20–13:00</td>
<td>Lunch Break</td>
</tr>
</tbody>
</table>

---
Theme III, Session 5 [Zoom Room 3]

Advances in Probing the Clay/Clay Mineral-Water Interface

Organizer: Omar R. Harvey, Geological Sciences, Texas Christian University

9:30–9:50  Artur Kuligiewicz and Arkadiusz Derkowski: Activation Energy of Smectite Rehydroxylation

9:50–10:10  Caitlin Payblas and Omar R. Harvey: Binding Dynamics of Mono- and Di-Carboxylates in a Boehmite-Bayerite Series: A Flow-Adsorption Microcalorimetry Study

10:10–10:30  Marie Aurore Niyitanga Manzi*, and Omar R. Harvey: Flow Experiments of Nanoparticles Interaction with Iron Oxide Surfaces

10:30–10:50  Michel Sassi, Zheming Wang, Eric D Walter, Xin Zhang, Hailin Zhang, Xiaohong S Li, Aashish Tuladhar, Mark Bowden, Hong-fei Wang, Sue B Clark, and Kevin M Rosso: Surface Hydration and Hydroxyl Configurations of Gibbsite and Boehmite Nanoplates

10:50–11:00  Break

11:00–11:20  Xinxin Mo, Matthew G Siebecker, Wenxian Gou, and Wei Li*: Surface Induced Ni(II) Precipitation at the Palygorskite-Solution Interface Revealed by EXAFS, HRTEM, and DRS

11:20–11:40  Hao Xiong, Deepak Devegowda, and Liangliang Huang: Unbalanced Adsorption of Cations at the Surface of Clay Minerals

11:40–12:00  Manyiel Mel and Omar R. Harvey: Zwitterion Effects of Amino Acids on Sorptive Behavior of Carboxylates at the Ferrihydrite- and Hematite-Water Interface
Theme IV, Session 2 [Zoom Room 4]

Stability of Mineral-Organic Matter Interactions Under Varying Biogeochemical Conditions

Organizers: Ravi Kukkadapu, Nancy Hess, Qian Zhao, and Nik Qafoku


10:00–10:30  Aaron Thompson* (invited), Nadia Noor, and Chunmei Chen: *Assessing the Bioavailability of Organic Carbon in Mineral-Associated Organic Matter Formed from Co-Precipitation of Short-Range Ordered Iron and Dissolved Organic Carbon*

10:30–10:50  Hailiang Dong* and Qiang Zeng: *Mutual Interactions Between Reduced Fe-Bearing Clay Minerals and Humic Acids Under Dark, Oxygenated Condition: Hydroxyl Radical Generation and Humic Transformations*

10:50–11:00  Break

11:00–11:30  Tyler Sowers* (invited), Owen Duckworth, and Don Sparks: *Bacteriogenic Iron Oxide and Permafrost Organomineral Interactions Impacting Terrestrial Carbon Cycling*

11:30–12:00  Steven Hall* (invited), Wenjuan Huang, Wenjuan Yu, Chenglong Ye, and Aaron Thompson: *Contrasting Roles of Reactive Iron vs. Aluminum Phases in Soil Carbon Persistence: A Multi-Scale Perspective*

12:00–12:20  Zihua Zhu* and Liuqin Huang: *Determining Active Adsorption Sites of Soil Organic Carbon on Clay Mineral Surface Using TOF-SIMS and PCA Analysis*
Theme V, Session 4 [Zoom Room 5]

Aqueous Processes in the Solar System: Evidence from Phyllosilicates

Organizers: Elizabeth Rampe, Patrick Gasda, Valerie Fox, and Sean Czarnecki

9:30–10:00  Victoria Hamilton*, Amy Simon, Hannah Kaplan, Philip Christensen, Dennis Reuter, Romy Hanna, and Dante Lauretta (invited): The Phyllosilicate-Dominated Mineralogy of Asteroid (101955) Bennu

10:00–10:30  Janice Bishop* (invited): Phyllosilicates Provide Clues about the Aqueous Environment and Climate on Early Mars

10:30–10:50  Valerie Fox*, Kristen Bennett, Ray Arvidson, Bethany Ehlmann, Erwin Dehouck, and Elizabeth Rampe: Martian Clay Minerals from Orbit to the Surface: MSL and MER Rover Investigations of Crism Smectite Detections

10:50–11:00  Break

11:00–11:20  Sean Czarnecki*, Craig Hardgrove, Patrick J Gasda, Travis S J Gabriel, and Ray E Arvidson: Hydration of a Phyllosilicate-Rich Unit on Mars using Neutron Spectroscopy


11:40–12:00  Erwin Dehouck*, Agnès Cousin, Nicolas Mangold, Jens Frydenvang, Olivier Gasnault, Gaël David, Jérémie Lasue, Pierre-Yves Meslin, William Rapin, Patrick Gasda, Olivier Forni, Valerie Fox, Kristen Bennett, Sylvestre Maurice, and Roger Wiens: Geochemical Signatures of Martian Clay Minerals at Glen Torridon, Gale Crater

12:00–12:30  Andrea Harrington*, Michael Thorpe, and Elizabeth Rampe (invited): Curation of Martian Phyllosilicates – Developing Strategies for a Unique Astromaterial Collection
Monday, October 19, 2020
Afternoon Sessions

Theme II, Session 5 [Zoom Room 1]

Clays and Layered Double Hydroxides in Extreme Environments – An IDREAM EFRC Session

Organizers: Trent R. Graham and Carolyn Pearce (PNNL) and Youjun Deng (Texas A&M)

13:00–13:20 Karolina Rybka* and Jakub Matusik: Mg/Al LDH Obtained via Transformation of Minerals for the Removal of Selected Elements from Acidic and Alkaline Wastewaters


13:40–14:00 Anna Koteja*, Paulina Maziarz, Agnieszka Solinska, and Jakub Matusik: Granulated and Functionalized Halloysite for Anions Adsorption

14:00–14:30 Jacob Reynolds* (invited): Gibbsite Solubility in Highly Concentrated Electrolyte and Sodium Hydroxide Solutions


15:00–15:20 ChiaWei Lin*, Ana L. Barrientos Velazquez, Youjun Deng, and Julie A. Howe: Evaluation of Dewatering and Stabilizing Bauxite Residue by Controlling pH, Double Layer Thickness, and Surface Hydrophobicity as well as Cementing Methods


15:50-16:00 Break

16:00-16:20 Trent Graham*, Jian Zhi Hu, Xin Zhang, Mateusz Dembowski, Nicholas R. Jaegers, Chuan Wan, Mark Bowden, Andrew S. Lipton, Andrew R. Felmy, Sue Clark, Kevin Rosso, and Carolyn Pearce: Transformation Pathways of Gibbsite into LiAl-LDH in Concentrated Lithium Hydroxide

16:20-16:50 Alexandra Navrotsky* (invited): Thermodynamics of Hydrotalcite Formation and Adsorption


17:50-18:00 Break

Poster Presentations

18:00–19:00 Karolina Rybka* and Jakub Matusik: Different Approaches to Transformation of Selected Minerals into Layered Double Hydroxides

Jueun Kim*, Jaehyuk Kang, and Wooyong Um: Simultaneous Removal of Both Cesium And Iodate Using Prussian Blue Functionalized Layered Double Hydroxides (PB-LDH)
Theme III, Session 2 [Zoom Room 2]

Mineral Clay Nucleation, Crystallization, and Aggregation

Organizers: Guomin Zhu and Benjamin Legg

13:00–13:20 Guomin Zhu, Maria L. Sushko, John S. Loring, Benjamin A. Legg, Miao Song, Jennifer A. Soltis, Xiaopeng Huang, Kevin M. Rosso, and James J. De Yoreo: Hematite Mesocrystal Formation Through Near Interface Nucleation and Oriented Aggregation


13:40–14:00 Tao Jiang: Investigation of Aggregation and Particle Size Analysis of Illite

14:00–14:20 Hejian Zhu*, Andrew Whittle, Roland Pellenq, Katerina Ioannidou, and Guoping Zhang: Multiscale Modelling of Clay Aggregate Behaviour


Theme V, Session 7 [Zoom Room 2]

General Clay Science

Organizers: Amanda Lawter, Nik Qafoku, and Jim Amonette

16:00–16:20 Marta Kisiel, Michal Skiba*, Piotr Jaglarz, Beata Zymelka, Katarzyna Maj-Szeliga, Beata Zymelka, Roksana Wozniak, Magdalena Makiel: Clay Mineralogy of the Tomanova Formation – Deposits of Periodic Swamps and Lakes Developed on River Flood Plains During Upper Triassic

16:20-16:40 Marta Kisiel*, Michal Skiba, Artur Kuligiewicz, Magdalena Makiel, Mateusz Damrat, Katarzyna Maj-Szeliga, and Marek Żajaczkowski: Formation of Chlorite During Early Diagenesis in Recent Sediments of Gdańsk Bay (Baltic Sea)

16:40-17:00 Warren Huff* and Andrei Dronov: Tectonic Setting of Explosive Volcanic Eruptions in the Upper Ordovician of the Siberian Platform

17:00-17:20 Jian Liu*, Pete McGrail, Praveen Thallapally, Michael Sinnwell, and Paul Martin: Rare Earth Elements Extraction from Geothermal Brine Using Magnetic Nanofluids
Theme III, Session 6 [Zoom Room 3]

Experimental and Computational Advances for Studying the Structure and Reactivity of Nanoscale Metal Oxides in Geochemical Environments

Organizers: Owen Duckworth, Nadine Kabengi, and Marc Michel

13:00–13:20  Vivien Ramothe*, Pauline Simonnin, Laurent Charlet, Benjamin Gilbert, Michel Sassi, and Kevin Rosso: Adsorption Mechanism of Sulfide on Silver Nanowires Surfaces


13:40–14:00  Presentation withdrawn


14:20–14:30  Break

14:30–15:00  Anxu Sheng, Juan Liu, Xiaoxu Li, Odeta Qafoku, Richard Collins, Adele Jones, Carolyn Pearce, Chongmin Wang, Jinren Ni, Anhuai Lu, and Kevin Rosso*: Labile Fe(III) from Sorbed Fe(II) Oxidation is the Key Intermediate in Fe(II)-Catalyzed Ferrihydrite Transformation


15:40–16:00  Runliang Zhu* and Hongping He: Adsorption of Heavy Metal Cations on Iron Oxides: The Effects of Coexistent Oxyanions and Light Irradiation

16:00–16:20  Paulina Maziarz* and Jakub Matusik: Kaolin Particles Coated with Zero-Valent Iron – Competitive Adsorption Of Pb/Cd, Regeneration and Reuse Possibilities
Theme IV, Session 2 [Zoom Room 4]

Stability of Mineral-Organic Matter Interactions Under Varying Biogeochemical Conditions

Organizers: Ravi Kukkadapu, Nancy Hess, Qian Zhao, and Nik Qafoku

13:00–13:30 Jennifer A R Willemsen* (invited) and Ian C Bourg: Molecular Dynamics Simulations of the Associations Between Smectite Clay Nanoparticles, Soil Organic Matter Coatings, and Organic Contaminants

13:30–14:00 Ludmilla Aristilde* (invited): Control of Binding Structures on Reactivity in Mineral-Organic Associations: Insight with Clays and Iron Oxides

14:00–14:20 Itamar Shabtai*, Srabani Das, Thiago Inagaki, and Johannes Lehmann: Soil Mineralogy and Water Content Interact to Control Soil Organic Matter Stabilization

14:20–14:30 Break

14:30–15:00 Mohammad Afsar* (invited), Bruce Vasilas, and Yan Jin: Colloidal Organic Carbon: Molecular Composition and Dynamics in Seasonally Flooded Depressional Wetland

15:00–15:30 Mike C Rowley* (invited), Stephanie Grand, Jorge Spangenberg, and Eric P Verrecchia: Investigating the Influence of Ca on Soil Organic Carbon Dynamics in Swiss Subalpine Grassland


15:50–16:00 Break

16:00–16:10 SSSAJ Special Issue Discussion

16:10–16:30 Jackson Nkoh Nkoh*, and Renkou Xu: Interaction of Variable Charge Soils with Bacteria: The Important Role Bacteria Play in Maintaining a Healthy Soil

Poster Presentation


**Theme V, Session 5 [Zoom Room 5]**

**Extraterrestrial Clays: Insight from Earth-Based Studies**

**Organizers:** Rebecca Lybrand, Tanya Peretyazhko, and Brad Sutter


13:30–14:00  Keisuke Fukushi* (invited speaker), Yasuhito Sekine: *Water Chemistry of Early Mars Recorded in Interlayer of Smectite and Secondary Minerals from Gale*

14:00–14:20  Anthony Feldman*, Elisabeth Hausrath, Elizabeth Rampe, Tanya Peretyazhko, and Oliver Tschauner: *Serpentine Soils Provide Constraints on Clay Mineral and Amorphous Material Relationships in Ferromagnesian Environments Similar to Gale Crater, Mars*

14:20–14:30  Break

14:30–14:50  Aditi Pandey*, Paul Schwab, and Doug W. Ming: *Analysis of X-Ray Amorphous Phase Abundance and Composition in Basaltic Samples as Potential Amendments for Martian Soil Analogues*


15:10–15:30  Matthew A Nellessen*, Laura Crossey, Patrick Gasda, Eric Peterson, Nina Lanza, Adriana Reyes-Newell, Dorothea Delapp, Christopher Yeager, Roger C Wiens, Sam Clegg, Shelbie Legett, and Debarati Das: *Boron Adsorption onto Clay Minerals: Implications for Martian Groundwater Geochemistry*


15:50–16:00  Break

**Poster Presentations**

16:00–17:30  Debarati Das*, Patrick Gasda, Kim Berlo, Richard Leveille, and Roger Wiens: *Fluid-Clay-Evaporite Interaction: An Analog for Evaporite Geochemistry in Gale Crater*

Tanya S Peretyazhko*, Arlaine Sanchez, Silas J Ralston, Brad Sutter, and Douglas W Ming: *Formation of Fe(III)-Bearing Dioctahedral Smectite on Mars*

Valerie M Tu*, Elizabeth B Rampe, Richard V Morris, Sarah E Perry, and Joanna Clark: *Partially Chloritized Smectites: Analogues for Smectite in Gale Crater, Mars*

Brad Sutter*, Silas J Ralston, Tanya S Peretyazhko, and Douglas W Ming: *Smectite Formation Under Acidic Conditions on Early Mars: An Experimental Flow-Through Assessment*
Tuesday, October 20, 2020
Morning Sessions

Theme I, Session 2 [Zoom Room 1]

Fundamental Shale Research at the DOE National Laboratories Focusing on Fossil Energy (Department of Energy, Office of Fossil Energy)

Organizers: Christina Lopano and Dustin Crandall

9:30–10:00 Elena Melchert (Keynote Talk DOE): Basin-Specific Oil and Gas Research Strategy: Increase Ultimate Recovery and Operational Efficiency


10:40–11:00 Wei Xiong*, Johnathan Moore, Mengling Stuckman, Hang Deng, Dustin Crandall, Alexandra Hakala, and Christina Lopano: Barite Scaling in Stagnation and Flow Zones During Hydraulic Fracturing in Marcellus Shale

11:00–11:20 Shane Butler*, Alexander Azenkeng, Blaise Mibeck, and Bethany Kurz: Advanced Image Analysis of SEM Photomicrographs to Enhance Understanding of Unconventional Reservoir Pore Space and Matrix Materials in the Bakken Formation in the Williston Basin


11:40–12:00 Marco Voltolini*, Timothy Kneafsey, Seiji Nakagawa, Sharon Broglin, and Adam Jew: Influences of Acid Treatment on Proppant Behavior in Fractured Shales Reservoirs: Insights from In-Situ Synchrotron X-Ray Micro-Imaging


Theme II, Session 6 [Zoom Room 2]

Redox Reactions of Clays and Clay Minerals in Natural and Engineered Systems

Organizers: Anke Neumann and Keith D. Morrison

9:30–9:50 Jordan Stanberry, Ilana Szlamkowicz, David Magno, and Vasileios Anagnostopoulos*: TcO2 Oxidative Dissolution by Manganite and Bixbyite Under Anaerobic Conditions

9:50–10:10 Drew E. Latta*, Kevin M. Rosso, and Michelle M. Scherer: Searching for a “Reactive” Ferrhydrite Phase During Fe(II)-Catalyzed Ferrhydrite Transformation Using Mössbauer Spectroscopy


10:50–11:00 Break

11:00–11:20 Pauline Simonnin*, Hailiang Dong, Anke Neumann, and Kevin M. Rosso: Transverse Electron Exchange Pathways in Nontronite From First Principles

Poster Presentations

11:20–12:20 Ethan Coffin* and Hailiang Dong: Stimulation of Microbial Fe(III) Reduction in Nontronite by Biochar

Olufemi Dayo-Olagbende* and Babatunde Sunday Ewulo: Ionic Mobility of Cations as Affected by Redox Status of Two Different Soil Types

Małgorzata Lempart*, Arkadiusz Derkowski, and Artur Blachowski: Forgotten Minnesotaite as Relevant Fe(II)-Bearing and H2-Releasing Phyllosilicate
Theme II, Session 1 [Zoom Room 3]

Impacts of In Situ Remediation and Waste Disposal on Local Mineralogy

Organizers: Hilary Emerson and Katherine Muller (PNNL), Amy Hixon and Ashleigh Kirstin Sockwell (Notre Dame), Lindsay Shuller-Nickles (Clemson), and Timothy Dittrich (Wayne State)


9:50–10:10 Emerson, HP, CI Pearce, BA Powell, KJ Cantrell, DI Kaplan, CH Delegard, MMV Snyder, M-L Thomas, DD Reilly, VL Freedman: Comparison of Tetravalent Actinide Interactions with Sediments at the Hanford Site and Savannah River Site

10:10–10:30 Presentation withdrawn

10:30–10:50 Sockwell, AK, F Zengotita, A Vento, D T Reed, J Swanson, J Dickson, Y Katsenovich, and H P Emerson: Mobility of Actinides (+3, +4, and +6) in the Presence of Dolomite – Effect of EDTA and Ionic Strength

10:50–11:00 Break

11:00–11:20 Katsenovich, Y, RT Gort, R Gudavalli, N Qafoku, J Szecsody, V Freedman, and L Lagos: Incorporation of Iodate in Calcium Carbonate at Variable pH and Si Concentrations

11:20–11:40 Kerisit, SN, MP Prange, SA Saslow, NP Qafoku, FN Smith, ME Hoover, AR Lawter, EJ Bylaska, and ES Ilton: Elucidating the Modes of Contaminant Incorporation in Minerals Using Molecular Simulation

11:40–12:00 L R Sadergaski, M Said, and A E Hixon*: Calcium-Facilitated Aggregation and Precipitation of U_{60} in the Presence of Na-Montmorillonite

12:00–12:20 Bollinger, D, ID Akin, and J McCloy: Transformation of Sodalite/Cancrinite Minerals to and from Clays in the Context of Industrial Wastes
Theme III, Session 3 [Zoom Room 4]

Clay Swelling and Aggregation: Modeling and Experiments

Organizers: Louise Criscenti (Sandia National Laboratory) and Laura Lammers (University of California, Berkeley)

9:30–10:00 Abhay Goyal, Hejian Zhu, Benoit Carrier, Matthieu Vandamme, Katerina Ioannidou, Andrew Whittle, Emanuela Del Gado, and Roland Pellenq*: Clays and Cement Under the Nanoscope: Bridging the Gap… from Atomic-scale Descriptions to the Micron-scale

10:00–10:20 Xinyi Shen* and Ian C Bourg: Free Energy of Aggregation of Charged Colloids (Smectite Clay) in Liquid Water from Molecular Dynamics Simulations

10:20–10:50 Thomas Underwood* and Ian Bourg: From Atoms to Aggregates: Large-Scale Molecular Dynamics Simulation of the Dehydration of a Suspension of Smectite Clay Nanoparticles

10:50–11:00 Break

11:00–11:20 Inna Kurganskaya* and Andreas Luttge: Charge and Aggregation Properties of Illite Nanoparticles Studied by Kinetic Monte Carlo Approach

11:20–11:40 Louise Criscenti*, Jeffery Greathouse, and Tuan Ho: Simulations of Gibbsite Nanoparticles and Aggregates

11:40–12:20 Michael L Whittaker*, David Ren, Colin Ophus, Laura N Lammers, Laura Waller, Benjamin Gilbert, and Jillian F. Banfield: Coupling Between Solution Chemistry and Clay Minerals

12:20–13:00 Lunch Break

Theme V, Session 1 [Zoom Room 5]

Clays and Rare-Earth Elements Cycling

Organizers: Chris Brown and Eirik Krogstad (PNNL)

9:30–9:50 Chares Nye* and Davin Bagdonas: Permissive Evidence for REE Concentration in Association with Clay-Rich Bounding Layers of Coal


10:10–10:30 Debora Berti*, Niall Slowey, and Youjun Deng: Rare Earth Nanominerals Formed by Alteration of Volcanic Ash in the Late Eocene Texas Coastal Plains

10:30–10:50 Christina Lopano*, Mengling Stuckman, Scott Montross, and Circe Verba: Synchrotron mXRF and mXANES Analysis on Rare Earth Speciation and Distribution in Select Appalachian Basin Underclays

10:50–11:00 Break

11:00–11:20 Steve Shen*, Eirik Krogstad, Chris Brown, and Elise Conte: Rapid Unseparated Rare Earth Element Analysis by Isotope Dilution Multicollector Inductively Coupled Plasma Mass Spectrometry (ID-MC-ICP-MS)
Tuesday, October 20, 2020
Afternoon Sessions

Theme I, Session 3 [Zoom Room 1]

Advancements in the Application and Characterization of Clay Minerals in the Petroleum Industry

Organizers: Dr. Hasmukh A. Patel (Aramco Americas) and Dr. Rolland Pellenq (MIT)


13:40–14:00 Ali Ettehadi* and Gurşat Altun: Comprehensive Evaluation of Sepiolite Clay Based Drilling Fluid Under Viscous and Viscoelastic Deformation at Hostile Drilling Conditions

14:00–14:20 Jeffery Greathouse*, Daniel Long, Guangping Xu, Hongkyu Yoon, and Katherine Jungjohann: Molecular-Scale Studies of Surfactant Partitioning on Muscovite Surfaces

14:20–14:30 Break


15:10–15:30 Ashok Santra*, Hasmukh Patel, and Carl Thaemlitz: Applications of Clay and Minerals in Drilling and Cementing Fluids

Poster Presentations

15:30–16:30 Ahmed Radwan* and Mohsen M Attia: The Influence of Clay Mineralogy on Reservoir Damage of Carboniferous Sandstone in Gulf of Suez Rift Basin, Egypt

Jothibasu Ramasamy*: Applications of Laponite Nanoclay in Drilling Fluids
Theme II, Session 4 [Zoom Room 2]

Colloid Mobilization and Colloid-Facilitated Contaminant Transport in the Subsurface

Organizers: Fred Zhang, Jianying Shang, and Kenton Rod

13:00–13:30  Scott Bradford*: Clay Mobilization and Facilitated Transport of Contaminants in the Subsurface

13:30–14:00  Jie Zhuang*: Colloid-Mediated Transport of Antibiotics Through Chemically Heterogeneous Porous Media

14:00–14:20  Bei Yan, Yanjie Shen, Jennifer Yao, Xiao-ying Yu, and Jinxia Liu: Distribution of Novel Per- and Polyfluoroalkyl Substances on Montmorillonite

14:20–14:30  Break


15:30–15:50  Peyman Babakhani: Size Dynamics Control the Fate and Transport of Nano-Particulate in the Environment: Toward an Accurate and Efficient Model

15:50-16:00  Break

16:00-16:20  Presentation Withdrawn

16:20-16:40  Fred Zhang, Christopher Strickland, Markus Flury, and Ziru Liu: Colloid-Facilitated Radionuclide Transport Under Field Conditions

16:40-17:00  Jianying Shang and Chaorui Yan: Dissolved Organic Matter Plays Important Role in Clay Colloid Transport
Theme II, Session 2 [Zoom Room 3]

Role of Minerals in Concentrating Radionuclides at the Molecular and Landscape Scales

Organizers: Daniel I. Kaplan, John C. Seaman, and Yuji Arai

13:00–13:20  
Debashish Banerjee and Andrey G. Kalinichev*: Molecular Dynamics Simulation of the Effects of Small Organic Molecules on the Adsorption and Transport of Radionuclides in Clay Materials

13:20–13:40  

13:40–14:00  
Daria Boglaienko*, Tatiana Levitskaia, Ravi Kukkadapu, Yingge Du, Jennifer Soltis, Hilary Emerson, and Yelena Katsenovich: Heterogeneous Tc4+ Sequestration by Iron Granules

14:00–14:20  
Daria Boglaienko*, Odeta Qafoku, Libor Kovarik, Ravi Kukkadapu, Hilary Emerson, Yelena Katsenovich, and Tatiana Levitskaia: Unique Geological Formations in the Iron Based Tc-99 Reductive Removal Aqueous Media

14:20–14:30  
Break

14:30–14:50  
Nur Shahidah Abdul Rashid*, and Wooyong Um: Oral Bioaccessibility Fraction of Uranium and Thorium in Contaminated Soil

14:50–15:10  
Nikolla Qafoku*: The Role of Natural, Incidental, and Engineered Nanoparticles in Controlling Contaminant Behavior in Nuclear Waste Contaminated Sites: A Review

15:10–15:30  

15:30–15:50  
Daniel I. Kaplan*, Ralph Nichols, Chen Xu, Peng Lin, and P. H. Santschi: Aqueous Radioiodine Concentrations over 20 Years in a South Carolina Wetland

15:50–16:20  
Masahiko Okumura, S. Kerisit, I. Bourg, L. Lammers, T. Ikeda, M. Sassi, K. Rosso and M. Makida.: Mechanism of inhomogeneous concentration of Cs in 2:1 clay minerals: Systematic numerical studies
Theme III, Session 3 [Zoom Room 4]

Clay Swelling and Aggregation: Modeling and Experiments

Organizers: Louise Criscenti and Laura Lammers

13:00-13:20  Laura Lammers*, Nithya Subramanian, Michael Whittaker, Francis Claret, Stephane Gaboreau, Michael Sitar, and Benjamin Gilbert: Solid Solution Thermodynamics Regulate Swelling in Chemo-Mechanically Coupled Clay


14:00-14:20  Tasneem Ahmadullah* and Maria Chrysochoou: Evaluation of Reaction Kinetics in Chemical Soil Stabilization

14:20-14:30  Break

14:30-14:50  MD Amanullah* and Mohammed Al Arfaj: Inhibition Durability Index – Impact on Time Dependent Borehole Instability of Reactive Shales and Mudrocks
Theme V, Session 7 [Zoom Room 4]

General Clay Science

Organizers: Amanda Lawter, Nik Qafoku, and Jim Amonette

14:50-15:10 Narendra Adhikari*, Aashish Tuladhar, Zheming Wang, and Kevin Rosso: Molecular Hydrophobicity of the Water Monolayer on MgO Single Crystal Surfaces


15:30-16:00 Break

Poster Presentations

16:00-17:40

J Marion Wampler*: Propagation of a Misconception in Mainstream Scientific Literature: A Failure of Peer Review

Seungyeol Lee* and Huifang Xu: Using Synchrotron Radiation Powder Diffraction and X-Ray/Neutron Pair Distribution Function to Refine Kaolinite Structure

Jeremy Jones*, Moticha Franklin, and Antonio Lara: Efficacy of Fired Natural Clays for the Sequestration of Aqueous Uranium and Lead

Sarah Bockisch* and Antonio Lara: The Effects of Firing Temperature on the Sorption Efficacy of Fired Clay Pellets

Moticha Franklin*, Jeremy Jones, and Antonio Lara: Nitrogen, Carbon Dioxide, and Argon Adsorption for Surface Area of an Unknown New Mexico Clay in order to Elucidate Uranium Abatement

Joshua Herrera* and Antonio Lara: Effect of Chloride Salt Solutions (LiCl, NaCl, and KCl) on Unconfined Compressive Strength of Heat-Treated Clay Pellets Made for the Abatement of Uranyl in Contaminated Water

Di Pietro S., H.P. Emerson, N. Qafoku, and J.E. Szecsody: Variable Redox Conditions and Alkaline Treatment in Phyllosilicate Minerals
**Theme V, Session 6 [Zoom Room 5]**

**Clays for Antibacterial/Medicinal Applications**

*Organizers: Youjun Deng and Jakub Matusik*

<table>
<thead>
<tr>
<th>Time</th>
<th>Presentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>13:00–13:20</td>
<td>Youjun Deng*: <em>Common Features in the Bonding of Biological Toxins and Pharmaceutical Medicine to the Surfaces of Clay Mineral</em></td>
</tr>
<tr>
<td>13:20–13:40</td>
<td>Bidemi Fashina* and Youjun Deng: <em>Adsorption of Pyocyanin by Smectites</em></td>
</tr>
<tr>
<td>13:40–14:00</td>
<td>Jakub Matusik* and Youjun Deng: <em>Fumonisin FB1 Interaction with Mg-Al and Mg-Fe Layered Double Hydroxides: Removal Efficiency and Mechanisms</em></td>
</tr>
<tr>
<td>14:00–14:20</td>
<td>Bidemi Fashina* and Youjun Deng: <em>Mechanism of Adsorption of Atrazine on Smectites</em></td>
</tr>
<tr>
<td>14:20–14:30</td>
<td>Break</td>
</tr>
<tr>
<td>14:30–14:50</td>
<td>Bidemi Fashina* and Youjun Deng: <em>Adsorption of Pyocyanin by Smectites</em></td>
</tr>
<tr>
<td>14:50–15:10</td>
<td>Presentation withdrawn</td>
</tr>
<tr>
<td>15:10–15:30</td>
<td>Presentation withdrawn</td>
</tr>
<tr>
<td>15:30–15:50</td>
<td>Bidemi Fashina* and Youjun Deng: <em>Mechanism of Adsorption of Atrazine on Smectites</em></td>
</tr>
<tr>
<td>15:50–16:10</td>
<td>Presentation withdrawn</td>
</tr>
</tbody>
</table>
Wednesday, October 21, 2020

Plenary Morning Session

7:30-9:30

The Clay Mineral Society Reception and Award Presentations

Reynolds Cup Award Winners

CMS Business Meeting
Wednesday, October 21, 2020
Morning and Afternoon Session

Workshop and Panel Discussion

A Hanford Perspective on Environmental Remediation

Organizers: Debra Barnett and Frances Smith

10:00-10:10  Frances Smith* and Debra Barnett: A Hanford Perspective on Environmental Remediation: Workshop Overview

10:10-10:40  Brett Simpson*, Mark Triplett, and Mark Freshley: Hanford Soil and Groundwater: Production Mission Overview

10:40-11:10  Katherine Muller*, Christopher Bagwell*, Mike Truex, and Mark Triplett: Overview of the Hanford Site’s Cleanup Mission

11:10-11:20  Break


12:20-13:00  Lunch Break

13:00-13:30  Hilary Emerson*, Mike Truex, and Vicky Freedman: Environmental Remediation of the Hanford Site’s Central Plateau Vadose Zone

13:30-14:00  Adam Mangel*, Judy Robinson*, Inci Demirkanli, and Mike Truex: Hanford Central Plateau Groundwater: Strategies and Implementation for Cleanup and Monitoring

14:00-14:10  Break

14:10-14:40  Carolyn Pearce*, Mark Triplett, and Vicky Freedman: Central Plateau Tanks

14:40-15:10  Nicolas Huerta and Vicky Freedman: Environmental End States Considerations for the Hanford Site

15:10-15:30  Break

15:30-16:30  A Hanford Perspective on Environmental Remediation: Workshop Discussion Panel
Thursday, October 22, 2020
Morning Sessions

Theme II, Session 3 [Zoom Room 1]

Advances in Understanding Clay-Based Barrier Systems for Deep Geological Repositories

Organizers: Sarah Saslow, Matthew Asmussen, Carlos Jove-Colon, Stephan Kaufhold, and Mark Nutt

9:30–9:50 Stephan Kaufhold*, Reiner Dohrmann, and Kristian Ufer: About the Effect of Reactive Silica on the Bentonite Performance at Interfaces

9:50–10:10 Nadine Kanik*, Fred Longstaffe, and Arkadiusz Derkowski: Impact of Interlayer Cation Composition on Smectite δ2H


10:50–11:00 Break

11:00–11:20 Huifang Xu*, Wenbin Yu, Eric Roden, and Quan Wan: Nano-Tubular Clay Minerals of Chrysotile and Halloysite as Barrier Materials for Immobilizing Radioactive Iodine

11:20–11:40 Presentation withdrawn

**Theme III, Session 1 [Zoom Room 2]**

**Visualizing Solution Structure at the Mineral Aqueous Interface**

*Organizers: Elias Nakouzi and Joanne Stubbs*

9:30–10:00 Sander Brugman and Elias Vlieg: *Interface Structure of Mica and Calcite with Electrolyte Solutions*

10:00–10:20 Benjamin Legg and James De Yoreo: *Visualizing Aluminum Ions, Clusters, and Crystalline Films at the Mica-Water Interface with In-Situ AFM*

10:20–10:40 Aashish Tuladhar, Marcel D Baer, Benjamin A Legg, Narendra M Adhikari, Zheming Wang, Christopher Mundy, Hong-fei Wang, and James J De Yoreo: *Probing Cation Speciation at Mica-Aqueous Interface using Vibrational Sum Frequency Generation Spectroscopy*

10:40–11:00 Break


11:20–11:40 Geoffrey Monet, Erwan Paineau*, Gilberto Teobaldi, Stéphane Rols, and Pascale Launois: *Control of the Structure and Dynamics of Water by Clay Nanotubes*

11:40–12:10 Piotr Zarzycki and Benjamin Gilbert: *Dielectric Properties of Clay/Electrolyte Interface and Clay Interlayers – Implications for Swelling, Aggregation, and Sorption*

12:10–12:30 Sebastien Kerisit, Elias Nakouzi, and James De Yoreo: *Molecular Simulation of Interfacial Water Structure and Effects on Particle Attachment*

12:30–13:00 Lunch Break

---

**Theme III, Session 4 [Zoom Room 3]**

**Nanomechanical Properties of Layered Materials: Toward Hierarchical Theories of Bulk Properties**

*Organizers: Michael Whittaker and Benjamin Gilbert*

9:30–10:00 Tianhao Wu: *Nanomechanical Properties of Organic-Rich Shale and Kerogen by Nanoindentation and Molecular Dynamics Simulations*

10:00–10:30 Harrison Lisabeth, Brian Bonner: *The role of water in anelasticity of clay materials*

10:30–10:50 Evgeny V Tararushkin* and Andrey G Kalinichev: *Atomistic Simulations of Brucite Compressibility Over Wide Ranges of Pressure and Temperature*
Theme IV, Session 1 [Zoom Room 4]

Clays and Climate Change

Organizers: Jim Amonette, Nancy Hess, and Ravi Kukkadapu


10:00–10:20  Susannah Burrows*, Isabelle Steinke, Gavin Cornwell, Gourihar Kulkarni, Swarup China, and Alla Zelenyuk: *Atmospheric Ice Nucleation by Soils and Dusts, and its Role in Climate*

10:20–10:40  Judy Q Yang*, Xinning Zhang, Ian C Bourg, and Howard A Stone: *4-D Imaging of Clay Reveals Soil-Carbon Dynamics*

10:40–11:00  Break

11:00–11:30  Cassandra Gaston: *The Impact of African Dust Transport on Biogeochemical Cycles in the Amazon Basin and Tropical Atlantic Ocean*

**Poster Presentation**

11:30–12:30  Gourihar Kulkarni*, Susannah Burrows, and Swarup China: *Quantification of Aerosol Particles Generated Through Raindrop Impaction*
Theme V, Session 2 [Zoom Room 5]

‘Putting Numbers’ on Clay Mineral Analyses, Approaches, and Applications across Ocean, Earth, and Extra-Terrestrial Sciences

Organizers: Steve Hillier, Mark Raven, and Kristian Ufer


9:50–10:10 Ruijun Sun and Lesley McGilp: Automated On-line Active Clay Analyzer in Mineral Slurries

10:10–10:30 Huseyin Demir* and Paul Schroeder: Comparison of X-Ray Powder Diffraction and Geochemical Data Using Principal Component Analysis (POSTER)

Theme V, Session 3 [Zoom Room 5]

Incipient Weathering of Primary Minerals to Clay Minerals: Biological and Physical Factors

Organizers: Paul Schroeder, David D’Amore, Ashlee Dere, Rebecca Lybrand, Raquel Portes, Diogo Spinola, and Tom Trainor


11:40–12:00 Rebecca Lybrand*, Paul Schroeder, Dragos Zaharescu, and Odeta Qafoku: A Focused View of an Incipient Fungal-Mineral Interaction and its Putative Weathering Product

12:00–12:20 Magdalena Makiel*, Michal Skiba, Katarzyna Maj-Szeliga, Marta Kisiel, Artur Blachowski, and Wojciech Szymański: Weathering of Glauconite in Soils of Temperate Climate

Thursday, October 22, 2020
Afternoon Sessions

Theme I, Session 1 [Zoom Room 1]

Oil Sands Tailings Clay Challenge

Organizer: Heather Kaminsky

13:00-13:30  Bradley Komishke* and Lucas Barr: Cosia’s Clay Challenge

13:30-13:50  Jason Ng* Heather Kaminsky, and Andrea Sedgwick: An In-Depth Look at Methylene Blue Index Titration

13:50–14:10 Narain Hariharan*, Nikolas Romaniuk, Mike Tate, Jesse Fox, and Dallas Little: Physicochemical and Geotechnical Evaluation of Lime Treated Fluid Fine Tailings

14:10-14:30 Yeling Zhu*, Michael Chae, Birendra Adhikari, Vinay Khatri, Heather Kaminsky, Paolo Mussone, and David Bressler: Consolidation of a Kaolinite Suspension Using a Protein-Based Flocculant

14:30-14:50 Wrap up discussion led by Heather Kaminsky

Theme III, Session 1 [Zoom Room 2]

Visualizing Solution Structure at the Mineral Aqueous Interface

Organizers: Elias Nakouzi and Joanne Stubbs

13:00-13:30 Yuanzhong Zhang, Rundong Huang, Xuanlin Du, Sang Bum Kim, and Younjin Min*: Nanoscale Forces and Nonlinear Transport Behaviors of Geocolloids Under Nanoconfinement

13:30–13:50 Mavis Boamah*, Xiaopeng Huang, Zheming Wang, and Kevin Rosso: Determination of the Reaction Dynamics and Electron Transfer Processes at Oxide/Aqueous Interfaces

Theme I, Session 4 [Zoom Room 4]

The Evolution of Micro- and Nanoporosity in Black Shales

Organizers: W. Crawford Elliott, R. Douglas Elmore, and Lawrence M. Anovitz

13:00-13:20 David Cole*: Multiscale Assessment of Pore Structures in Unconventional Gas Shale Systems

EMERGING METHODS IN CLAY SCIENCE

Organizers: Eugene S. Ilton and Ravi K. Kukkadapu


15:00–15:30 Jim De Yoreo*: High-Speed, Atomically Resolved AFM as a Tool for Investigating Solvent Structure and Surface Dynamics at Clay-Water Interfaces


16:00–16:10 Break

16:10–16:40 Amity Andersen*: Investigating Organic-Mineral Interactions with Large-Scale Classical Molecular Dynamics

16:40–17:10 Discuss Special Issue
Friday, October 23, 2020
Morning Sessions

CMS Workshop

Emerging Methods in Clay Science

Organizers: Eugene S. Iltan and Ravi K. Kukkadapu

7:30–8:00  Joanne E. Stubbs*: Interfacial Scattering from Small Surfaces: Adapting Mineral-Fluid Structure Methods for Microcrystalline Material

8:00–8:30  Olaf J. Borkiewicz*, Sebastian T. Mergelsberg, Micah P. Prange, and Uta Ruett: In Situ and Operando Structural Analysis of Amorphous Thin Films and Interfaces by Grazing-Incidence High-Energy Total X-Ray Scattering

8:30–8:45  Break

8:45–9:15  Niri Govind* and Micah P. Prange: Simulating X-Ray Spectroscopies: Theory and Applications

9:15–9:45  Eric J. Bylaska*: Development of Novel First Principles Simulations for Reactions and Spectroscopic Analysis at Complex Geochemical Interfaces

ICDD Workshop

X-ray Diffraction Applications: JADE software

International Centre for Diffraction Data

10:00 am – 13:15 pm
Friday, October 23, 2020
Afternoon Session

Virtual Geology Field Trip

13:30–15:00

Geologist-author Bruce Bjornstad will present "Ice Age Floodscapes of the Pacific Northwest" highlighting informative aerial images of Ice Age flood features captured via drone and fixed-wing airplane. Photos and images will be included in his new book, with the same name, published by Springer-Nature and available in early 2021.

www.BruceBjornstad.com
ABSTRACTS (IN ALPHABETICAL ORDER BY FIRST AUTHOR)

Frenchman Coulee (looking west), Grant County, WA, USA
Oral bioaccessibility fraction of Uranium and Thorium in Contaminated Soil

Nur Shahidah Abdul Rashid¹ and Wooyong Um¹,*

¹Division of Advanced Nuclear Engineering (DANE), Pohang University of Science and Technology (POSTECH), Republic of Korea.
*Corresponding author. Tel: +82-542799563 , Email: wooyongum@postech.ac.kr

Thorium-232 (²³²Th) and uranium-238 (²³⁸U) are naturally occurring radioactive materials (NORM) and are considered as primordial radionuclides, which can be found at trace levels in the biosphere. Virtually all materials found in nature contain some concentration of terrestrial radionuclides. Due to human activities, such as ²³²Th and ²³⁸U milling, enrichment, nuclear energy production and decommissioning, nuclear industry occupational workers and members of the public can be exposed to ²³²Th and ²³⁸U. The general population is chronically exposed to ²³²Th and ²³⁸U mainly through oral ingestion. In the case of the nuclear decommissioning process and severe accident, incidental ingestion of contaminated media can compromise a significant risk to animals and humans. Thus, toxicity and exposure assessment to quantify the human intake of ²³²Th and ²³⁸U in the contaminated media via oral ingestion is necessary. In this context, to obtain a better description of the toxicological mechanisms associated with actinides on a molecular scale, ²³²Th and ²³⁸U oral bioaccessibility fraction (²³²Th/²³⁸U-BAF) were assessed using the in vitro Unified BARGE Method (UBM) in the contaminated soil. In the present work, the results of both ²³²Th- and ²³⁸U-BAF in contaminated IAEA-312 standard reference soil showed that the ²³²Th-BAF in the gastric phase and gastrointestinal phase ranged from 0.035-0.059% and 0.014-0.022%, respectively. On the other hand, ²³⁸U-BAF in the gastric phase and gastrointestinal ranged from 0.020-0.037% and 0.003-0.021%, respectively. Generally, ²³²Th tends to hydrolyze in the gastric phase to form Th(OH)₂²⁺ species, whereas in the gastrointestinal phase, the formation of Th(OH)₃(CO₃)- had caused retention. The presence of high concentrations of phosphate may cause the precipitation of (UO₂)₃(PO₄)₂·4H₂O(s), following the decrease in pH between the gastric and intestinal (gastrointestinal) assay. Therefore, ²³²Th- and ²³⁸U-BAF are largely dependent on the chemistry of lixiviants and the influence of precipitate formation in the digestive assay. Additionally, the coexistence of ferum, calcium, and phosphorus in the gastric and gastrointestinal phases played a crucial role in reducing ²³²Th- and ²³⁸U-BAF. These findings will promote the development of robust exposure narratives for ²³²Th and ²³⁸U contaminated soil in nuclear decommissioning and nuclear facilities.
MOLECULAR HYDROPHOBICITY OF THE WATER MONOLAYER ON MgO SINGLE CRYSTAL SURFACES

Narendra M. Adhikari*, Aashish Tuladhar, Zheming Wang, James J. De Yoreo, and Kevin M. Rosso

Pacific Northwest National Laboratory, Richland, WA 99352

Due to its simple crystal structure, MgO is a model system for the study of surface structure and reactions of oxides. Many theoretical and experimental studies have been carried out to understand how the MgO surface interacts with water, yet the molecular-level picture of the surface structure of the MgO-water interface is not clear. It is generally agreed that water molecularly physisorbs on the defect-free MgO surface and the presence of the low coordinated defect sites such as step edges, corners, kinks, divacancies, valleys, etc. results in the dissociative chemisorption of the water on the surface. In this study molecular structure at the air and water interface of the single crystal MgO surface is studied using the surface-specific second-order non-linear vibrational sum frequency generation (vSFG) spectroscopy. Results show that the surface of the single crystal MgO is hydroxylated at the ambient conditions and the vSFG spectra from the MgO/water interface are mainly dominated by spectral features from the MgO surface. The vSFG spectra in the MgO-water interface are significantly different than the spectra reported for the silica-water or alumina-water interface. For silica or alumina-water interface, the vSFG spectra are dominated by the vibrational signature from the H-bonded water in the electric double layer. However, MgO-water interface spectra show very little to no signature from such water molecules. This observation is unique and shows that there is minimal to no spectral signature from the H-bonding interaction between MgO surface hydroxyl groups and the water which is consistent with the relatively non-wetting behavior of water at the hydroxylated MgO surface.
Colloidal organic Carbon: Molecular composition and dynamics in seasonally-flooded depressional wetland

Mohammad Z. Afsar, Bruce Vasilas, and Yan Jin

Department of Plant and Soil Sciences, University of Delaware, Newark, DE-19716, USA.

Redox-induced biogeochemical transformations are the key processes that control the stability of soil organic carbon (OC) via association with metal oxides in seasonally-inundated depressional wetlands. Given the particularly significant role of wetland soils in C storage (20-30% of terrestrial C) and cycling, the dynamics of soil colloids (1-1000 nm) and colloidal OC and their molecular composition remain a critical knowledge gap. Here we present size distribution, concentration, and composition of organo-mineral associations in pore water samples from a depressional wetland located in Delaware, USA, as influenced by seasonal fluctuations in water table level. The samples were collected from piezometers installed at multiple depths (50 cm, 100 cm, and 200 cm) and in three zones (upland, transitional, and wetland), respectively. Four size fractions were analyzed: dissolved (<2.3 nm), natural nanoparticle (2.3-100 nm, NNP), fine colloid (100-450 nm), and particulate (450-100 nm). Our results revealed that dissolved, NNP, fine colloid, and particulate fractions comprised 47 ± 4.1%, 37 ± 4.0%, 8 ± 2.8% and 8 ± 2.7% of the bulk OC (<1000 nm) concentration, respectively. Isotope ratio mass spectrometry analyses demonstrate enrichment of heavier δ¹³C stable isotopes in the upland in comparison to the transition and wetland zones. NNP was more enriched in δ¹³C than the larger size fractions. X-ray photoelectron spectroscopy further confirmed that the NNP fraction had a greater proportion of mostly oxidized OC, while the particulate fraction had more aliphatic/aromatic OC functional groups. These findings clearly demonstrate that there are significant differences in elemental composition among the different organo-mineral size fractions, which imply the importance of taking into consideration of NNP and fine colloid fractions separately, as opposed to lumping them into “dissolved” fraction following the conventional definition of 450 nm. Ignoring the contribution of COC would cause significant oversight in the assessment of the cycling and transport of various elements and associated OC in depressional wetlands.
EVALUATION OF REACTION KINETICS IN CHEMICAL SOIL STABILIZATION

Tasneem Ahmadullah¹, Maria Chrysochoou¹

¹Department of Civil and Environmental Engineering, University of Connecticut, Storrs, CT, USA

This study looks into the reaction between two abundant clay minerals (bentonite and kaolinite) and lime, the most common treatment method applied in geotechnical processes for treating the subgrade soil. The pozzolanic reactions in the lime-clay system are monitored over time in the solid by quantitative $^{29}$Si and $^{13}$Al NMR, TGA-DTA, XRD and in the extracted pore water solution via chemical analysis. A thermodynamic and kinetic model of the system will be developed using cement-based models as reference. A substantial difference between cement hydration and clay pozzolanic reactions is the slower dissolution rate of the clay minerals, requiring years to reach equilibrium compared to months in cement. Therefore, the geochemical model will be refined and extended to field-relevant time frames, and its relationship to strength evolution will be investigated. Finally, the model developed for the pure lime-clay systems will be applied to a real clay soil.
HEAT TREATMENT INDUCED STRUCTURAL CHANGES AND AFLATOXIN ADSORPTION BY DIFFERENT CLAYS

Saba Akbar*1,2, Mohammad S. Akhtar1, Ahmad Khan1,2, Ana L. Barrientos-Velázquez2 and Youjun Deng2

1Institute of Soil Science, PMAS Arid Agriculture University Rawalpindi, Punjab, 46300, Pakistan; 2Department of Soil and Crop Sciences, Texas A&M, Texas, 77843-2474, USA

Aflatoxin causes aflatoxicosis in poultry and livestock and poses serious health hazard to the consumer. Bentonites as binder are effective and used as non-nutritive additive to the prepared feed. Palygorskite and sepiolite with their specific tunnel type structure act as molecular sieve and may be an alternative as aflatoxin binder. Known palygorskite, palygorskite-smectite mix, sepiolite and smectite were tested before and after structural changes through heat treatments.

The clays consisted of (i) a palygorskite and (ii) palygorskite-smectite mix from Pakistan, (iii) palygorskite from Georgia, US, (iv) palygorskite from Xuyi, China, (v) sepiolite from Canabas, Spain, and (vi) smectite 37GR. Bulk clays were powdered and passed through a 150 µm sieve, heat treated at 25 °C, 250 °C, 400 °C, 500 °C and 600 °C for 2 h, and analyzed through X-ray diffraction. Structural changes were determined by comparing infrared spectroscopic patterns before and after the heat treatments. One mg clay was suspended in 10 mL of distilled deionized water, sonicated and a drop of suspension was positioned on ZnS disc, air dried and desiccated overnight. IR spectra was recorded in transmission mode while purging N2. Aflatoxin adsorption was determined in aqueous and synthetic gastro-intestinal fluid. One mg clay in 50 mL of 4 mg L⁻¹ aflatoxin B1 was agitated at 37 °C overnight, and aflatoxin concentration was measured using UV-VIS spectrophotometer at 365 λ.

The Ca-smectite, 37GR, had 001 diffraction at 15.6 Å when dried at room temperature or heated at 250 °C, and it shifted to 9.7 Å after heating at 400 °C or at higher temperatures. In all the palygorskites dried at room temperature or heated at 250 °C, the 10.5 Å diffraction peak (110 hkl) shifted to 10.0 Å after heating at 400 °C and higher temperatures. Sepiolite’s 110 diffraction at 12.2 Å shifted to 10.0 Å upon heating at 400 °C or higher, and its 060 diffraction at 4.51 Å and 080 at 3.36 Å disappeared after heating at 400 °C and above. The X-ray data suggested change in tunnel size and tube length of palygorskite and sepiolite and a change in the interlayer space in smectite. The IR bands associated adsorbed water (1630 cm⁻¹) in smectite and zeolitic and coordinated water at 3550 cm⁻¹ and 3580 cm⁻¹ disappeared upon heating palygorskite and sepiolite at and above 400 °C. Smectite adsorbed greater aflatoxin compared to sepiolite and palygorskite, and the heat treatments increased aflatoxin adsorption up to 250 °C in smectite and declined thereafter as par decrease interlayer space. In sepiolite aflatoxin adsorption reduction with heat treatments occurred almost progressively which may be associated with structural change. In palygorskite-smectite mix aflatoxin adsorption increased slightly after heating at 400 °C. In gastro-intestinal fluid, pepsin caused a decline in aflatoxin adsorption by all clays though smectite adsorbed three times than sepiolite. The palygorskite and palygorskite-smectite mix clays had the least adsorption both in gastro-intestinal fluid and aqueous solution.

Heat treatments in smectite, palygorskite and sepiolite induced structural changes especially at 400 °C and above differently which increased aflatoxin adsorption in smectite up to 250 °C and reduced in palygorskite and sepiolite.
INHIBITION DURABILITY INDEX — IMPACT ON TIME DEPENDENT BOREHOLE INSTABILITY OF REACTIVE SHALES AND MUD ROCKS

Md. Amanullah* and Mohammed Arfaj

Saudi Aramco

The clay-rich shale and mud rocks encountered while drilling are the major sources of various drilling problems, including time dependent bore problems that can create severe operational problems after successful drilling of a reactive shale section using an inhibitive drilling mud system. The factors that govern the time dependent borehole instability problems are: (a) near wellbore in situ stresses, (b) borehole erosion due to hydrodynamic effect of mud circulation, (c) borehole destabilization due to drilling string movement, (d) time dependent effect of shale drilling fluid interactions, and (e) poor durability of shale inhibition mechanisms that protect the reactive shales from the detrimental action of reactive water molecules of freshwater, non-inhibitive and low inhibitive water-based muds (WBMs). Currently, the industry has no clues about the long-term inhibition potential of conventional shale inhibitors and ways to measure the inhibition durability of conventional, novel, and specially designed shale inhibitors. This paper highlights the development of a novel method for inhibition durability assessment of various shale inhibitors, inhibition durability index (IDI) of several conventional shale inhibitors and their technical and economic significance for current and future drilling operations.

The first stage of the three-stage inhibition durability assessment method is the conventional shale dispersion test, the second stage is the innovative inhibition permanency evaluation test, and the third stage is the determination of the inhibition durability index based on the experimental data. The Inhibition Durability Index (IDI) has been defined as the inhibition breakdown point of the inhibited shale mass recovered after the inhibition permanency assessment stage of the test and the time curves.

Experimental evaluation of the newly developed IDI assessment method demonstrated the suitability of the method to evaluate the long-term inhibition potential of the traditional and specially designed shale inhibitors. The method also provides a fast moving avenue for the synthesis and development of long-life shale inhibitors using the emerging nanotechnology, nanomaterials, dendrimers, hybranes, and their hybrids.

The study indicates that due to the poor durability of the protective inhibition shield or water repelling barrier created by conventional shale inhibitors, a successfully drilled reactive shale section using an inhibitive drilling mud can create a time dependent borehole instability problem, if there is a need to change to a simple WBM or a non-inhibitive water mud, due to some technical and economic reasons. As the time dependent borehole instability problems are one of the major challenges for current and future drilling operation, there is a need to develop long-life shale inhibitors that have a high IDI to prevent or mitigate time-related drilling problems. The newly developed method will act as a powerful catalyst to develop a new generation of shale inhibitors to improve the IDI and prevent the time dependent borehole instability problems.
INVESTIGATING ORGANIC-MINERAL INTERACTIONS WITH LARGE-SCALE CLASSICAL MOLECULAR DYNAMICS

Amity Andersen

*Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland WA 99352*

Molecular dynamics is a powerful tool in studying a broad range of phenomena at the molecular level including those in structural biology, materials science and geochemistry. Soil structure with complex mixtures of organic matter and minerals is a burgeoning and especially challenging application of molecular dynamics techniques. Molecular dynamics for mixtures of soil-relevant bio-organic molecules over mineral surfaces is challenging due to the large number force-field assignments for multiple bio-organic and inorganic molecular topologies. We have been developing software tools to address this challenge, and we will demonstrate the application of molecular dynamics techniques to complex soil-relevant bio-organic molecular mixtures interacting with mineral surfaces including clay mineral surfaces.
CONTROL OF BINDING STRUCTURES ON REACTIVITY IN MINERAL-ORGANIC ASSOCIATIONS: INSIGHTS WITH CLAYS AND IRON OXIDES

Ludmilla Aristilde

1Department of Civil and Environmental Engineering, Northwestern University, Chicago, IL 60608.

Mineral oxides such as clays and iron oxides have long been implicated in controlling the fate of organic compounds, including emerging organic contaminants and biomolecules, in soils and sediments. Of particular interest are the reactivity mechanisms of adsorption and transformation of polar organic compounds by mineral oxides. These organic compounds contain several functional groups and can adopt various structural conformations in solution. However, specific adsorbate structures are required to mediate the favorable intermolecular interactions and thus facilitate recorded reactions at the mineral interfaces. In my group, we have sought to investigate the three-dimensional binding structures that control the reactivity in these mineral-organic associations. In this talk, I will present findings from two main research activities in my group: 1. the selective trapping of antimicrobial compounds within smectite clay interlayers and 2. the selective transformation and trapping of biomolecules by iron oxide minerals (Fig. 1). We have applied experimental techniques (X-ray diffraction, infrared, nuclear magnetic resonance, mass spectrometry, X-ray absorption) coupled with molecular modeling (Monte Carlo and molecular dynamics simulations) to gain new insights on the mechanisms of interactions that serve as precursors to the resulting reactivity in these processes.

Fig. 1. Study of reactivity and adsorbate structures of (A) fluoroquinolone antimicrobials within montmorillonite interlayers and (B) ribonucleotides reacted with goethite.
IMPACT OF ETTRINGITE STABILITY AND TRANSFORMATION ON IODINE RETENTION IN CEMENTITIOUS WASTE FORMS

Nancy M. Avalos*1, Tamas Varga2, Sebastian T. Mergelsberg3, Joshua A. Silverstein1, and Sarah A. Saslow1

1Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, USA; 2Environmental and Biological Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, USA; 3Physical and Computational Sciences Directorate, Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352, USA

Ettringite \([\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}]\) found in cementitious waste forms (CWFs) is known to immobilize iodate \((\text{IO}_3^-)\) via sulfate \((\text{SO}_4^{2-})\) substitution; however, limited studies have investigated the effects of leaching on the long-term fate and behavior of \(\text{IO}_3^-\) retained in ettringites. In this study, ettringite mineral transformation and iodine release from \(\text{IO}_3^-\)-incorporated ettringite \(((\text{IO}_3^-)\text{-Ett})\) were investigated using batch experiments to determine the mechanisms likely to drive \(\text{IO}_3^-\) release/retention within ettringite in environmentally relevant solutions of varying composition, pH, and alkalinity. \((\text{IO}_3^-)\text{-Ett}\) was leached in six simulated solutions relevant to the Hanford Site (Washington State, USA) for a period of 56 days: double deionized water, 24 ppm \(\text{CO}_3^{2-}\), 1400 ppm \(\text{SO}_4^{2-}\), Hanford groundwater, Hanford vadose zone porewater and a cement-equilibrated solution. By monitoring \(\text{IO}_3^-\) uptake and removal and characterizing changes in the solid material, incongruent dissolution of ettringite to calcite and oxyanion substitution into the ettringite structure (e.g., \(\text{SO}_4^{2-}\) or \(\text{CO}_3^{2-}\)) were identified as contributing \(\text{IO}_3^-\) release mechanisms. However, the formation of calcium carbonates, e.g., calcite, may re-incorporate \(\text{IO}_3^-\) (pH < 10) or prevent the release of \(\text{IO}_3^-\) when formed on solution-exposed surfaces of ettringite. These results provide valuable insights into iodine release from CWFs that may be used to improve current CWF formulations for the treatment of iodine-containing nuclear waste.
Size dynamics control the fate and transport of nano-particulate in the environment: toward an accurate and efficient model

Abstract for “Clay Minerals Society 57th Annual Meeting”

Peyman Babakhani
Earth Surface Science Institute, School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK

The size of nano-particulates (NP), whether manufactured or naturally occurring, controls their fate and transport behaviours in the environment. Once manufactured NP are introduced into groundwater environments or naturally-occurring NP are remobilized in such media, the initial particle size distribution (PSD) changes spatiotemporally due mainly to NP aggregation and selective removal of certain size fractions. If such dynamics of the particle size lead to higher mobility of NP within subsurface environments, this can bring about risks of facilitated transport of dissolved contaminants adsorbed onto NP surfaces with potentially higher surface area than their counterpart nonporous colloids. Considering the aggregation of NP in current fate and transport models is imperative whereas it is hindered by high computational expenses, mathematical complexity, and the variable used in current population balance models of aggregation, i.e., particle number concentration being different from that of fate and transport models, i.e., mass concentration.

In this study an accurate population balance model, known as the fixed pivot technique, is combined with an accurate 3-D groundwater numerical model, MT3D-USGS, to investigate the impact of NP aggregation on their transport behaviours in groundwater environments. Special attention is devoted to investigate concurrent occurrence of aggregation with size exclusion mechanism, which has long been known as being responsible for unexpectedly high mobility of colloidal particles in subsurface environments and carrying hazardous contaminants over long distances.

Model simulations at a field-scale shows that aggregation increased NP mobility at regions close to the injection point and retains them at greater distances through alteration of their diffusivities, secondary interaction-energy minima, and settling behaviour. This results in a change of residual concentration profiles from exponential for non-aggregating dispersions to non-monotonic for aggregating dispersions. In order to address high computation expenses encountered in these simulations, further work was conducted to develop a new paradigm for modelling aggregation phenomenon in aquatic environment. This model is based on a chain-reaction expression and uses mass concentration instead of the commonly used state variable in population balance model, i.e., particle number concentration. Assessing the new model against batch experiment data of aggregation and sedimentation of NP, showed that the model fits are comparable or better than a current population balance model in terms of accuracy and efficiency; offering the potential for being combined with various NP fate, transport, and reaction models.
MOLECULAR DYNAMICS SIMULATION OF THE EFFECTS OF SMALL ORGANIC MOLECULES ON THE ADSORPTION AND TRANSPORT OF RADIONUCLIDES IN CLAY MATERIALS

Debashish Banerjee¹, Andrey G. Kalinichev*¹

¹Laboratoire SUBATECH (UMR 6457 - Institut Mines-Télécom Atlantique, Université de Nantes, CNRS/IN2P3), 44300 Nantes, France

Low permeability Callovo-Oxfordian clay formation is under consideration in France as a possible host rock for long-term disposal of radioactive waste in a deep geological repository. The Callovo-Oxfordian rock serves as an efficient natural geochemical barrier for radionuclides mobility, but complexation of radionuclides with organic molecules, naturally present in the pore solution or generated by the waste, may significantly affect their adsorption and transport properties. These organic species, such as small carboxylic acids, can be retained by clay through chemical interactions or physical immobilization [1]. Fundamental molecular scale understanding of the physical and chemical mechanisms controlling their interactions with radionuclides (metal cations) and clay minerals is crucial for the development of reliable predictive models of the long-term behavior of the repositories. We use molecular dynamics (MD) computer simulations [2] in order to quantify the effects of small organic molecules on the adsorption and transport of radionuclides in clay materials.

The structural models of montmorillonite (MMT) with randomly distributed Al/Si and Mg/Al substitutions in the tetrahedral and octahedral clay layers incorporating different interlayer cations i.e. (Na-MMT and Ca-MMT) were systematically developed and generalized as models for Callovo Oxfordian clay [2,3]. Cs⁺ and Sr²⁺ were selected as representative radionuclides having substantial amount of diverse experimental data on its interactions with clay, thus allowing for thoroughful comparison with experiments. Acetate, benzoate, oxalate, phthalate and terephthalate were selected as representative small organic molecules to probe the interaction mechanisms on the molecular scale.

MD simulations of binary systems (clay/radionuclides) have been initially performed in order to obtain the reference data for the investigation of more complex ternary systems (clay/radionuclides/organic molecules). Structural, energetic, and dynamic aspects of the sorption processes on the basal surfaces of clay are quantitatively modelled by MD techniques. Constrained MD simulations for selected specific adsorption sites were performed to determine the adsorption free energy profiles using potential of mean force calculations (PMF).

References
Molar volume changes of montmorillonite and the activity of H₂O in deep saline aquifers: Geologic considerations for CO₂ sequestration

Paolo Andre Benavides*, Jacqueline Kowalik, Stephen Guggenheim and August F. Koster van Groos

Department of Earth and Environmental Sciences, University of Illinois at Chicago, IL, 60607, USA

The effects of the activity of H₂O \([a(H₂O)]\) on the molar volume of montmorillonite (SWy-2) were determined by varying temperature \((T)\), CO₂ pressure \([P(CO₂)]\), and brine concentration. These parameters are important to assess deep saline aquifers as possible reservoirs for CO₂ sequestration. Previous workers have found that CO₂ adsorption in the interlayer is dependent on the H₂O content of montmorillonite, which is dependent on \(a(H₂O)\). At conditions of limited H₂O presence, CO₂ can enter the interlayer of montmorillonite if there is less than one plane of H₂O present, whereas the present study considers conditions of excess H₂O. To determine if CO₂ enters the interlayer under the conditions of this study, we assume that inert gases will not enter the montmorillonite interlayer, and thus, the effects of helium pressure \([P(He)]\) were compared to those of \(P(CO₂)\) at similar \(P-T\) conditions. It is concluded that \(T\) and brine concentration can have a major effect on \(d(001)\) with either a loss or addition of interlayer H₂O, causing molar volume changes in montmorillonite, whereas \(P(CO₂)\) is of less importance.

Na-rich montmorillonite (Na-SWy2), in eight NaCl brine concentrations (0.17 M to saturation) was exposed to increasing \(T\) and \(P\) in an X-ray high-pressure environmental chamber. The \(d(001)\) value was measured after each 25 °C increment (to 150 °C), and after each 100-bar increment (to 500 bars) for \(P(CO₂)\) and \(P(He)\). For \(P(CO₂) = 1\) bar and \(T \sim 33\) °C, increasing brine concentration from 0.34 M to saturation, a 22% decrease in \(d(001)\) from 20.1 to 15.7 Å was observed. A 17% decrease from 18.7 to 15.7 Å was observed when \(T\) was increased from 50 to 150 °C at a brine concentration of 1.71 M. A decrease in \(d(001)\) was observed when \(P(CO₂)\) is increased from 56 to 500 bars at \(T \sim 33\) °C. At 0.17 M brine, an increase in \(P(CO₂)\) showed a decrease in \(d(001)\) from 20.4 to 19.6 Å (8%). Experiments performed with \(P(He)\) shows identical results with \(P(CO₂)\), suggesting that CO₂ does not enter the interlayer and that the \(a(H₂O)\) is the same for \(P(CO₂)\) and \(P(He)\) for these experiments.

Montmorillonite is commonly present in varying abundances in an aquifer and a caprock. In an aquifer, montmorillonite can occur as coatings on sandstone grains. Increasing the \(a(H₂O)\) can lead to the expansion of montmorillonite, reducing the porosity and permeability. In contrast, a decrease in \(a(H₂O)\) resulting to the contraction of montmorillonite can lead to formation of secondary structures, e.g. fractures, compromising the caprock to seal stored CO₂.
PREPARATION OF ILLITE-COATED GEOMATERIAL SURFACE FOR MICROFLUIDIC STUDIES

Rupom Bhattacherjee\textsuperscript{1}, Sushobhan Pradhan\textsuperscript{2}, and Prem Bikkina\textsuperscript{1,2}

\textsuperscript{1}Petroleum Engineering Program, Oklahoma State University, Stillwater, OK 74078, USA; \textsuperscript{2}School of Chemical Engineering, Oklahoma State University, Stillwater, OK 74078, USA

Caney, a Mississippian unconventional play in Southern Oklahoma, USA, is an emerging clay-rich shale and considered to have a huge reserve of hydrocarbons. However, the unique characteristics of clay even though make any clay abundant shales a good source of adsorbed gas, make them equally difficult to produce. Clay increases the ductility of rock. Moreover, the laminated structure of clay, high interlayer distance, and the deficiency of positive charges make those shales highly vulnerable to water-based drilling, fracking, and other injection fluids. The clay-water interaction can cause significant swelling, and fines migration in shale formation both of which can contribute to rock wettability alteration, and damage to formation porosity, and permeability and hence, can significantly impair the overall hydrocarbon recovery from shale.

The objective of this study was to develop a clay coating procedure in order to prepare clay-coated geo-material microfluidic chips so that the pore-scale behavior of the clay upon exposure to injection fluids can be investigated before using them in the field during drilling, completion, and production periods.

Since the spectral gamma-ray and the X-ray diffraction (XRD) data of the samples from different wells drilled in Caney shale exhibited illite as the dominant clay mineral, it has been chosen as the clay to be studied. 1 wt.% clay slurry made of illite clay particles and brines were prepared and injected into the glass capillary tubes at a flow rate fast enough to prevent the clay deposition in the glass tubes. The motivation for using brine to prepare the slurry was to avoid potential low salinity shock. Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) data of the clay-coated surfaces were collected to study the clay coating density, coverage, and chemistry. After developing a procedure to obtain quasi-homogeneous coating of illite, the procedure will be used to prepare clay-coated geo-material microfluidic chips to study clay swelling potential, and the influence of fines migration on formation damage and wettability alteration. This information will then be used to design injection fluids to avoid the clay-induced problems and for improved recovery of hydrocarbons from Caney shale.
Understanding water (H2O), carbon dioxide (CO2), and small hydrocarbon molecules (such as CH4) interactions in subsurface is relevant to CO2 geologic sequestration and enhanced gas recovery in shale and depleted reservoirs. However, in computational molecular simulations for H2O-CO2-CH4 ternary mixture in clay minerals, accurate force field parameters for unlike-pair LJ interactions usually cannot be derived from simple mixing rules due to thermodynamic nonideality. Here we report our recent force parameter developments for the ternary system using the Gibbs ensemble Monte Carlo (GEMC) and a coupling parameter approach.

We first use GEMC simulation to calculate mutual solubilities of three binary systems: CO2-H2O, CH4-H2O, and CH4-CO2 under different T/P conditions, to which all experiment data are available. Initially, the unlike-pair LJ interaction parameters between different species are estimated from simple mixing rules. The GEMC simulation results are then compared with experimental data. An iterative procedure is developed based on the coupling parameter approach to optimize the LJ parameters. In simulations we employ the compatible CLAYFF force field for a montmorillonite clay interlayer, the SPC water model, the flexible EPM CO2 model used in our previous studies, and the OPLS all-atom model for CH4. CO2-clay surface interaction parameters also adopt the re-optimized CO2-H2O unlike-pair LJ parameters.

Grand canonical Monte Carlo (GCMC) simulations with the optimized force parameters are performed to investigate the compositions of H2O–CO2 binary mixture in a Na-montmorillonite interlayer under $T/P = 323 \text{ K}/90\text{ bar}$ condition. Simulation results are compared with available experimental data and showed the importance of computational model to interpret experimental findings, from which we could use more realistic computational model to predict new data sets. We further employ GCMC and molecular dynamics (MD) simulations to investigate CO2-H2O-CH4 ternary mixture in Na-montmorillonite clay interlayer under geological conditions ($T = 323 \text{ K}, P = 90 \text{ bar}$) with relative humidity (RH) in the ranges of 5% – 40%. We studied the effects of RH on the intercalation of different species. The stable clay interlayer distances at different RH values are determined based on the normal pressure and free energy curves of H2O–CO2–CH4–Na+ complex in the clay interlayer. As expected, our simulation results showed that high RH values facilitate water molecules entering clay interlayers and decrease the CO2 and CH4 intercalation. Different CO2/CH4 ratios in the ternary mixture are investigated. The presence of CO2 significantly influences the CH4 sorption. CO2 and CH4 molecules are partially hydrated, especially at low RH, while sodium ions are fully hydrated due to its relatively high hydration energy with water molecules.
References
SIMULATING EXPERT KNOWLEDGE FOR QUANTITATIVE PHASE ANALYSIS WITH X-RAY POWDER DIFFRACTION

Barry R. Bickmore¹

¹Department of Geological Sciences, Brigham Young University, Provo, UT 84602.

One of the clear lessons drawn from the results of past Reynolds Cup competitions is that the exact methods used for quantitative phase analysis (QPA) via X-ray powder diffraction (XRPD) are of secondary importance in comparison to the analyst’s experience. Two of the most popular methods, full-pattern summation and Rietveld QPA, in essence are simply optimization routines, where the analyst must choose in advance the individual phases used to model the XRPD pattern of a sample mixture. Typical QPA software might employ simple peak-matching routines to give the analyst suggestions about which phases might be present, but given how common it is for the XRPD patterns of different minerals to have coincident peaks, it is no wonder how common it is for inexperienced analysts to propose exotic mineral phases, or geologically strange combinations of phases.

My group is attempting to address this problem in RockJockML, our MATLAB-based full-pattern summation QPA program, by finding ways to automatically mimic processes expert analysts use to select phases for QPA analysis of mineral mixtures. In one approach, we are developing a suite of simple progressive optimization strategies, where phases are chosen for inclusion in the analysis based on information such as 1) the correlation between each phase’s XRPD pattern and the difference pattern (real minus calculated), 2) how common it is, as indicated by the number of locations it appears in the Mineral Evolution Database (MED), 3) the probability of the selected phases occurring together in the MED, and 4) X-ray fluorescence analyses. In a second approach, we will be using supervised learning algorithms to develop models to predict likely combinations of phases to select for analysis. For an approach like this to work, however, we need a very large set of training data—so large that it would be impossible to produce it experimentally. Instead, we are using published crystal structures to generate a training set of synthetic data for mineral mixtures—including XRPD patterns generated using the Rietveld equations and synthetic XRF analyses. The synthetic samples will be randomly generated mixtures of minerals reported at the same locations in the MED. We will compare the results of the automation methods when applied to a similar test set.
PHYLLOSILICATES PROVIDE CLUES ABOUT THE AQUEOUS ENVIRONMENT AND CLIMATE ON EARLY MARS

Janice L. Bishop

1Carl Sagan Center, SETI Institute, Mountain View, CA 94043.

A new climate model was developed for Mars that better explains how clay minerals formed on the surface (1). Short-term warm and wet environments, occurring sporadically in a generally cold early Mars, are proposed to explain formation of phyllosilicates on the surface of Mars. In this model, smectites are distinguished from Mg-rich mixed clays that liked formed in subsurface environments. Further, the geologic horizons of phyllosilicate-bearing outcrops at sites including Mawrth Vallis indicate changing sedimentary (2) and geochemical environments (3) on Mars.

Clay formation on Mars. a) map of dioctahedral smectites, b) nontronite formation versus temperature, c) nanophase aluminosilicates over Al-rich phyllosilicates over Fe-rich smectites, d) fluvial features cutting through ancient, light-toned phyllosilicate rocks at Mawrth Vallis.

References:
DETERMINATION OF THE REACTION DYNAMICS AND ELECTRON TRANSFER PROCESSES AT OXIDE/AQUEOUS INTERFACES

Mavis D. Boamah, Xiaopeng Huang, Zheming Wang, and Kevin Rosso

Pacific Northwest National Lab, Physical and Computational Sciences Directorate, Richland, WA 99354.

We use time-resolved transient absorption spectroscopy to investigate the reaction dynamics and energy/electron transfer properties between Fe-oxide and aqueous dye molecules as a function of solution pH and concentration. Due to the likely low signal strength in transient absorption for thin-film samples, our analyses are performed on nanoparticle suspensions of Fe-Oxide, taking advantage of the in-house nanoparticle synthesis capabilities and expertise at PNNL. One advantage of our measurements is the possibility to study the reactivity at specific crystal facets as the particle shape and crystal facet distribution can be varied quantitatively by controlling the synthesis conditions. Preliminary results show there is a possibility of electron transfer from the excited rhodamine B dye molecules to the hematite nanoparticles as reflected by the delayed decay rate when hematite nanoparticles are introduced to the dye suspension.
The Effects of Firing Temperature on the Sorption Efficacy of Fired Clay Pellets

Sarah Bockisch*1, Jeremy Jones1, Antonio Lara1

1New Mexico State University, Department of Chemistry and Biochemistry, Las Cruces, NM, 88003

Uranium contamination in drinking water is prevalent in the Four Corners area of the Southwest. Ingestion of heavy metal uranium greater than 30 ppb in the water has long been known to cause a variety of serious health effects as per the EPA. Traditional methods for uranium removal are often too expensive and complex to be a viable option for lay persons suffering from this contamination and require utilities such as electricity that many of these persons do not have access to. A cost-effective and sustainable technology is necessary. Fired clay pellets offer a good solution to this problem. However, a means to measure the concentration of uranium in the water is essential, and enhanced fluorimetry is an instrumental method with several advantages over other analysis methods. It is relatively inexpensive, nondestructive, and can be designed to be small and portable for field application. It also allows for real time analysis of uranium sorption by the clay pellets, which is especially useful for kinetic studies. Firing the clay powder into a pellet gives it a manageable structure while still retaining its sorption properties, and the firing temperature affects its relative ability to sequester uranium. Upon abatement, the uranium concentration can be analyzed using fluorimetry. To this end, low, medium, and high firing temperatures for the clay were tested. These fired clay pellets were subsequently exposed to a 125 ppb uranium solution for 24, 48, and 72 hour periods. The resulting solutions were analyzed using polyphosphate enhanced fluorimetry and ICP-MS, an orthogonal analytical method, for comparison. Subsequent analysis showed similar sorption by both low-temperature fired clay and mid-temperature fired clay, with slightly better sorption by the mid-temperature fired clay. There was almost no uranium sequestration by the high-temperature fired clay. Additionally, similar trends between data obtained by fluorimetry and data obtained by ICP-MS could also be seen, although ICP-MS showed better sensitivity. With further study and modification, it is possible that fluorimetry could supplement ICP-MS as a viable alternative for drinking water analysis, especially for rural field analysis.
HETEROGENEOUS Tc$^{4+}$ SEQUESTRATION BY IRON GRANULES

Daria Boglaienko$^1$, Tatiana G. Levitskaia$^*$$^1$, Ravi K. Kukkadapu$^1$, Yingge Du$^1$, Jennifer A. Soltis$^1$, Hilary P. Emerson$^1$, and Yelena Katsenovich$^2$

$^1$Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99354; $^2$Florida International University, Applied Research Center, 10555 W Flagler St, Miami FL 33174.

Substitution and incorporation of metal ions into mineral crystal structures is widespread in the natural environment. Here, we report heterogeneous or clustered partial incorporation of Tc$^{4+}$ into iron minerals. Even though incorporation of Tc$^{4+}$ into iron minerals has been studied before, those studies were conducted in a controlled environment to achieve syntheses of targeted iron minerals, using Fe$^{2+}$ solutions or pre-synthesized iron oxides/oxyhydroxides. Thus, the mechanisms of the transformation of iron phases leading to incorporation of Tc$^{4+}$ in less-controlled, aerobic environments remain poorly understood.

We investigated granular metallic iron for reductive sequestration of elevated concentrations (17 mM) of Tc$^{7+}$ under ambient conditions. X-ray absorption and X-ray photon spectroscopies showed that approximately 30% of Tc$^{4+}$ (of the reduced TcO$_4^-$ removed from the aqueous phase) was incorporated into iron mineral structure. Moreover, microscopy revealed a heterogeneous, i.e. with areas of local enrichment, distribution of Tc$^{4+}$ in magnetite crystals. Mossbauer spectroscopic evidence further clarified formation of non-stoichiometric magnetite during oxidation of iron granules and allowed to conclude retarded transformation of ferrihydrite to magnetite in the presence of Tc, observed for the first time.
Periodic sedimentation and precipitation in geological environments are observed from the micro to macro scale, and often periodic layers are composed of iron-based constituents. These phenomena likely occur because of the transport of aqueous Fe through porous or amorphous substrates, and are known to acquire rhythmical or oscillatory character, causing formation of layered precipitates, or geological features called Liesegang rings and orbicular rocks.

Here, we present a similar phenomenon that was observed during the redox reaction between Tc-99 with zero valent iron (ZVI) particles, in an aqueous environment. Energy dispersive x-ray analysis in combination with scanning electron and transmission electron microscopies were employed to elaborate on the nature of the unique ZVI (trans)formations. Surprisingly, the mathematical models for pattern formation, widespread in the natural environment, are applicable for the description of the observed patterns. Mossbauer analysis was also used to gain insight into the iron oxidation state and transformation into Fe (oxy)hydroxide solids.

We will present the effect Fe solids as well as the effect of impurities present within, in the redox reduction of Tc. This study reveals a unique ZVI dissolution behavior, representing similar phenomena to those observed in porous media in subsurface environments and may be used to better understand our natural surroundings.
Mineral transformations between feldspathoids and clays play an important role in interactions between the environment and wastes from industrial processing. For example, it is known that Al-containing hyperalkaline liquids leaking from tanks at the Hanford site have reacted in the vadose zone to dissolve smectites and precipitate cancrinite and sodalite [1, 2]. Similar reactions take place during the Bayer process for aluminum extraction from bauxite ore, where phyllosilicate minerals including clays are converted to a highly alkaline desilication product (DSP) consisting mainly of sodalite and cancrinite [3]. Some of the considered options for reuse of this DSP waste, which comprises some 150 million tons worldwide with over 7 million tons produced per year, are in civil and building construction or agronomic applications [4]. For the latter application, in situ bioremediation has been considered, but several key gaps have been presented, including understanding of the dissolution mechanisms and ion exchange in the DSP, as key components – Na+, OH-, Al^{3+}, CO_{3}^{2-} – are toxic to plants and microbes at high pH and affect soil properties such as porosity, permeability, and aggregation [5]. A successful understanding of the interconversion between clay minerals and sodalite/cancrinite could help quantify long term effects of leaking alkaline waste at Hanford and potentially provide a path for repurposing of other alkaline industrial wastes. Industrializing the production of 2:1 clay from waste provides many potential applications as a useful material in geoenvironmental engineering, notably its use in hydraulic barriers for waste containment systems and as soil amendments for mine reclamation. Many studies have been undertaken to investigate the creation of sodalites/zeolites from clay minerals, particularly using hydrothermal methods (e.g., [6-9]). However, relatively less work has been done exploring the opposite reaction, that of conversion of feldspathoids like sodalite back to clay minerals.

In the current research, we studied the synthesis of feldspathoids and their subsequent dissolution and mineral transformation. A synthetic mixture of sodalite/cancrinite was designed to be similar to DSP. Powders were made by a low temperature reaction from kaolinite, sodium aluminate/hydroxide/carbonate, and colloidal silica. The synthesis reaction was studied as a function of pH and temperature using Geochemists’ Workbench. Secondly, dissolution and reprecipitation of clay minerals was attempted under various conditions. The results of these experiments are discussed, as characterized by X-ray diffraction, infrared absorption spectroscopy, cation exchange capacity, and water vapor sorption tests.


SORPTIVE FRACTIONATION OF DISSOLVED ORGANIC MATTER TO IRON-RICH MINERALS

Thomas Borch

Department of Soil and Crop Sciences, Colorado State University, Fort Collins, CO 80523-1170

Water transports organic matter through soils, where mineral-organic associations form to retain dissolved organic matter (“DOM”), influencing terrestrial carbon cycling, nutrient availability for plant growth, and other soil organic matter functions. Adsorption of dissolved organic matter to mineral surfaces is also an important process determining DOM bioavailability and carbon sequestration in soils. However, little is known about preferential adsorption of DOM at the molecular level. Thus, we combined Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS) with novel data analysis techniques and classic spectroscopy techniques to examine sorptive fractionation. In particular, DOM was analyzed in order to elucidate DOM sorptive fractionation by iron-rich minerals as a function of DOM concentration and composition as well as temperature. Our findings suggest that a significant amount of DOM was irreversibly stabilized by mineral surfaces, and that DOM sorption on iron minerals was positively correlated with increasing temperature. The study demonstrates that both DOM composition and DOM concentration need to be considered in order to predict DOM reactivity and carbon stabilization in soils, and that non-selective sorption can contribute substantially to the formation of mineral-organic associations.
IN SITU AND OPERANDO STRUCTURAL ANALYSIS OF AMORPHOUS THIN FILMS AND INTERFACES BY GRAZING-INCIDENCE HIGH-ENERGY TOTAL X-RAY SCATTERING

Olaf J. Borkiewicz1, Sebastian T. Mergelsberg2, Micah P. Prange2, and Uta Ruett1

1Argonne National Laboratory, Lemont IL 60439
2Pacific Northwest National Laboratory, Richland WA 99352

Atomic pair distribution function (PDF) analyses using high-energy (> 50 keV) total X-ray scattering data have demonstrated a unique capability for structural analysis, providing atomic-scale insights into material structure with sub-Angstrom spatial resolution. Total X-ray scattering measurements in transmission geometry and subsequent PDF analyses for bulk materials are well-established for numerous materials, both amorphous and crystalline, in a wide range of sample environments. However, application of PDF analyses to central questions in geochemistry relating to interfacial, near-surface, and thin film processes is presently limited. The main challenge to thin film PDF analyses using the standard transmission geometry is that the signal is dominated by substrate contributions rather than the sample structure. Recent measurements at beamline 11-ID-B of the Advances Photon Source demonstrate the possibility of achieving grazing-incidence high-energy total X-ray scattering data capable of producing high-quality GI-PDF data on thin films and interfaces. This newly commissioned, dedicated setup will allow for routine data acquisition in grazing-incidence geometry on a wide range of materials in various sample environments, with particular emphasis on operando and in situ conditions. Structural measurements of previously inaccessible materials provide a unique opportunity to refine current computational efforts to model interfacial processes, greatly improving our current understanding of geochemically relevant near-surface processes.
Characterizing Fluid-Solid Interactions and Chemistry at Reservoir Conditions Using High Pressure NMR and IR Spectroscopy with High Pressure X-ray Diffraction


1St. Mary’s College of Maryland, Department of Chemistry and Biochemistry, St. Mary’s City, MD 20686; 2Pacific Northwest National Laboratory, William R. Wiley Environmental and Molecular Sciences Laboratory, Richland, WA 99354; 3Pacific Northwest National Laboratory, Physical and Computational Sciences Directorate, Richland, WA 99354.

A molecular-scale understanding of how methane and carbon dioxide interact with the organic and inorganic components of shale at the hydrostatic conditions of a typical reservoir is crucial to design and implementation of cleaner, more effective hydrocarbon extraction methods such as methane recovery via injection of supercritical carbon dioxide (scCO2). This presentation focuses on the types of information we can learn by studying wet supercritical CH4 and CO2 interactions with clay minerals and clay-rich rocks in situ at reservoir conditions using advanced instrumentation available at Pacific Northwest National Laboratory, with a primary focus on NMR methods. Studies by our group using 13C NMR have shown that clay minerals adsorb both types of molecules in their interlayers and in small pores between particles, with the relative populations of each pore environment varying with the humidity of the fluid phase. We find that CO2 can actively enter clay layers when the smectite charge-balancing cation is large and has a low affinity for H2O, inducing interlayer expansion, while CH4 enters interlayers via a passive mechanism only when the interlayer spacing is large enough to accommodate the CH4 molecule and the humidity is low. Interestingly, the 13CH4 chemical shift is sensitive to the size and surface properties of the pore in which it is adsorbed, providing a potential new mechanism for characterizing pore sizes/chemistry, while 13CO2 tends to have only subtle differences in the spectra with pore size/composition. As humidity increases, H2O more effectively competes with CH4 for adsorption sites, essentially displacing all CH4 from small pores, while some CO2 is retained in all types of pores at all humidities. The combination of multiple high-pressure laboratory techniques also permitted us to characterize and understand a chemical mechanism of CO2 trapping by clays when the charge-balancing cations can produce carbonates with very low Ksp. NMR can also characterize the dynamics behavior of the fluids on multiple timescales, allowing us to constrain the types and rates of molecular motion. For example, recent exchange-correlation spectroscopy (EXSY) NMR experiments have allowed us to characterize site exchange rates for CH4 between different pore environments on the 1 kHz to Hz rate scales. Finally, these tools can also be applied to real shale samples, as we recently demonstrated using 13CH4 NMR of supercritical CH4 in contact with a natural shale.
CLAY MOBILIZATION AND FACILITATED TRANSPORT OF CONTAMINANTS IN THE SUBSURFACE

Scott A. Bradford

United States Department of Agriculture, Agricultural Research Service, US Salinity Laboratory, 450 W. Big Springs Road, Riverside, CA 92507

An understanding of factors that influence clay mobilization in the subsurface is needed to accurately assess the potential for facilitated contaminant transport. This presentation highlights our group’s research activities to improve the description of clay interaction energies, and the measurement and modeling of clay release and facilitated contaminant transport. We demonstrate that the strength of clay interactions is highly dependent on the hydration force (as well as double layer, van der Waals, and capillary forces), the shape and orientation of clay particles with surfaces, and the presence of nanoscale roughness and charge heterogeneity. It is shown that alterations of these forces by changes in solution chemistry and/or water saturation can produce significant amounts of clay release and the potential for clay-facilitated contaminant transport. We demonstrate how continuum scale models can be modified to simulate these clay release and facilitated transport processes to predict potential risks.
Redox cycling of Fe-bearing clay minerals via biologically mediated, abiotic reduction: impact on clay mineral redox reactivity and structure

Harry Brooksbank, Anke Neumann

h.brooksbank2@newcastle.ac.uk

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

In natural sediments, Fe is one of the most abundant elements and the Fe(II)-Fe(III) redox couple plays a vital role in the cycling of nutrients and the fate of various environmental contaminants. Clay minerals often contain octahedral Fe in their mineral structure and this structural Fe can reductively degrade a variety of organic contaminants. Unlike other natural Fe-bearing minerals, clay minerals are mostly resistant to reductive dissolution and are thus viewed as a renewable source of reduction equivalents in the environment. Recent research however suggests that reduction of clay mineral Fe can cause irreversible mineral alterations. The extent of the effects and reversibility vary depending on reduction pathway (i.e microbial or chemical) and mineral Fe content. However, to date it is unclear how the recently discovered processes of biologically mediated, abiotic reduction, i.e. reduction by aqueous Fe(II), impacts clay mineral structure and, consequently, redox reactivity over multiple cycles of reduction and oxidation.

Here, we compared clay minerals with different Fe contents (high: NAu-1, 22.1 wt%; low: SWy-3, 2.8 wt%) that were subjected to three cycles of reduction and oxidation. Biologically mediated, abiotic reduction with aqueous Fe(II) was contrasted with chemical reduction with dithionite to high (75% Fe(II)/Fe(total)) and low (25% Fe(II)/Fe(total)) reduction extents. In both cases, almost complete re-oxidation of clay mineral Fe(II) was achieved using hydrogen peroxide. The redox reactivity of the resulting Fe(II)-containing clay minerals and, in case of reduction with Fe(II), additional reactive secondary precipitates was evaluated using the reductive degradation of the reactive probe compound 3-chloronitrobenzene (3-CNB). The 3-CNB degradation data was analysed with both a one-site and a two-site kinetic model. Concomitant mineralogical and structural alterations of the redox-cycled clay minerals, both reduced and re-oxidised, were investigated using 57Fe-Mössbauer spectroscopy, electron microscopy, and X-ray diffraction.

Degradation of 3-CNB with dithionite-reduced NAu-1 was quicker for high than for low clay mineral Fe reduction extents and could be fit only with the two-site kinetic model. Interestingly, the kinetic rate constants were highly similar for both reduction extents and all redox cycles, suggesting that the reactive Fe entities within the clay mineral were unaffected by reduction extent and redox cycling. This observation is further supported by the high similarities in Mössbauer spectra of redox-cycled NAu-1. Additional complementary analyses of aqueous solution and solids after each chemical reduction, using ICP-OES and electron microscopy equipped with EDX, respectively, also indicated the absence of preferential dissolution of Fe from the clay mineral structure, in contrast to previous reports. Interestingly, kinetic rate constants of 3-CNB degradation by Fe(II)-reacted NAu-1 were of values comparable to those of dithionite-reduced NAu-1 for the first reduction cycle, suggesting that the precipitates formed contributed only to a small extent to 3-CNB degradation. However, rate constants increased significantly, by about one order of magnitude, after the first cycle and we suspect that the initially formed precipitates, once oxidised, reacted preferentially with the added Fe(II) in subsequent redox cycles to form reactive Fe(II) species in addition to clay mineral Fe(II). Experiments with combinations of Mössbauer-invisible 59Fe(II) and Mössbauer-visible 57Fe(II) are underway to comprehensively understand Fe precipitate formation and its role for the observable redox reactivity of Fe(II)-redox-cycled clay minerals.

References:
Decades of space exploration have shown that three to four billion-year-old surface environments of Mars may have once been habitable. Surface paleoenvironments of Earth are represented by paleosols (buried, lithified soils) which contain some of the oldest (> 2 Ga) biosignatures including carbonaceous microfossils and isotopically light carbon and sulfur. However, the factors controlling the preservation and degradation of organic matter in paleosols with Mars-like mineralogy have not yet been determined. We examine clay mineralogy and organic preservation in the Eocene and Oligocene (43-28 Ma) volcaniclastic paleosols at the John Day Fossil Beds National Monument in easter Oregon which have vertical profiles of dioctahedral Al-smectite clays which overlay Fe / Mg smectite deposits that exhibit striking spectral similarity to Noachean (4.1-3.7 Ga) sequences at Mawrth Vallis, Oxia Planum, and elsewhere on Mars. Smectites and amorphous phases offer a favorable setting for the preservation of organic matter and both have been significant components of drilled samples at Gale Crater. We hypothesized that chemically reduced paleosols with abundant (> 80 wt %) dioctahedral Fe/Mg smectites and amorphous colloids would have the highest total organic carbon (TOC). We identified clay minerals with visible/near infrared (VNIR) spectroscopy and used a Mars flight-analog instrument calibrated to operate like the Sample Analysis at Mars - Evolved Gas Analysis (SAM-EGA) instrument to constrain mineralogy and organic matter composition. We determined that clay mineralogy and depth in profile are significantly correlated with TOC. The highest amounts of TOC were detected in the surface horizons of paleosols with Al smectites that formed under reducing conditions and the lowest amounts of TOC in paleosols with kaolinite and oxides which formed under oxidizing condition. Our results suggest that redox state and clay mineralogy are two principal controls on organic carbon preservation in these paleosols. Interestingly, paleosols with > 80 wt. % dioctahedral smectite paleosols appear to have resisted diagenetic alteration relative to less clayey paleosols which show illitization and severe celadonization. These results suggest that dioctahedral smectite-rich paleosols with evidence of reducing conditions should be prioritized in the search for biosignatures across ancient soil environments on Mars.
Knowledge of the atomic-scale structure of an interface is one of the requirements of understanding the processes that occur at such interfaces. X-ray diffraction is the tool of choice for the structure determination of crystals, and can also be applied to crystal-liquid interfaces provided the interface is well-defined and synchrotron radiation is used. We will show how many details can be revealed for two minerals: muscovite mica and calcite. The crystal part gives very reliable results, but even under the best conditions, it’s difficult to draw firm conclusions on the disordered liquid part. For this reason, we have supplemented the X-ray diffraction results with a surface complexation model (for mica) and molecular dynamics simulations (for calcite), leading to a consistent picture in both cases.

For muscovite mica, charge plays a major role in the interface structure, but the competition between monovalent and divalent ions also reveals the importance of hydration forces. For calcite charge is less important and the interface structure is determined by covalent-type interactions. These differences explain the different bonding of carboxylic acids at these interfaces.

A schematic of the interface structure of muscovite mica in contact with a CsCl solution.
ATMOSPHERIC ICE NUCLEATION BY SOILS AND DUSTS, AND ITS ROLE IN CLIMATE

Susannah M. Burrows¹, Isabelle Steinke¹, Gavin Cornwell¹, Gourihar Kulkarni¹, Swarup China², Alla Zelenyuk-Imre¹

¹Pacific Northwest National Laboratory, Atmospheric Sciences and Global Change Division, Richland, WA; ²Pacific Northwest National Laboratory, Environmental and Molecular Sciences Laboratory, Richland, WA.

Soil and dust particles aerosolized by wind-driven erosion and human activities represent a major source of atmospheric particulate matter, with implications for both human health and climate. In particular, mineral dusts and soils are a globally important source of atmospheric ice nucleating particles (INPs). Clay minerals such as kaolinite and illite are among the best-studied particles that participate in atmospheric ice nucleation, and their efficacy as INPs can further be modified by adsorption or coating with other molecules (such as organic vapors).

Because of their rarity, INPs require specialized methods to collect and characterize chemically and physically. In experiments at PNNL’s Environmental and Molecular Science Laboratory, we have chemically characterized ice nucleating particles in soils using both microscopic imaging, molecular methods and highly sensitive single-particle mass spectrometry methods. Additionally, we use Monte Carlo simulations of freezing by complex particle populations under laboratory conditions to link particle size and composition to freezing events, and to better understand the experimental uncertainties of laboratory and field measurements.

We find that ice-nucleating particles in agricultural soil samples are a chemically distinct population that differs in its elemental and molecular composition from the overall soil particles. Additionally, we show that laboratory preparations such as heating and suspension in water, which are often used in the analysis of INP samples, can have effects on the physical and chemical properties of soil particles that are unintended in such experiments, potentially limiting the conclusions that can be drawn from such methods. These findings further motivate the need for advanced molecular and single-particle characterization methods to understand the characteristics that enable some particles to more efficiently nucleate ice.

For particles to participate in ice nucleation, they also need to be elevated to cloud altitudes. To better understand the vertical transport of dust particles, we have carried out trajectory simulations of particle lofting in a region surrounding the DOE-ARM Southern Great Plains measurement site in Oklahoma, leveraging wind predictions from the LES ARM symbiotic simulation and observation workflow (LASSO) and the FLEXWRF trajectory model. Particle removal by either gravitational sedimentation or rainout is a strong function of particle size, and so we simulate significantly less transport to cloud elevations (e.g., above 1 km) for larger particles (e.g., 10 µm diameter) than for smaller ones (e.g., 1 µm diameter). We place these findings in context with measurements of aerosol and meteorological variables from the site and discuss implications for the participation of agricultural dusts from the Southern Great Plains region in cloud processes and long-range transport.
Advanced Image Analysis of SEM Photomicrographs to Enhance Understanding of Unconventional Reservoir Pore Space and Matrix Materials in the Bakken Formation in The Williston Basin

Shane K. Butler¹,* Alexander Azenkeng¹, Blaise A.F. Mibeck¹, and Bethany A. Kurz¹

Energy & Environmental Research Center, 15 North 23rd Street, Grand Forks, ND 58202-9018

Advanced characterization of the Bakken Formation, an unconventional oil and gas play of the Williston Basin, was performed via analytical microscopic investigation that employed machine learning techniques in concert with standard laboratory methods. Unconventional reservoirs represent systems with high specific surface area and low mean free path for fluid molecules. These reservoir properties require new methods of image analysis for predicting the transport or storage capacity of CO2 and other fluids. Characterizing the composition and distribution of framework grains, organic matter (OM), clay minerals and porosity in this type of medium is difficult because of the extremely lithified nature of the small grain and particle sizes that constitute the formation. In this study, corroborative methods aimed to define micro- and nanoscale fabrics that impact parameters such as maturity, oil recovery, clay content, micropore networks, and CO2 interactions for either gas storage or enhanced oil recovery (EOR). Each sample underwent high-resolution field emission scanning electron microscopy (FESEM) to capture back-scattered electron (BSE) images at multiple magnifications to maximize particle morphology in the fine-grained rock of the Bakken reservoir. An advanced image analysis technique known as shared border analysis was performed on the high-resolution FESEM images to characterize key features of interest within the lithofacies. Shared border analysis is a machine learning tool that allows for detection and quantification of the rock matrix composition surrounding pore and fracture networks using segmented images. The shared border analysis was supplemented with data derived from the Advanced Mineral Identification and Characterization System (AMICS), which was used to map, classify and quantify mineralogy, OM, and porosity from FESEM images. For validation purposes, x-ray diffraction was used to obtain bulk mineral and clay mineral data and x-ray fluorescence was used to obtain bulk chemical compositions of the samples.

The data highlighted trends related to factors that impact CO2 transport and sorption in unconventional reservoirs. Segmented BSE images from the FESEM made it possible to estimate OM, clays, and porosity for each sample. The shared border analysis and AMICS analysis of matrix porosity, OM porosity, and mineralogical composition maps provided context for the potential of unconventional reservoirs as CO2-based EOR targets or CO2 storage targets. Shared border analysis specifically was able to quantify the amount of pore space that shares borders with other defined classes in the FESEM images, based on the understanding that a limiting factor involved in CO2 storage and transport is the contact of pores with organic minerals and clays.
UNDERSTANDING THE CORROSION POTENTIAL OF SULFATE-REDUCING BACTERIAL COMMUNITIES IN BENTONITE, AN ENGINEERED BARRIER FOR RADIOACTIVE WASTE DISPOSAL

Sarah Butterworth*, Carolyn I. Pearce2, Dirk Engelberg3 and Jonathan R. Lloyd1

1 Williamson Research Centre for Molecular and Environmental Science and Department of Earth and Environmental Sciences, The University of Manchester, M13 9PL, UK.; 2 Pacific Northwest National Laboratory, Richland, WA 99352, US; 3 Materials and Performance Centre & Corrosion and Protection Centre, Department of Materials, The University of Manchester, The Mill, M13 9PL, UK.

High level radioactive waste (HLW) must be stored safely for at least 100,000 years and isolated from the environment, due to long-term radioactivity. Several countries, including the UK, are committed to a geological disposal facility (GDF). The general disposal concept for a HLW-GDF is encapsulation in a canister of a corrosion-resistant material such as copper, buried several hundred metres underground and backfilled with bentonite clay.

For many years, extreme environments associated with radioactive waste disposal have been assumed to prevent microbial metabolism. However, viable sulfate-reducing bacteria (SRB) have been successfully cultured from commercial bentonite clays, and shown to withstand extreme conditions, including high temperatures and radiation. Understanding the impacts of SRB and their metabolic capacity under GDF-relevant stresses is of great importance, as SRB can produce highly corrosive hydrogen sulfide, which may impact canister longevity.

The aim of this research is to identify how SRB communities change with varying groundwater chemistry and whether differences in community composition impact on copper corrosion rates. Through an interdisciplinary combination of microbiological, geochemical and electrochemical techniques, this work aims to develop an understanding of the relationship between groundwater chemistry, microbial-driven processes, and subsequent corrosion, to aid in the development of generic safety cases for geological disposal of radioactive waste.
DEVELOPMENT OF NOVEL FIRST PRINCIPLES SIMULATIONS FOR REACTIONS AND SPECTROSCOPIC ANALYSIS AT COMPLEX GEOCHEMICAL INTERFACES

Eric J. Bylaska

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland WA 99352

In the last two decades, first principles methods of simulations based on ab initio molecular dynamics (AIMD) have been developed and applied to formerly computationally intractable geochemical problems such as (1) Interpretations of structure, reactivity and electron transport in mineral/fluid interfaces of complex highly correlated transition metal oxide minerals; (2) the interpretation of EXAFS, Mössbauer, IR and Raman spectroscopies of the fluid, interfacial, and bulk structures; and (3) reaction mechanisms involving charge transfer (e.g., electron transfer and proton exchange reactions at partially hydrated mineral surfaces). Unfortunately, these simulations can quickly become prohibitive as the system sizes become larger. While advanced HPC algorithm and software development has been able to overcome many of these barriers, the computation cost of AIMD is still prohibitive for many systems and project resources. In this presentation, we will give an overview of the current state-of-the-art of AIMD simulations in geochemistry and we will also discuss the development of new algorithms and approaches for AIMD that are currently being developed by us and other researchers, including $O(N)$ DFT methods and machine learning methods, to more efficiently sample fluid and interface structures.

To make these types of simulations more accessible to larger numbers of scientists and engineers, we have recently been creating modern interfaces (e.g., web APIs) between the user and NWChem, taking full advantage of the GPU and Intel MIC capabilities of NWChem. Our first app called, ESML Arrows (https://arrows.emsl.pnl.gov/api/), is an interface that generates and uses coupled thermochemical databases (DFT, MP2, CCSD(T), and composite methods such as G2MP2) to enable large numbers of quantum chemistry calculations needed for triaging among possible chemical reaction pathways, generating descriptor data in QSAR development, or just generating potential energy surfaces. This service is designed to be used by experts and non-experts alike. Experts can carry out and keep track of large numbers of complex calculations with diverse levels of theories present in their workflows. Additionally, due to streamlined and easy-to-use input, non-experts can carry out a wide variety of molecular and condensed modeling calculations previously not accessible to them.
CHARACTERIZATION AND QUANTIFICATION OF ION EXCHANGE IN SODALITE AND CANCRINITE

Darren A. Chevis¹, Mackenzie Jeter¹, Youjun Deng¹, and Julie A. Howe¹

¹Texas A&M University, Department of Soil and Crop Sciences, College Station, TX 77843

Hyperalkaline solutions such as radioactive waste from processing uranium fuel, and the digestions solutions used in Bayer process for aluminum ore refining often end up in interacting with minerals in soils and sediments in the environment. The interaction of hyperalkaline solutions with clays and other aluminosilicate minerals commonly result in the formation of the feldspathoids sodalite (Na₈Si₆Al₆O₂₄X₂) and cancrinite (Na₈Si₆Al₆O₂₄X₂). Due to the importance of these minerals in regulating the geochemistry of radioactive elements, the ability of these two minerals to incorporate a variety of cations (e.g., radioactive Cs⁺ and Sr²⁺) and anions (radioactive TeO₄⁻ and I⁻) into their structures has been studied extensively; however, little information is available on their ion exchange characteristics. The objectives of this study were to characterize and quantify ion exchange in synthetic cancrinite (Na₈Si₆Al₆O₂₄SO₄) and sodalite (Na₈Si₆Al₆O₂₄Cl₂) with common cations (Ca²⁺, Cs⁺, K⁺, Mg²⁺, NH₄⁺, and Sr²⁺) and anions (NO₃⁻, Cl⁻, F⁻, HPO₄²⁻). The ion exchanged feldspathoids were characterized by FTIR, SEM/EDS, and XRD, while the exchanged fluids were analyzed for Na⁺ released into solution by flame AAS to quantify the extent of ion exchange. Generally, no structural or morphological change occurred in either feldspathoids during the ion exchange procedure; however, EDS analysis detected the presence of the exchanged cations in the structure of both feldspathoids. Quantification of the cation-specific exchange capacities showed the greatest exchange occurred with K⁺ with values of 697 and 425 cmolc kg⁻¹ for sodalite and cancrinite, respectively, and yielded a lyotropic series for both feldspathoids (K⁺ > NH₄⁺ ≈ Mg²⁺ > Sr²⁺ > Ca²⁺ > Cs⁺). The exchange of Na⁺ for K⁺ in sodalite caused up to a 20 cm⁻¹ shift in IR band positions and a systematic shift of the peaks in the XRD spectra that corresponded to a 3% expansion in the unit cell size compared to the initial synthesized sodalite. In contrast to the cation exchange experiments, FTIR, SEM/EDS, and XRD provided no evidence for anion exchange occurring in either sodalite or cancrinite. Further work to evaluate the potential mechanisms that sequester anions in the structures of sodalite and cancrinite while allowing cations to freely exchange is necessary to fully understand how both feldspathoids interact with aqueous chemical species in the environment.
Layered Al Hydroxide/Oxyhydroxide Minerals in Extreme Environments: Resolving Challenges with Managing Legacy Radioactive Waste

Sue B. Clark

1Pacific Northwest National Laboratory, Richland, WA 99353, USA

*sue.clark@pnnl.gov

In the U.S., decades of nuclear materials production for the Cold War have resulted in large quantities of high-level radioactive wastes that are currently stored in large tanks at Department of Energy sites located in the states of South Carolina and Washington. The wastes are highly alkaline concentrated electrolytes containing significant quantities of fission products and actinides, along with non-radioactive constituents such as aluminum (Al). Al came from cladding materials and was added as Al nitrate in certain nuclear materials processing. It is precipitated as layered Al hydroxide/oxyhydroxide minerals, such as gibbsite (Al(OH)₃) and boehmite (AlOOH).

These wastes have been aging in an environment of ionizing radiation for decades. Planned removal of the wastes from the tanks will involve controlled manipulation of aluminum solids and speciation, followed by processing to separate the bulk of the radionuclides. Separations will result in a low-level waste that will be solidified and disposed of on-site, with the remaining radioactive waste stream managed as high-level waste (HLW). Current efforts to treat high level radioactive wastes are slow and costly because processing schemes are limited to narrow conditions based on uncertainties in waste characteristics and behavior during processing. The need for a fundamental understanding of the behavior of layered Al hydroxide/oxyhydroxide phases in these highly alkaline and extremely concentrated electrolyte systems is being addressed by PNNL’s Energy Frontier Research Center focused on interfacial dynamics in radiation environments and materials (IDREAM), in partnership with Washington State University, Oak Ridge National Laboratory, Georgia Institute of Technology, Notre Dame Radiation Laboratory and University of Washington.

In the concentrated electrolytes that represent the chemical conditions of the waste, the solvent shells of relevant cations and anions are complex because water is a limited species, which leads to sharing of hydration waters between dissolved species. Also, in highly alkaline conditions, Al is present as the aluminate anion (Al(OH)₄⁻), which can polymerize into dimeric species, impacting on the dissolution and precipitation behavior of Al(OH)₃ and AlOOH. Ionizing radiation adds additional complexity, due to radiolysis both in the bulk solution and in the interfacial regions of the Al hydroxide/oxyhydroxide. In this presentation, the role that these layered Al hydroxide/oxyhydroxide minerals play in controlling observed solution and interfacial speciation will be discussed.
Iron redox reactions are essential to many major biogeochemical processes in soils including supporting life under anoxic conditions, controlling nutrient availability, altering minerals along with a wide range of environmental remediation and industrial applications. Biochar produced from pyrolyzing organic matter has been receiving more attention as a soil amendment and its impacts on these processes must be understood. Solid biochar has been shown to stimulate microbial reduction of Fe (III) in common iron oxide minerals under anaerobic conditions as it contains redox-active functional groups. Recently it has been shown that the rate and extent of reduction of Fe (III) oxides is heavily dependent on biochar concentration. Little is known about the impact of biochar concentration on the bioreduction of Fe (III) bearing clay minerals. Here we designed bioreduction experiments with lactate (20.0 mM) as electron donor, structural Fe (III) in nontronite (NAu-2) as electron acceptor (5.0 g/L) and *Shewanella putrefaciens* CN32 (8.5*10^8 cells/mL) as a mediator. Biochar enhanced the rate of Fe (III) bioreduction in a concentration-dependent manner but has a varying effect on the extent. High concentrations (2.5, 3.5, 5, and 10 g/L) of wood-derived solid biochar increased the reduction extent, in contrast low concentrations of biochar (0.5 and 1.5 g/l) had an inhibitory effect. The enhancement effect may result from electron shuttling of biochar, but the inhibitory effect is difficult to explain and may be due to redox activity of individual functional groups of biochar. To confirm this speculation, NAu-2 was treated with chitosan to reverse the surface charge of NAu-2. For this chitosan-modified NAu-2, the inhibitory effect of biochar on the extent of bioreduction remained at 0.5 g/L, but the enhancement effect became negligible, likely because the close attachment of CN32 cells to positively-charged NAu-2 surface facilitates electron transfer without a need for an electron shuttle. To further explore the negative effect of biochar the iron source was replaced with 2.5 g/L ferric citrate with a range of biochar concentrations (0, 0.5, 1.0, and 10 g/L). In this case, the extent of bioreduction showed a negative correlation with biochar concentration, i.e., a high concentration of biochar (10.0 g/L) resulted in the lowest extent of bioreduction followed by 1.0 g/L, 0.5 g/L and 0 g/L biochar concentration. In contrast, the rate of Fe (III) bioreduction was still enhanced by the low biochar concentrations (0.5 and 1 g/L). This suggests that biochar may be retaining a portion of the electrons during the bioreduction even when there cannot be any degree of aggregation between the iron source and biochar. The inhibitory effect of low concentrations of biochar in the presence of excess lactate (20.0 mM) may be due to saturation of the redox-active functional groups inhibiting electron accepting capacity while higher concentrations have an excessive amount of these functional groups and can continue to shuttle electrons even if a larger proportion of electrons are retained by the biochar. Our study suggests that relative biochar concentrations control the rate and extent of microbial reduction of Fe (III) in nontronite.
Multiscale Assessment of Pore Structures in Unconventional Gas Shale Systems

David R. Cole*¹, Julia Sheets¹, Lawrence M. Anovitz², Susan Welch¹

¹School of Earth Sciences, The Ohio State University, Columbus, OH; ²Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN,

Geological formations that host unconventional oil and gas fields and coal bed methane are extraordinarily heterogeneous and exhibit a wide range of physical and chemical features that can vary over many orders of magnitude in length scale. In the context of subsurface geochemical and mineralogical processes relevant to unconventional hydrocarbon deposits, we need to consider both the sedimentologic and diagenetic processes that formed the deposits and the present-day nature of fluid and rock properties and the complex interactions among fluids and between solids, fluids and even microbial communities over broad ranges of temperature, pressure, fluid composition, spatial and temporal scales. Of particular importance is the nature of the microstructure and evolution of pore space in rocks, which are critically important factors controlling fluid flow. The size, distribution and connectivity of these confined geometries dictate how fluids migrate into and through these micro- and nano-environments, wet and react with the solid. The abundance, and secondarily the shape and size distribution of clasts of clay size and above largely determine the distribution of the angles of repose of clay folia. An unexpected result is that, in mudstones with both abundant clasts and clay, this perturbation reduces anisotropy more at the nanometer scale of clay folia than at the microscale of the clasts themselves. The wrapping of clay folia around clasts of every size may be expected to mediate local diffusivity and permeability, and potentially enhance the ability of fractures to propagate in directions other than the horizontal, even in lithologies with sufficient clay to be ductile.

This presentation will provide an overview on pore types and their relationship with organic matter in gas shale formations with special emphasis on the Utica/Pt. Pleasant and Marcellus. We will highlight multi-scale results a complementary set of “tools” with a focus on scanning electron microscopy (SEM) with backscattered electron imaging (BSE), dual-beam focused ion beam scanning electron microscope (FIB-SEM), Mercury intrusion porosimetry (MIP), and small- and ultra-small angle neutron scattering (SANS/USANS) that contribute to two key science questions areas:

(a) What are the size, distribution, connectedness, and contribution to total porosity of nano- to micropores in a representative gas shale?

(b) How do these pore features vary with the distributions of clay and carbonate matrix and organic matter?

Some key ‘global’ observations include:
(1) Total porosity exhibiting bimodality may be typical of mudstones,
(2) Connected porosity exhibiting bimodal tendencies may not be uncommon in mudstone and seal rocks,
(3) Fissile mudstones can contain a far greater abundance of nanopores,
(4) Connected porosity commonly mimics the bimodal total porosity trends with connected nanopores observed below about 5 nm typically associated with kerogen and connected nanopores between 20 and 100 nm associated with clays (e.g., illite, chlorite) or clay-detrital grain contacts.
SIMULATIONS OF GIBBSITE NANOPARTICLES AND AGGREGATES

Louise J. Criscenti, Jeffery A. Greathouse, and Tuan Anh Ho

Geochemistry Department, Sandia National Laboratories, Albuquerque, NM 87185

The porosity of clay aggregates is one of the most important properties used to determine the permeability, ion exchange capacity, gas loading, and fluid migration in mudstones and shales. The location of adsorbed species in compacted soils is difficult to assess because compaction results in lower water-rock ratios, heterogeneous porosity, and nanoconfined mineral-water interfaces. Pore spaces in clay-rich rocks include interlayer (i.e., space in between TOT layers) and interparticle (i.e., space between platelets) pores. Classical molecular dynamics (MD) simulation can provide information regarding the formation of these aggregates.

We developed model nanoparticles of gibbsite to investigate interparticle porosity as a function of water content and dewatering conditions. Using gibbsite as a clay proxy, we developed an MD method to construct realistic clay-like nanoparticle aggregates with interparticle pores and grain boundaries. The results suggest that slow dewatering creates more compact aggregates with more neatly stacked gibbsite platelets than fast dewatering.1 We are now investigating the energetics of particle-particle interaction to better understand the forces driving the oriented, stacked packing of gibbsite.

We also investigated the adsorption of Na+, Ca2+, Ba2+, and Cl− ions on gibbsite edge (100) and basal (001) surfaces as well as on a gibbsite nanoparticle (NP). Surface coverages for cations on the gibbsite NP are always higher than those calculated for the (100) and (001) surfaces. This result is consistent with larger-scale surface complexation models that require two types of surface sites to fit adsorption data collected from batch experiments on unconsolidated particles. The two types of surface sites are qualitatively described as one that has a high affinity for metal cations but a low site density that is attributed to the presence of defects, edges, and corners; and another that has a lower affinity for metal cations and a high site density that represents the average properties of ideal mineral surfaces.2

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

SAND2020-2555

References

Metal uptake mechanisms in extreme chemical environments relevant to nuclear waste are much less understood than at environmental conditions. We report a multiscale study of selective Cr(III) adsorption on boehmite nanoplates in highly caustic sodium hydroxide solution up to 3 M. Empirical modeling of measured adsorption isotherms and kinetics suggests monotonic uptake of Cr(OH)$_4$$^-$$^$ monomers until saturation coverage of about half the aluminum surface site density. High resolution AFM combined with EXAFS and EPR reveal self-assembly of monolayer Cr(III) clusters on (010) basal surfaces with a structural motif similar to guyanaite ($\beta$-CrOOH) entailing corner-sharing Cr-O-Cr bonds and edge-sharing Cr-O-Al bonds. The selective uptake appears related to short-range surface templating effects, with bridging metal connections likely enabled by hydroxyl anion ligand exchange reactions at the interface. Cluster formation, which stops short of more laterally extensive heteroepitaxy, may be a selective metal uptake mechanism more prevalent than currently recognized.
Hydration of a phyllosilicate-rich unit on Mars using neutron spectroscopy

S. Czarnecki*1, C. Hardgrove1, P. J. Gasda2, T. S. J. Gabriel1, and R. E. Arvidson3

1Arizona State University, Tempe, AZ, sean.czarnecki@asu.edu; 2Los Alamos National Laboratory, Los Alamos, NM, 3Washington University in St. Louis, St. Louis, MO

The primary goal of the NASA Mars Science Laboratory (MSL) Curiosity rover mission is the identification of habitable environments. The ~150 km-wide Gale crater was selected as the landing site in part due to the Glen Torridon (GT) phyllosilicate-bearing interval on its ~5 km-tall central sedimentary mound. Orbital hyperspectral data from the CRISM instrument show strong absorption bands at 2.29 µm in GT, characteristic of metal-OH smectites. XRD results from the first GT drilled samples show the largest smectite abundances found in Gale crater (~30 wt.%). The MSL Dynamic Albedo of Neutrons (DAN) is a neutron spectrometer sensitive to H as well as neutron absorbers (e.g., Cl, Fe, B, Mn) in the top ~60 cm of the subsurface. We report results from DAN’s active mode, in which neutrons are produced by the instrument, interact in the subsurface, and return to be detected. DAN measured a distinct neutron count rate increase as Curiosity drove into GT (Figs. 1, 2), corresponding to increased hydration (WEH, measured hydrogen abundance converted to water abundance), consistent with increased hydrated smectite abundance, and in agreement with CRISM. Curiosity left the area of CRISM smectite observations on sol (martian day) 2559, after which neutron count rates decreased, again correlating DAN and CRISM. These low neutron count rates could also be due to abundant Fe- and Mn-rich diagenetic features in this area. Comparison to simulations for the DAN measurement over the first drilled samples in GT provided a best-fit WEH of 2.4 wt.%, lower than the best-fit 4.4 wt.% WEH measured adjacent to it. Although GT is on average more hydrated than this smectite-rich outcrop, there is no significant difference in the overall bedrock hydration (3.9 wt.% WEH) compared to hydration of unconsolidated material (4.1 wt.% WEH) in GT. We examine the correlation of DAN-derived bulk hydration with surficial hydration features in CRISM spectra and explore constraints on smectite abundances where samples were not acquired.

Fig. 1: Map of a section of the MSL traverse and CRISM relative 2.29 µm band depth parameter, produced by Valerie Fox. (inset) Section of traverse in GT. Select sols (martian days) and GT drill targets are labeled.

Fig. 2: DAN neutron counts acquired while entering GT. Horizontal axis is detection time after PNG pulse. As neutron counts increase, WEH of the best-fit model also increases.
FLUID-CLAY-EVAPORITE INTERACTION: AN ANALOG FOR EVAPORITE GEOCHEMISTRY IN GALE CRATER

Das. D¹, Gasda. P. J², R. Berlo. K¹, Leveille. R. J¹, Wiens. R. C²

¹Department of Earth and Planetary Sciences, McGill University, Quebec, Canada H3A 0E8; ²Los Alamos National Laboratory, New Mexico, USA.

Boron was discovered in light-toned calcium sulfate veins throughout the traverse of NASA’s Curiosity rover in Gale crater, most recent in the Vera Rubin ridge (VRR). The lacustrine mudstones of Gale crater are clay rich, containing up to ~30 wt% Fe- and Mg-rich smectites [1]. Based on the presence of jarosite and akageneite in the clay-rich sedimentary rocks [1] and the presence of B and Li in the veins on VRR, it is inferred that acidic weathering of the clays may have driven B and Li into solution on VRR. In the veins of VRR, it is also observed that relative concentrations of B and Li are inversely proportional to each other and it is inferred that the two elements separated in the brine through differences in solubility, and crystalized in different strata as water disappeared by either evaporation or freezing [2]. In this project, we aim to study B and Li-rich terrestrial veins to understand the interaction between these soluble elements with clays. Boron cannot be measured in Fe-rich clays with ChemCam due to interference between the B and Fe emission in the laser-induced breakdown spectroscopy (LIBS) spectra. Hence, analog studies involving Fe-Mg-rich clays are needed to better understand the observations on Mars. Samples for this study were collected from Rio Tinto borate mine, CA, where borate deposits are hosted by clay-rich rocks. Clay samples collected near these veins have bulk compositions of ~12 wt% MgO, 3.5 wt% Fe₂O₃T and a basal spacing of 12.6Å (comparable to clay minerals detected in Gale crater), compared to 14.8Å spacing of nontronite standard (determined by ICP-MS and XRD) [3]. A sample was mapped using LIBS (J200, Applied Spectra) at McGill University (Fig 1a). Borate at this level of the mine is primarily kernite (sodium borate) [4], which is reflected in the results by the presence of Na (purple hues) within the borate vein (Fig 1b). Li is primarily observed adsorbed to the clay (Fig 1b) which is a similar observation to Li-containing clays in VRR, Gale crater [5]. Figure 1c shows the presence of Fe, Mg, and Si in clay surrounding and within the vein. Pure borate within the vein could indicate boric acid, a product of acidic weathering of the primary borate, which may be similar to the observations at VRR on Mars, but more work is needed to confirm borate structure. Future work will include Raman spectra to understand fine scale structure of borates in the veins, as well as quantification of elements using standard materials for gaining insights on martian B-rich vein mineralogy and geochemistry.

Figure 1. a. 10x image of a borate vein-clay sample (red box shows area mapped by LIBS). False color composite of b. B, Li, & Na. c. Fe, Mg, and Si.

IONIC MOBILITY OF CATIONS AS AFFECTED BY REDOX STATUS OF TWO DIFFERENT SOIL TYPES

*Dayo-Olagbende, G.O. and Ewulo, B.S.

Department of Crop Soil and Pest Management, Federal University of Technology Akure, PMB 704, Ondo State Nigeria

Movement of ions within the soil plays a key role in nutrient availability as well as soil management. Various reactions in the soil contribute to soil ionic mobility and consequently nutrient availability, one of which is the oxidation-reduction reaction. Hence, this study sets out to evaluate the effect of redox status of the soil on ionic mobility of cations. A 3x2x2 factorial experiment was set up on two different soil types (clay loam and sandy clay loam), arranged in a completely randomized design (CRD) with three replicates. The treatment combination involved three levels of Poultry manure (0tha-1, 6tha-1 and 8tha-1), two levels of NPK 15-15-15 (0gha-1, 200kgha-1) and two watering regimes (field capacity and waterlogging). Twelve treatments were obtained giving rise to different redox potential. Redox potential was measured using the method similar to that described by Rabenhorst et al., 2009; Ionic mobility was calculated using the mobility equation.

\[ \mu = \frac{Diq}{KBT} \]

The conductivity was measured using the method of Rayment and Lyon, 2011. Microsoft excel 2010 edition was used to generate graphs. Results from this study show that highly reduced soils recorded the highest ionic mobility, mobility of cations in descending order is \( K^+ > Na^+ > Ca^{2+} > Mg^{2+} \) and sandy clay loam has higher mobility than clay loam.
Advances in atomic force microscopy in the past decade have created new opportunities to probe the mineral-solid interface with unprecedented temporal and spatial resolution. High speed systems now provide imaging at over a frame per second in non-contact mode in fluid. Increases in sensitivity and changes in tip design have enabled atomic resolution of ions on mineral surfaces, even at high imaging speeds. This increase in sensitivity coupled with an analysis of cantilever response to forces imposed by the fluid acting on the oscillating cantilever has led to 3D mapping of fluid density with sub-nm resolution. Here I illustrate the contributions of these capabilities to establishing a picture of ion adsorption, cluster formation, nucleation and fluid structure at mineral-water interfaces.
ENVIRONMENTALLY BENIGN CUNPS@HNT COMPOSITE AND ITS CATALYTIC PERFORMANCE

Amal K Deb*1,2,3,4, Bhabananda Biswas3,4, Ravi Naidu1,3, and Mohammad M Rahman1,3

1Global Centre for Environmental Remediation (GCER), University of Newcastle, the Australia, 2Institute of Leather Engineering and Technology, University of Dhaka, Bangladesh, 3Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE), the University of Newcastle, Australia, 4Future Industries Institute, University of South Australia, Australia.

Azo dyes are well-known carcinogen and a significant amount of dyes is present in the wastewater generated from various industries. Catalytic degradation of dye is often useful but the technique suffers from poor reusability, stability and eco-compliance of the bare catalysts. Catalyst supported on nontoxic and reusable material such as clay mineral could be an alternative effective material. In this study, ultrafine Cu nanoparticles (NPs) were synthesized using biocompatible glutathione (GSH) as both reducing and stabilizing agents and localized them on the surfaces of halloysite nanotubes (HNTs). The composite (CuNPs@HNT) was synthesized by wet chemical method and characterized by TEM, FTIR, XPS, TGA and ICP-MS.

The TEM image of the powder-like composite CuNPs@HNT (Fig. 1A) reflects the uniform localization of ultrafine CuNPs (2-3 nm) on both outer and inner surfaces of HNT. No characteristics peaks of Cu2O and CuO at 623 cm\(^{-1}\), 588 cm\(^{-1}\), 534 cm\(^{-1}\) and 480 cm\(^{-1}\) were observed in FTIR spectra indicating the formation of metallic CuNPs stabilized by GSH on HNT surfaces, which was further supported by the spectra of XPS (data not shown). The Cu content determined by ICP-MS was 118.1 µg/mg composite. TGA proves that the CuNPs@HNT was more stable (1.5 times) than bare NPs at high temperature due to their confinement with HNTs. The material was tested to degrade a widely used azo dye, methylene blue (MB) by following the reduction pathway of catalysis. As evidenced by UV-vis spectra, the CuNPs@HNT exhibited faster catalytic performance than bare CuNPs while only HNT was non-catalytic (Fig. 1B). The MB degradation (99.9%) time was only 4 min by CuNPs@HNT, while bare CuNPs required 6 min for the same. The same degradation efficiency was achieved by only 17.5±2.5 s with the aid of mechanically stirring of the solution, and it was even faster (5 times) than bare NPs. Furthermore, the composite catalyst was reused with similar efficiency consecutively eight times without any purification while the bare CuNPs were not reusable. In conclusion, the CuNPs@HNT may be an ecofriendly, sustainable and potential novel catalyst for the degradation of azo dyes from industrial wastewater.

![Fig. 1: A-TEM image of CuNPs@HNT, B-Catalytic degradation of MB by CuNPs@HNT.](image-url)
The Curiosity rover landed in August 2012 inside Gale, a 150-km impact crater located near the Martian equator. Since September 2014, the rover has been climbing the sedimentary layers of Aeolis Mons, the ~5-km tall central mound of Gale. Most rocks encountered on the mound are laminated mudstones and indicate a lacustrine depositional environment. In January 2019, Curiosity started to investigate the Glen Torridon area, a section of Aeolis Mons stratigraphy where spatially extensive spectral signatures of smectite clay minerals were detected from orbit. The ongoing scientific campaign aims at characterizing the nature, abundance and context of formation of these Martian clay minerals. Here, we present the main results of the geochemical measurements performed by the ChemCam LIBS instrument throughout this campaign.

From orbital observations, three subunits were identified in Glen Torridon, based on terrain texture and spectral properties: the “smooth clay-bearing unit”, the “fractured clay-bearing unit”, and the “fractured intermediate unit” (from bottom to top). The first two subunits are now referred to as the Jura and Knockfarril Hill members, respectively. Rover observations have revealed additional diversity not resolvable from orbit. For example, the Jura member turned out to be composed of two main facies: the “coherent” bedrock, forming relatively large but sparse slabs; and the “rubbly” bedrock, composed of smaller fragments but much more spatially extensive. Compositionally, the coherent bedrock is characterized by higher MgO (~6 to 10 wt%), whereas the rubbly bedrock is characterized by higher K₂O (>1.5 wt%) and SiO₂ (>55 wt%). X-ray diffractions analyses of the coherent bedrock performed by the CheMin instrument show the presence of ~30 wt% of (mostly dioctahedral) smectites. The rubbly bedrock was not analyzed by CheMin, but the enrichment in K₂O and the K/Al ratio measured by ChemCam suggest incipient illitization. The Knockfarril Hill member also shows geochemical diversity, with measured compositions spanning the two endmembers described above. In addition, a layer located near the transition into the fractured intermediate unit displays remarkable similarities with the Jura rubbly bedrock, both in terms of surface expression and composition.

Values of the Chemical Index of Alteration (CIA) calculated using ChemCam data throughout the Jura and Knockfarril Hill members are quite elevated for Mars (~55-60), and are indicative of open-system alteration. Nonetheless, these values are in the same range as those measured in some other sections of Aeolis Mons stratigraphy, which suggests that the distinct orbital signature of Glen Torridon is not primarily explained by the abundance of clay minerals (which CheMin shows to be only marginally higher than in previous terrains). Finally, chemical compositions recently measured in the fractured intermediate unit give decreasing CIA values, which may indicate that Curiosity has reached the onset of the clay-to-sulfate mineralogical transition that is observed from orbit.
COMPARİSON OF X-RAY POWDER DİFFRACTİON AND GEOCHEMİCAL DATA USİNG PRİNCİPAL COMPONENT ANALYSİS

Demir, Huseyin, Schroeder, Paul A.

University of Georgia, Department of Geology, 210 Field St., Athens, GA 30602-2501

Determination of the relative mineral proportions in earth material is an essential part of understanding almost every geologic process. X-ray powder diffraction (XRD) has long been used in identifying minerals and their relative abundances by modeling experimental XRD patterns. The quantitative Rietveld method (Rietveld, 1969) uses the full XRD intensity pattern and fits observed intensities to calculated structures (Bish and Howard, 1988; Chipera and Bish, 2013). The end product of the Reitveld method is a very useful weight percent listing of minerals, despite some inaccuracy resulting from misfit. Clay mineral rich samples present a challenge to the Rietveld method because the model algorithms do not currently include complex defect factors, particularly effects of interstratification and mixed layering. In this present study, we employ the raw intensity XRD data (corrected for instrument and sample sensitive aberrations) by using multivariate statistical principal component analysis (PCA). This PCA approach embraces every X-ray scattering aspect of a sample. To further demonstrate the utility of classifying XRD full intensity patterns, complete major and trace geochemical data for the same samples were also evaluated using PCA.

Samples were gathered from the Sile Region, Turkey. They include clay-rich Miocene lucustrian deposits and nearby rocks consisting of both fresh and weathered andesites, sandstones, and shales. These clays are being studied on the context of a broader effort to better define the geologic history of the Miocene deposits. The geochemical analysis was conducted by Actlab (Canada) using fusion and subsequent ICP and AA methods. A Bruker D8 Advance with Co radiation was used for XRD experiments using Topas software. All data were processed in R software, with log transformations applied to both of the data frames to fullfil multivariate normality required for PCA. PCA of geochemical data demonstrates that 75 % of the variation was defined by the three highest ranking principal components and can be defined by elemental groupings related to ionic potentials and hydrolysis/redox behavior under Earth surface conditions. The three highest ranking principal components were taken into consideration for XRD data (each sample has a data set of n > 7000) with 54% of the variation and sample grouping very similar to the geochemical data. The observed mineral assemblages as defined by quantitative Rietveld further relate the principle components of the full pattern data. Potential parent rocks and clay samples were clustered similarly for all of the PCA, thus revealing insights into provenance studies of these clay deposits.


COMMON FEATURES IN THE BONDING OF BIOLOGICAL TOXINS AND PHARMACEUTICAL MEDICINE TO THE SURFACES OF CLAY MINERALS

Youjun Deng

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

Clay minerals play unique roles in detoxifying biological toxins such as those produced by fungi (mycotoxins) and bacteria. Adsorption and degradation of the toxins by the minerals are the two major detoxification mechanisms. Clay minerals have also been used extensively in pharmaceutical products for the delivery of medicine or for the controlled release of the drugs in targeted organs or tissues. In these applications and many other organic-mineral interaction related areas, it often comes to a basic question on the effectiveness of the clays: how do the clay minerals interact with the interested compounds? If the clays can adsorb or transform so many different organic compounds, how can they be used to selectively adsorb a specific compound but maintain a relative weaker affinity for the coexisting compounds in the system? In this presentation, we will review our own work on mycotoxin, bacterial toxin -clay mineral interactions conducted in the last 15 years, compare them with the interactions of clay minerals with common medicines that have similar functional groups as the toxins. We emphasized the mineral crystal and surface structure-functionality relationship in these studies. Infrared spectroscopic data and computational calculation on energy and surface interaction dynamics were used to reveal the bonding of the toxins and medicine on the surfaces.

Even though the biological toxins and pharmaceutical products have drastically different formulas and functions, they share many common functional groups that are important in their binding to mineral surfaces. The O- and N- containing functional groups are the most important players in the bonding of these large organic compounds to the minerals. Electrostatic interaction, ion-dipole interaction, and coordination are the major driving forces for the strong interactions. Yet, hydrophobic interactions, and entropy gain can play important role in the binding. If adsorption occurred, most of the large biological toxins and medicines cannot be desorbed with water or common electrolytes solution. It appeared that matching the polarity and size of the adsorbing domains and the organics and charge coupling are the most critical factors in determining the mineral’s affinity and capacity for the toxins or medicines. Simple treatments such as replacing the exchange cations in smectite or exchange anions in layer double hydroxides with inorganic or organic compounds, reducing the charge density of the layer structures, and grafting inorganic and organic pillars with controlled size and polarity, can modify the selectivity of the minerals for the toxins and medicines.

Studying the common features and difference in the bonding of the different biological toxins and pharmaceutical medicines with clay minerals offers unique insight to the local structure and surface features e.g, the polarity, adsorbing domain size, and charge of the surface on an atom-size and nanometer scales. The knowledge gained from these studies can guide the selection and modification of the clays for their uses in binding targeted toxin and medicine compounds.
VARIABLE REDOX CONDITIONS AND ALKALINE TREATMENT IN PHYLLOSILICATE MINERALS

Silvina A. Di Pietro1*, Hilary P. Emerson2, Nikolla Qafoku2, James E. Szecsody2, and Yelena Katsenovich1

1Applied Research Center, Florida International University, 10555 West Flagler Street, Miami, FL 33174; 2Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99354

Application of reactive gases including ammonia (NH3) is being considered for remediation of radionuclides by pH manipulation in unsaturated zones. Ammonia gas injection may decrease radionuclide mobility without addition of liquid amendments into the vadose zone. Gas reaction with pore waters elevates the pH inducing soil mineral dissolution with co-precipitation processes occurring and potentially sequestering radionuclides as NH3 dissipates and the pH returns to neutral. However, the mineral dissolution and secondary precipitate formation processes are not well understood in these conditions. We studied the dissolution of clay minerals (illite, montmorillonite, and muscovite) under anaerobic (oxygen-free) and aerobic conditions in NH4OH and NaOH as comparable alkaline treatments. Major cations (Si4+, Al3+, Fe2/3+) as well as pH and oxidation reduction potential (ORP) in the aqueous phase were monitored for over 60 days. Results show that there is a rapid decrease in aluminum dissolution (< 240 hrs) and slow increase in aqueous silica over time (up to 1440 hrs). While the pH remained elevated (11.5 - 12.3) throughout the experiment, there was a difference in dissolution trends when comparing basic solutions. Illite and muscovite (mica) minerals dissolved more with the strong base NaOH, while montmorillonite clay mineral dissolved more with the NH4OH treatment. This is likely due to their mineralogical tetrahedral-octahedral-tetrahedral (T-O-T) interlayer structure as solution cations react differently with the minerals’ surfaces. In the case of mica minerals, dissociated Na+ cations from the strong base (NaOH) bonded with the silicate anion-containing layer. In the case of montmorillonite, the larger NH4+ cation (1.43 Å atomic radius) from the weak base solution intercalated into the expandable montmorillonite layer (~ 10-17Å). Results further show that incongruent dissolution is occurring in batch experiments and suggests formation of secondary precipitates during alkaline treatment. These observations suggest secondary precipitates may be an effective method for sequestration of contaminants within newly formed, low solubility minerals as a result of pH manipulation.
MUTUAL INTERACTIONS BETWEEN REDUCED FE-BEARING CLAY MINERALS AND HUMIC ACIDS UNDER DARK, OXYGENATED CONDITION: HYDROXYL RADICAL GENERATION AND HUMIC TRANSFORMATIONS

Hailiang Dong¹,² and Qiang Zeng¹

¹ Center for Geomicrobiology and Biogeochemistry Research, State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing, China; ²Department of Geology and Environmental Earth Science, Miami University, OH 45056, USA.

Hydroxyl radicals (•OH) exert a strong impact on carbon cycle, due to their nonselective and highly oxidizing nature. Reduced iron-containing clay minerals (RIC) one of the major contributors to the formation of •OH in dark environments, but their interactions with humic acids (HA) are poorly-known. Here we investigate the mutual interactions between RIC and HA under dark and oxygenated conditions. HA decreased the oxidation rate of structural Fe(II) in RIC, but significantly promoted the •OH yield. HA dissolved a fraction of Fe(II) from RIC to form aqueous HA-Fe²⁺ complex. •OH was generated through both heterogeneous (through oxidation of structural Fe(II)) and homogeneous pathways (through oxidation of aqueous HA-Fe²⁺ species). RIC mediated •OH production by providing H₂O₂ to react with HA-Fe²⁺ and electrons to regenerate HA-Fe²⁺. This highly efficient homogeneous pathway was responsible for increased •OH yield. Abundant •OH significantly decreased the molecular size, bleached chromophores, and increased the oxygen-containing functional groups of HA. These molecular changes of HA resembled photochemical transformation of HA. The mutual interaction between RIC and HA in dark environments provides a new pathway for fast turnover of recalcitrant OM in clay- and HA-rich ecosystems such as tropical forest soils and tidal marsh sediments.
CAN TIP-ENHANCED RAMAN NANOSCOPY AND IMAGING REVOLUTIONIZE OUR UNDERSTANDING OF ORGANIC-MINERAL INTERACTIONS?

Patrick Z. El-Khoury

Pacific Northwest National Laboratory, Richland WA 99352

Tip-enhanced Raman spectroscopy (TERS) is an emerging analytical technique that affords single molecule detection sensitivity and (1-few) nanometer spatial resolution under ambient laboratory conditions; in a nutshell, this is the ‘TERS promise’. Indeed, TERS has been used to examine biological, chemical, and catalytic processes at solid-air, and more recently, at solid-liquid interfaces. Unfortunately, rich fundamental physics is often swept under the rug in the rush to demonstrate the many potential applications of this powerful technique. In this regard, I will first discuss the fundamental physical and chemical processes that are broadcasted through TERS. Particular attention will be devoted to understanding hyperspectral TERS nanographs of chemically functionalized plasmonic silver and gold nanoparticles. We will then expose the technique’s pros and cons and explore the potential of TERS for answering fundamental scientific questions regarding organic-mineral interactions.
Comparison of transuranic actinide interactions with sediments at the Hanford Site and Savannah River Site

Hilary P. Emerson*1, Carolyn I. Pearce1, Brian A. Powell2, Kirk J. Cantrell1, Daniel I. Kaplan3, Calvin H. Delegard1, Michelle M.V. Snyder1, May-Linh Thomas1, Dallas D. Reilly1, and Vicky L. Freedman1

1Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99354; 2Clemson University, 342 Computer Court, Anderson, SC 29625

Significant releases of the radioactive actinide elements have occurred from historic development and testing of nuclear weapons worldwide including at the Hanford Site and Savannah River Site located in the U.S. The mobility of actinides at these sites is strongly dependent on oxidation state with their solubility following the trend +5 > +6 ~ +3 > +4 and sorption affinity following the opposite trend. Plutonium (Pu) is generally predominant in the +4 oxidation state in the solid phase in environmental systems and, therefore, exhibits relatively strong sorption and low solubility. The initial phase characteristics, time since release, and presence of ligands and organic compounds also affect their mobility in the environment based on complexation and sorption behavior as particulates, colloids, or dissolved species.

In this research, we consider the mobility of actinides released at different periods from different sources. These experiments represent different actinide phases in Hanford Site sediments, Savannah River Site sediments, and clean quartz sand. The actinides are present in these samples as micron-sized particles, intrinsic (PuO2-type particles) and pseudo-colloids (Pu associated with mineral colloids), and dissolved species. In the Z-9 trench at the Hanford Site, the mobility of micron-sized PuO2 particles was limited while some Pu transported to greater depths potentially as dissolved or intrinsic colloidal species based on a comparison of aqueous concentrations measured in leach experiments with speciation models. It may also be controlled by interactions with phosphate in deeper sediments. However, Pu in the Z-12 trench was more homogenously distributed suggesting its presence primarily as adsorbed Pu species or significantly smaller PuO2 particles. These two trenches received different waste streams likely leading to the different phases in the sediments beneath. Similarly, Pu is relatively immobile in Savannah River Site sediments as shown by laboratory scale batch and column and field lysimeter experiments. Experiments with initially solid Pu\(^{4+}\) source materials in unsaturated lysimeters and saturated columns transported less than a few centimeters. Desorption from Savannah River Site sediments showed that sediments out-competed ligand complexation. However, in pure quartz columns, the mobility as dissolved and colloidal species was observable following the trend: dissolved > intrinsic colloids > pseudo colloids (hematite nanoparticles) with a significant impact of complexing ligands. Overall, these data highlight the importance of the initial waste chemistry and release characteristics as well as sediment characteristics on long-term Pu transport.
ENVIRONMENTAL REMEDIATION OF THE HANFORD SITE’S CENTRAL PLATEAU VADOSE ZONE

Hilary P. Emerson*, Mike Truex, and Vicky L. Freedman

Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99354

The Hanford Site was constructed in 1943 primarily for production of plutonium for the Manhattan Project with the Central Plateau area of the site designated for chemical separations. Significant amounts of radioactive waste were generated as a result of these activities with releases to the subsurface through historic disposal operations in cribs and trenches as well as leaks from underground tanks built to house the most hazardous liquid wastes. Today, cleanup of this site is part of the largest environmental remediation effort in the world led by the Department of Energy. The Central Plateau’s deep vadose zone (up to 80 m below the ground surface) contains radioactive and chemical contamination from these historic operations. The risk-driving contaminants represent long-term sources to groundwater, including uranium, technetium, and carbon tetrachloride. The objective of this seminar is to communicate the essential interdisciplinary knowledge for environmental remediation as developed through the ongoing cleanup of the Hanford Site’s Central Plateau vadose zone.
Circulating in the wellbore, drilling fluid shows both fluid and solid-like behavior under large and small deformations. Therefore, understanding actual rheological behavior of the drilling mud requires to monitor the viscoelastic behavior of drilling fluid as well as their respective properties in a steady shear flow at relatively high shear rates. An exhaustive experimental study was performed on investigating the rheological properties of sepiolite based drilling fluids under small and large deformation at hostile drilling conditions. Conventional aging method using classic viscometer and direct measurement method using high temperature-high pressure (HTHP) rheometer were followed to accomplish elaborate evaluation on the thermal rheological variation of sepiolite fluid systems. Discovery Hybrid Rheometer was used to evaluate linear and nonlinear viscoelastic properties of drilling fluids. The full characterization of real rheological behavior for a drilling fluid system requires considering the results of these three measuring methods.

1. American Petroleum Institute (API) Method

Classic Couette type rotational viscometer is traditionally used to measure the viscosity of drilling fluids in ambient condition. Through this traditional method according to API standards (API RP13B-1, 2004) [1], following procedure is applied to investigate the effect of temperature on drilling fluid viscosity. The fluid samples are poured into pressurized cells that are placed in a roller oven for 16 hours of aging at elevated temperatures (thermal aging). The samples were subjected to ambient condition to be cooled, and then the rheological properties of the samples were measured using Couette type rotational viscometer (FANN 35SA) at different rotor speeds. The rheological properties of active-clay contaminated sepiolite base mud were investigated based on conventional aging method at elevated temperatures up to 204°C. The sepiolite base muds had exhibited particularly good rheological properties at temperatures above 177°C (350°F). The mud samples were not noticeably affected by the water salinity. In extreme temperatures, the sepiolite concentration of muds should be decreased to overcome problems related to degradation, particularly when formulating barite-weighted mud systems. Flocculation was observed when the sepiolite content exceeds 42.75 kg/m3 (15 lb/bbl) for the barite-weighted muds at temperatures above 177°C (350°F) coupled with high amount of active solid contamination.

Conventional viscometer along with thermal aging method commonly used to determine rheological properties of drilling muds can be fallacious to project the effect of temperature on drilling mud behavior. The effect of cooling after the thermal aging could be the major reason of possible misleading in the viscosity measurements. On the other hand, values measured with conventional viscometer might be away from reality due to temperature variations. For this reason, it is necessary to use more effective method in order to obtain accurate rheological behavior of drilling fluids. HTHP rheometer measurements can be used for this purpose. Figure 1 illustrates test procedure applied in API method.
2. Thermal In-Situ Rheological Properties of Sepiolite Mud Using HTHP Rheometer

Knowledge of in-situ rheological properties of a drilling fluid concerning temperature variations has indisputable importance for minimizing borehole instability and enhancing well design. It is also fact that safe drilling practices in environments with narrow mud weight windows dictate rigorous assessment and analysis of temperature and pressure effects on the rheological properties of drilling muds. Thermal rheological properties of sepiolite muds were measured using Model 50 SL high temperature rheometer. In addition, obtained results at elevated temperatures have been compared with those from the conventional viscometer relying on thermal aging method. Moreover, commonly used two drilling muds (bentonite/polymer and lignosulfonate mud) were also subjected to the test with HTHP rheometer to determine the thermal rheological properties and to provide a comparison with the sepiolite muds. Figure 2 shows the test procedure and the thermal rheological and filtration behavior of unweighted fresh water sepiolite mud. Thermal in-situ rheological properties of unweighted fresh water sepiolite mud indicated that the viscosity of sample decreased with increasing temperature up to the gelation temperature (193°C), and then tended to increase with the further temperature increase. This behavior was similar to what observed during rheological measurements using conventional aging method. However, the gelation event began at earlier temperatures based on viscometer data than those of obtained from HTHP rheometer. Compare to the commonly used drilling fluids (Bentonite/polymer and Lignosulfonate muds), sepiolite muds provided more efficient rheological and filtration properties particularly at temperatures above 149°C.

![Figure 1. API test procedure.](image)

![Figure 2. HTHP Rheometer test procedure and the thermal rheological and filtration behavior of unweighted fresh water sepiolite mud.](image)
3. Mechanical and Thermal Viscoelastic Properties of Sepiolite Mud Using DHR Rheometer

Discovery Hybrid Rheometer (DHR II) was used to evaluate linear and nonlinear properties of sepiolite drilling fluid (Figure 3). In order to examine the linear viscoelastic properties of drilling fluids, dynamic tests consisting of transient and oscillation experiments were applied. The most commonly used transient tests are creep-recovery and relaxation tests. Typical oscillation tests used to investigate the viscoelastic properties of materials; amplitude sweep, frequency sweep, oscillation time and temperature sweep tests. Oscillation tests are used to investigate the structural properties of a material. Furthermore, oscillation tests can be used to detect responses to small deformations of materials that cannot be measured from rotational tests. It can provide information about the reaction of a material under both long and short term deformations. The most important feature of the oscillation tests is the measurement of the material under very small deformation without destroying it. It is very important to have non-linear material properties that control the response of the system when the deformation is large and rapid. Therefore, large amplitude oscillatory shear (LAOS) test [2] was applied for the first time to examine nonlinear viscoelastic behavior of selected fluids systems at four different frequencies. As a result of LAOS test, Lissajous-Bowditch curves and nonlinear quantitative parameters were used to understand the variation in nonlinearity and its effects on drilling fluid performances. The results indicate that analyzing viscoelastic properties of drilling fluid and modelling effect of viscoelastic nonlinearities provide more details in understanding some critical problems encountered during fluid circulation.

Figure 3. Test procedure of viscoelastic properties evaluation using DHR II

ACKNOWLEDGEMENT

The authors would like to sincerely thank Scientific and Technological Research Council of Turkey (TÜBİTAK-217M723) as the lead sponsor of this R&D project.

References


MECHANISM OF ADSORPTION OF ATRAZINE ON SMECTITES

Bidemi Fashina*, and Youjun Deng

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

Atrazine is a synthetic herbicide used to prevent of pre- and postemergence broadleaf weeds in crops, golf courses, and residential lawns. Being cheap and highly effective, it is the second-most applied herbicides in the United States. Due to wide usage and mobility, atrazine is the herbicide most often detected in aquifers. This poses a problem since studies have shown that this herbicide is an endocrine-disrupting chemical that may have adverse effects on both animals and humans. Several studies have evaluated the potential of smectites to adsorb atrazine as well as the effects of mineralogical properties of smectites (type of interlayer cation, charge density, interlayer hydration, etc.) on adsorption. The proposed mechanism for smectite-atrazine adsorption being through (i) hydrogen bonding with interlayer water and basal oxygen of aluminate tetrahedra, (ii) van der Waals (hydrophobic interaction) and (iii) ion-dipole interaction through water-bridging. To the best of our knowledge the interlayer adsorption of atrazine by smectites as earlier proposed is yet to be experimentally validated. Though computational efforts have been made to validate the configuration and adsorption of atrazine in the interlayers of smectites. The absence of experimental evidence of the mechanism of interlayer adsorption makes it difficult for such computations to be guided. Therefore, the main objective of this research is to, through experimental investigations, answer the following questions: (i) Can atrazine be adsorbed in the interlayer of smectites as hypothesized? (ii) What are the bonding mechanisms of adsorption of atrazine by smectites?

An amount of 0.1 mg of smectite in water was equilibrated in 0, 0.1, 0.25, 0.5, 1, 2.5, 5 and 7.5 ppm atrazine followed by the quantification of adsorbed atrazine on a UV spectrophotometer. The adsorption capacity \( Q_{\text{max}} \) in mol/kg and binding affinity \( K \) in \( \mu \text{mol/L} \) was from the adsorption isotherms. To study adsorption mechanism, smectite-atrazine complex was prepared by equilibrating 1 mg of smectite several times in atrazine solution. Adsorption mechanism was elucidated using a combination of Fourier transform infrared (FTIR) spectroscopy at varying relative humidity (RH), x-ray diffraction (XRD) at varying temperatures and energy dispersive x-ray spectrometry (EDS).

The XRD of smectite-atrazine complex confirmed that atrazine was adsorbed in the interlayer of smectite. The mechanism of smectite-atrazine interaction was explained from the FTIR and EDS data.
ADSORPTION OF PYOCYANIN BY SMENTITES

Bidemi Fashina*, and Youjun Deng

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

Pyocyanin is one of the phenazine pigment secreted by Pseudomonas aeruginosa as a secondary metabolite. Through the secretion of phenazines (and other pigments) this opportunist bacterium can optimally exercise its pathogenic attacks on humans. P. aeruginosa infection can cause loss of pulmonary function and lung damage in cystic fibrosis patients. The bacterium is the main cause of death and sepsis in immunocompromised individuals such as those with burns, HIV or undergoing cancer chemotherapy. Pyocyanin plays an important role in P. aeruginosa infection by facilitating the development of biofilm, generation of toxic reactive oxygen species, and inhibition of the growth of competing microbes. P. aeruginosa develops resistance to antibiotics quickly and therefore, it is difficult to control with conventional antibiotics. The biofilm makes the total eradication of the bacterium by antibiotics impossible while the reactive oxygen directly damages or kill cells. Since pyocyanin is important in the development and residency of P. aeruginosa, an approach that controls the concentration and distribution of the metabolite might be an alternative effective treatment of P. aeruginosa infection. Herein, a clay-based approach in detoxifying pyocyanin is evaluated. The objectives of the study are to (1) investigate the influence of interlayer cations and source of layer charge of smectites on the adsorption of pyocyanin, and (2) to reveal the adsorption mechanism.

Different cation saturated smectites, M^{n+}—Montmorillonite (where M^{n+} = Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+} or Ba^{2+}) were used to investigate the influence of interlayer cations while four Na saturated smectites (montmorillonite, hectorite, beidellite and saponite) were used to investigate the influence of the source of layer charge. In either case, 0.1 mg of clay in water was equilibrated in 0, 0.1, 0.25, 0.5, 1, 2.5, 5 and 7.5 ppm pyocyanin solutions overnight followed by the quantification of the residual pyocyanin by UV spectrometry. From the adsorption isotherms, the adsorption capacity (Q_{max} in mol/kg) and binding affinity (K in μmol/L) were estimated. The mechanism of adsorption was studied using a combination of molecular simulation (MS), Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD) and energy dispersive x-ray spectrometry (EDS).

The Q_{max} ranged from 0.55 – 0.62 and 0.43 – 0.59 mol/kg for monovalent and divalent cations, respectively. The K was between 0.41 – 0.52 and 0.10 – 0.25 μmol/L for monovalent and divalent cations, respectively. Tetrahedral sheet charge originated smectites have higher K (0.376 – 0.768 μmol/L) compared to those who have their charge originating from the octahedral sheet (0.07 – 0.269 μmol/L). The XRD data, at room and 0% humidity, showed that the pyocyanin molecules are adsorbed in the interlayer. From the EDS data, the mechanism was by ion-exchange. FTIR spectra of pyocyanin-clay complex showed shifts in certain IR bands of the pyocyanin molecule. Results indicate that smectites can adsorb pyocyanin up to 12% of clay weight. Hence, smectites can be used to detoxify pyocyanin and in the treatment of P. aeruginosa infection.
Serpentine Soils Provide Constraints on Clay Mineral and Amorphous Material Relationships in Ferromagnesian Environments Similar to Gale Crater, Mars

Feldman A.D.1, Hausrath E.M.1, Rampe E.B.2, Tschauner O.1, Peretyazhko T.S.2

1University of Nevada, Las Vegas, Department of Geosciences, Las Vegas, NV, 89154; 2NASA Johnson Space Center, Houston, TX, 77058.

The presence of clay minerals interpreted as smectites and a suite of X-ray amorphous materials that are Fe/Mg-rich and Al-poor has been documented in Gale Crater by the CheMin instrument on the Curiosity rover and elsewhere on Mars from remotely sensed data. Based on the presence of volatile compounds measured by the SAM instrument on the Curiosity rover, at least some of the amorphous materials are likely to represent weathering products rather than primary glasses. The nature of and relationships between these amorphous materials and clay minerals remains poorly understood, hampering their usefulness as indicators of past aqueous weathering environments. To understand in greater detail the relationships between Fe/Mg-rich and Al-poor clay minerals and amorphous materials, we are examining changes in soil mineralogy with time in serpentine soils developing in a variety of climate types. Soil and bedrock samples were collected from serpentine bodies in the Candelaria Mining district in the arid desert of west-central Nevada, the Tablelands of subarctic, maritime Newfoundland, Canada, and the dry summer, wet winter Mediterranean climate Klamath Mountains of northern California. Within the Tablelands and Klamath Mountain sites soils were sampled in both recently deglaciated and substantially older locations. Whole rock, bulk soil, and clay size fraction samples were analyzed via X-ray diffraction on randomly oriented mounts and the clay size fraction via oriented mounts following Mg-saturation, air drying, and ethylene glycol solvation, and K-saturation followed by heating to 550°C. These X-ray diffraction analyses suggest two silicate weathering pathways exist, a chlorite to smectite transition through an intermediate randomly interstratified chlorite/smectite, and a dissolution/precipitation pathway where primary silicates (e.g., lizardite, amphibole, talc) dissolve, amorphous materials precipitate, and smectites crystallize out of these siliceous amorphous materials. The chlorite to mixed chlorite/smectite transition was observed in soils of all climatic zones. While the older soils in the Klamath Mountains and all described Candelaria Mining District soils possessed pure smectite phases, the Tablelands soils did not exhibit the development of pure phase smectites with increasing soil age. The Klamath Mountain soils saw large amorphous abundances in the clay size fraction of younger soils, with declining proportions of amorphous materials in older soils, while the Tablelands soils demonstrated continued production of amorphous content with increasing soil age but no development of pure phase smectites, indicating that cooler temperatures might inhibit the transition from amorphous materials to smectites. Comparing these findings to the silicate mineralogy of Gale Crater suggests that during the early Hesperian era (~3.5 Ga ago), Gale Crater experienced extended periods of cold conditions conducive to the preservation of amorphous silicates with brief warmer spells that permitted conversion of these amorphous materials to more crystalline smectites.
MARTIAN CLAY MINERALS FROM ORBIT TO THE SURFACE: MSL AND MER ROVER INVESTIGATIONS OF CRISM SMECTITE DETECTIONS.

V.K. Fox*, K. A. Bennett, R. E. Arvidson, B. L. Ehlmann, E. Dehouck, E. Rampe

Earth Sciences, University of Minnesota, Minneapolis MN (vfox@umn.edu), USGS Astrogeology Science Center, Flagstaff, Arizona, Washington University in Saint Louis, Missouri, CalTech and the Jet Propulsion Laboratory, Pasadena, California, LGL-TPE, Université de Lyon, France, NASA Johnson Space Center, Houston, TX

Coordinated investigation of Martian clay minerals by both orbital (particularly the Compact Reconnaissance Imaging Spectrometer for Mars, a near-infrared reflectance imaging system) and surface assets (the Mars Exploration Rover Opportunity and the Mars Science Laboratory Curiosity rover) has demonstrated a variety of phyllosilicate-favorable aqueous alteration pathways active during both the Noachian and Hesperian periods, and shown that a synergistic approach combining information obtained at many spatial scales is critical to determining geologic context and aqueous conditions as indicated by the presence of clay minerals.

Mt Sharp and Curiosity: The sedimentary central mound of Gale crater contains discrete strata identified as clay-bearing with CRISM observations, and the Curiosity rover reached these regions in January 2019 to explore the outcrops and geologic history. Quantitative mineralogy derived from the rover’s XRD instrument CheMin demonstrate that the mudstones and fine sandstones associated with the CRISM detections carry up to 30 wt.% clay minerals, consistent with the spectroscopic predictions. However, nearly every other mudstone and fine sandstone sample collected by Curiosity in its seven year traverse up the sedimentary mound that are not associated with a CRISM smectite signature have also contained phyllosilicate. In-situ observations of sand and dust cover, as well as the physical characteristics of the outcrops, provide key information to better interpret the observed distributions of mineral detections in orbital data sets.

Endeavour Crater and Opportunity: The Opportunity Rover also characterized several occurrences of smectite clay minerals while investigating the Noachian-aged Endeavour Crater, particularly a region called Marathon Valley that was associated with a CRISM Fe³⁺/Mg smectite detection. Rover compositional measurements demonstrated that the fractured bedrock within Marathon Valley was consistent with that of the commonly observed impact breccia formation that formed most of the crater rim. Thus it is inferred that the crater rim was likely pervasively isochemically altered by post-impact fluid permeation, particularly along fracture systems. That the smectite spectral signal detected from orbit was isolated within Marathon Valley again demonstrates signal detections are controlled by surface texture, dust content and bedrock exposure as well as alteration mineral abundance. Given that at the time of exploration Opportunity lacked an explicit means of measuring mineralogy, these discoveries were dependent on the combination of orbital and in-situ observations.

Alteration to smectite minerals is demonstrably more widespread than implied by the positive CRISM mineral identifications, implying that the thousands of clay-mineral detections seen from orbit represent only a fraction of the true extent of aqueous alteration on Mars.
Nitrogen, Carbon Dioxide and Argon Adsorption for Surface Area of an Unknown New Mexico Clay in order to Elucidate Uranium Abatement

Moticha Franklin, Jeremy Jones, Dr. Antonio Lara

Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, New Mexico 88003

Uranium contaminated drinking water on the Navajo Nation has been extremely detrimental to the surrounding Four Corners region. Contaminated water causes health hazards such as kidney failure, cancer, uranium incorporation into the bone matrix, and sometimes death. Technologies to purify water, such as reverse osmosis, are not appropriate for the Navajo Nation. Therefore, an appropriate solution is needed - inexpensive, simple to implement and needs readily available materials. Clays are the answer. Due to their cation exchange capabilities, clays bind and sequester heavy metals in water, especially uranium. However, muddy suspensions, on adding water to the clay in its powder form are difficult to manage. For this reason, we fabricated clay pellets, and they must maintain structural integrity. Preliminary sorption studies demonstrated uranium abatement with the clay pellets. The resulting uranium concentration levels were less than the established 30 ppb EPA MCL. A Gallup, New Mexico soil was used because it is found juxtaposed to the uranium affected area and has high clay composition. The capacity for clays to sorb heavy metals is directly related to the surface area of the clay. To this end, the ASAP 2050 Extended Pressure Adsorption Analyzer was used with nitrogen (N₂), carbon dioxide (CO₂) and argon (Ar) sorbates to determine the surface area of the Gallup clay in powder and pellet forms under the noted conditions above. Nitrogen is a standard for analysis, but due to its shape it may not best ‘mimic’ uranyl (UO₂²⁺) sorption. Conversely, argon is spherical, and due to its small size, it may represent maximum sorption potential. Carbon dioxide, however, has a linear structure with two oxygens and has the potential to ‘mimic’ uranyl cation (O=O vs. [O=U=O]²⁺). We hypothesize that fabrication of clay pellets will decrease the available surface area, relative to clay powder. Brunauer–Emmett–Teller isotherm sorption measurements follow: N₂ sorbate (powder 62 m²/g; pellets 37 m²/g); CO₂ sorbate (powder 42 m²/g; pellet 31 m²/g) and Ar sorbate (powder 63 m²/g; pellet 38 m²/g). The reduction of surface area on pellet fabrication verified the hypothesis. Even though surface area is reduced, our previous results indicate pellet surface area is more than adequate for uranium sorption. Despite the loss of surface area, pellet manageability, relative to the muddy clay suspension, is a desirable trade-off.
Water chemistry of early Mars recorded in interlayer of smectite and secondary minerals from Gale

Keisuke Fukushi*1, and Yasuhiro Sekine1,2

1Kanazawa University, Institute of Nature and Environmental Technology, Kanazawa, Japan; 2Tokyo Institute of Technology, Earth and Life Science Institute (ELSI), Tokyo, Japan.

There is a wealth of geomorphological and mineralogical evidence indicating the presence of liquid water on early Mars [1,2]. However, the chemical properties of the water such as pH and salinity, which are crucial to habitability on early Mars, have not been clarified so far. The almost all previous attempts to reconstruct the ancient water chemistry on Mars are bottom-up approach to reproduce the observed mineral assemblages by assuming the initial solution compositions, reactants minerals, water-rock ratio and the series of chemical reactions [3,4,5,6]. The water chemistries obtained from the bottom-up approaches must highly depend on the assumptions, which are always difficult to justify on early Mars.

The top-down approach for the quantitative reconstruction of the water chemistry of pore-water in terrestrial clay rocks was proposed by Gaucher et al [7]. This approach can reproduce the measured water chemistry in porewater in clay rocks without any estimated parameters [7]. Smectite is unique mineral that possesses the exchangeable cation (Na+, K+, Mg2+ and Ca2+) in the interlayer. The interlayer can record the major cationic composition of the surrounding solution. The geochemical modeling based on the cationic composition in smectite and the mineral assemblages of the secondary phases can provide the reasonable prediction of other solution parameters such as anion compositions including dissolved carbonate, pH and redox conditions [7,8,9].

The NASA rover Curiosity has conducted a geological survey of Gale crater, a former lake on Mars, and provided mineralogical and geochemical data on the lacustrine sediments [1]. The obtained X-ray diffraction patterns from the several layers of the sediments provide the information about the exchangeable cations of smectite as well as the secondary minerals such as calcium sulfates and iron oxides [10]. The smectite in the sediments can record the water chemistry in the pore-water at the last stage in the presence of liquid water. Present study quantitatively estimates the major components composition of pore water and reconstructs the environmental conditions to produce the water chemistry at Gale [11].

POROSITY ESTIMATES AND MINERALOGY OF THE LOWER PERMIAN WOLFCAMP SHALE, MID CONTINENT, UNITED STATES OF AMERICA

Morgan K. Garner¹, W. Crawford Elliott*¹, R.D. Elmore², K. Garrett², and L.M. Anovitz³

¹Department of Geosciences, Georgia State University, Atlanta, GA 30302-3965.
²School of Geosciences, University of Oklahoma, Norman, OK 73019
³Geochemistry and Interfacial Sciences Group Oak Ridge National Laboratory Oak Ridge, Tennessee 37830-6110

A set of representative samples of the lower Permian Wolfcamp Shale, a prominent tight shale play in the Midland Basin (Texas) in the mid-continent were investigated to test for an hypothesized relation among the sizes of pores, the extent of thermal maturity and the progress of smectite-to-illite reaction. The samples range in thermal maturity from 0.8-1.07% VRo. Authigenic minerals identified in this range of thermal maturity included illite (I-S with high percentage 80-90% of illite layers), quartz, kaolinite, pyrite, chlorite, dolomite, and albite. Both detrital and diagenetic illite were observed based on field emission scanning electron microscopy (FE_SEM) and microporosity was observed between clay aggregates, in organic material, and in pyrite framboids. Based on XRD analysis, the stacking order and percentage of illite layers in I-S were consistent with the measured thermal maturity. Measured pore lengths ranged from 109 nm to 940 nm from FE-SEM images.

The sizes of nanopores within the sample is described by a positively skewed log-normal distribution with a series of peaks at nano- to mesoscales from small angle X-ray scattering data (SAXS, USAXS). Overall, the pore sizes ranged from 20 nm to 150 nm. The shales having the lower thermal maturity values showed a range of pore sizes from 30-150 nm whereas the shales with the highest thermal maturity values had more abundant finer pore sizes in the range of 20-50 nm with some nanopores being as large as 100 nm. The nanopores decreased in size with increased thermal maturity. The small angle scattering data showed packets that are consistent with I-S being composed of fundamental particles as opposed to MacEwan crystallites. The results of this study suggest that compaction and diagenetic mineral formation occluded porosity at higher thermal maturities.
African dust is transported to the Amazon Basin and the Tropical Atlantic Ocean in the winter and spring where it can deposit vital nutrients that stimulate primary productivity and help facilitate the drawdown of atmospheric carbon dioxide. Despite interest in this topic and its potential importance for Earth’s climate, few measurements exist to document this phenomenon and quantify its impacts on biogeochemical cycles. Here I will discuss aerosol measurements collected at a site in Cayenne, French Guiana located on the coast of the Tropical Atlantic Ocean that also sits at the gateway to the Amazon Basin. This site only receives long-range transported and sea spray aerosol and is ideal for determining the impact of long-range transported African dust on the Amazon Basin. In this presentation, I will discuss seasonal variations in nutrient loadings, nutrient solubility, and aerosol sources derived from bulk and single particle measurements of both iron (Fe) and phosphorus (P) containing particles. Our measurements reveal the vital importance of African dust as a supply of P and Fe to the Amazon Basin and Tropical Atlantic Ocean during peak dust transport season, and that this dust contains bioavailable forms of Fe and soluble forms of P. However, our measurements also reveal that in addition to mineral dust, other particle sources are also important for supplying nutrients to these ecosystems. In particular, I will show that freshwater diatoms that are frequently transported from African paleolakes to South America are also an important source of Fe. I will also show the underappreciated role of African biomass burning as an important driver of P solubility even during peak dust transport season. Overall, our results yield a more complete view of how African dust transport contributes nutrients to both the Amazon Basin and the Tropical Atlantic Ocean.
SIMULATING X-RAY SPECTROSCOPIES: THEORY AND APPLICATIONS

Neri Govind\textsuperscript{1} and Micah P. Prange\textsuperscript{2}

\textsuperscript{1}The Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory, Richland WA 99352
\textsuperscript{2}Pacific Northwest National Laboratory, Richland WA 99352

The emergence of highly monochromatic, intense tunable synchrotron radiation in various energy regimes varying from relatively soft x-rays (1-5 keV) to hard x-rays (above 5-10 keV) has revolutionized x-ray spectroscopies. However, it has become increasingly apparent that accurate theory is required to harness the full potential of these methods for understanding and interpretation of the x-ray spectra. In this talk we will present an overview of state-of-the-art theoretical approaches for simulating x-ray absorption and emission spectra. Applications to molecular complexes and mineral systems relevant to environmental science will be presented. We will illustrate how these calculations can be used to interpret experimental data as well as to shed light on the chemical state, local structure and chemical bonding in complex environments. Current limitations and future developments will also be discussed.
We investigated the interactions responsible for the cohesion of colloidal materials such as clays, cement. The swelling/cohesive properties of these (lamellar) materials depend both on the nature of the (interlayer) cations and on the surface charge of the layers. The overall goal of this work is to determine the right level of modeling complexity required to capture the cohesive behavior of charged materials immersed in an electrolyte. We used various numerical modeling approaches of increasing complexity from the Primitive Model to full-atomistic description to get the so-called Potential of Mean Force (PMF) between elementary particles: platelets for smectite clay, tubes for imogolite clay and spheres for cement hydrates. In particular, we introduced the Explicit Solvent Primitive Model (ESPM), in which ions are modeled as charged hard spheres and solvent molecules as soft spheres with embedded point dipoles. We showed that taking explicitly into account the solvent in such a Primitive Model description, significantly impacts the system cohesion and allows refining atomistic scale results. Ionic correlation interactions are always present between charged objects immersed in an electrolyte and always play an important role, even in the case of system carrying a low surface charge balanced by monovalent counter-ions such as clays. Cement hydrate is used an example of highly charged systems while clay are examples of less charged systems. Overall, the Potential of Mean Force (PMF) strategy to get realistic interactions between elementary particles allows for a truly consistent multi-scale modeling approach of complex systems.
TRANSFORMATION PATHWAYS OF GIBBSITE INTO LiAl-LDH IN CONCENTRATED LITHIUM HYDROXIDE

Trent R. Graham¹,², Jian Zhi Hu¹, Xin Zhang¹, Mateusz Dembowski¹, Nicholas R. Jaegers¹,², Chuan Wan¹, Mark Bowden¹, Andrew S. Lipton¹, Andrew R. Felmy¹, Sue B. Clark¹,², Kevin M. Rosso¹, and Carolyn I. Pearce¹

¹Pacific Northwest National Laboratory, Richland, Washington 99352, United States
²Washington State University, Pullman, WA 99164, United States

Layered double hydroxides are widely used materials in areas including corrosion science, chemical separations, and catalysis. One strategy to synthesize these materials is through lithiation of the aluminum hydroxide mineral, gibbsite (α-Al(OH)₃), to form the layered double hydroxide, lithium aluminate hydroxide dihydrate (LiAl-LDH, Li[Al(OH)₃]₂OH·2H₂O). Due to the structural similarity between LiAl-LDH and gibbsite, previous transformation mechanisms suggested that phase transformation occurred through insertion of ions. However, in highly alkaline, hydroxide containing solutions, dissolution and precipitation pathways become available. By using in situ ²⁷Al magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) and complementary X-ray diffraction, scanning electron microscopy, and high field ²⁷Al MAS NMR, the phase transformation pathway is clearly demonstrated to be predominantly through dissolution of gibbsite and precipitation of the incipient, metastable aluminate ions. The elevated concentration of metastable aluminate ions correlated with the persistence of gibbsite at intermediate times, which was evident by both X-ray diffraction and high field ²⁷Al MAS NMR. This improved understanding of the gibbsite transformation pathway into layered double hydroxides presents intriguing opportunities to tune both the structure and reactivity through manipulation of reaction conditions and may help in the development of strategies to control aluminum concentrations in industrial applications, such as aluminum refining and high level nuclear waste processing. This work was conducted by the Department of Energy, Energy Frontier Research Center on Interfacial Dynamics of Radioactive Materials and Environments (IDREAM).
MOLECULAR-SCALE STUDIES OF SURFACTANT PARTITIONING ON MUSCOVITE SURFACES

Jeffery A. Greathouse*,1, Daniel M. Long2, Guangping Xu1, Hongkyu Yoon3, and Katherine L. Jungjohann2

1Geochemistry Department, 2Center for Integrated Nanotechnologies, and 3Geomechanics Department, Sandia National Laboratories, Albuquerque, New Mexico, USA.

Surfactants’ ability to manipulate properties of mineral surfaces and fluid properties (e.g., interfacial tension) has resulted in widespread industrial use, including application for increasing oil mobility during enhanced oil recovery processes, enhanced geological carbon storage, and environmental remediation. However, many of these attempts have been improved empirically with little fundamental understanding of the complex processes. To better control the flow of fluids in the subsurface, science-based improvements can be achieved from a molecular understanding of complex fluids at mineral interfaces. Our specific focus is on the effect of cation binding on anionic surfactant behavior at muscovite surfaces, as mica is a well-characterized mineral representative of clay phases present in many geologic formations. Previous neutron reflectometry studies indicate that some cations are able to bind one such surfactant (AOT) directly to the surface via a cation bridging mechanism (Allen et al., 2017; Allen et al., 2019). In oil production, this mechanism is believed to be responsible for enhanced reservoir output following low-salinity waterflooding (Lager et al., 2008). Divalent cations are replaced by monovalent cations, releasing bound polar organic molecules in the process.

We have applied molecular dynamics (MD) simulations to investigate the partitioning of AOT in aqueous fluids near a muscovite surface. Simulation results are compared with nanoscale cryogenic electron microscopy, macroscopic vibrational spectroscopy and contact angle measurements. The MD simulations show that AOT bilayers form in the aqueous region when sufficient numbers of AOT molecules are present. At lower AOT concentration, micelles form near the surface. The adsorption mechanism of bilayers and micelles depends on the cation present, ranging from cation bridging via adsorbed cations and AOT sulfate head groups to weaker adsorption via outer-sphere surface complexes. Other measurements at both molecular and continuum scales will validate the MD simulation results and improve the simulation applicability for more complex systems.


SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.
Sulfide-bentonite interactions: linking sulfide oxidation and iron reduction

Hadi J. Author and Presenter\textsuperscript{1}, Pekala M.\textsuperscript{1}, Grenèche J.M.\textsuperscript{2}, Wersin P.\textsuperscript{1}, Muuri E.\textsuperscript{3}, and Koho. P.\textsuperscript{3}

Collaborators

\textsuperscript{1}University of Bern, Institute of Geological Sciences, Bern, Switzerland; \textsuperscript{2}University of Le Mans, IMMM, Le Mans, France; \textsuperscript{3}Posiva Oy, Olkiluoto, Finland.

Geological repositories for nuclear waste disposal will employ bentonites as a buffer confining and protecting waste canisters. Anaerobic conditions will prevail and sulfate reducing bacteria, which may be present at the bentonite/host rock interface, may eventually produce sulfide, which presents a potential threat for metallic canisters. In this study, concentrated (4 to 100 mM) sulfide solutions were reacted with different types of low iron-bearing (from Wyoming, Milos, and Laviosa) and high iron-bearing (from India and Czech Republic) bentonites, along with isolated or blended common Fe-bearing components of the bentonite (purified montmorillonites, goethite, hematite and maghemite), in batch experiments lasting from 1 hour to 1 month, at pH values ranging from 7 to 13. Solutions were analyzed by colorimetry to determine final sulfide and polysulfide concentrations, and solids were analyzed by \textsuperscript{57}Mössbauer spectrometry to determine iron speciation.

Notable sulfide consumption was found, ranging between 150 and 700 mmol·kg\textsuperscript{-1}·bentonite. The main identified product of sulfide oxidation in the bentonite was elemental sulfur, which further partly reacted with excess sulfide to form polysulfides. Most of the sulfide consumption (>75\%) was observed within the first 48 hours of reaction. The main reactive pool of reactive iron was found to be smectite structural iron (reduced to up to 80\% in MX80), while the (oxyhydr)oxides pools were almost not impacted (cf. diagram below). The strong reduction of the clay is accompanied with dramatic color changes and possibly also structural changes. This study highlights that bentonites are efficient scavengers of sulfide.

![Fe speciation](image)

Iron speciation in a synthetic mixture of reference smectite SWy with 0.93 wt.% goethite reacted with a concentrated sulfide solution over a reaction time of 1 month (S:Fe = 1:1 mol:mol, L/S = 20 L·kg\textsuperscript{-1}, pH 7.8-8.5).
Contrasting roles of reactive iron vs. aluminum phases in soil carbon persistence: a multi-scale perspective

Steven J. Hall*1, Wenjuan Huang1, Wenjuan Yu1, Chenglong Ye1,2, Aaron Thompson3

1Iowa State University, Department of Ecology, Evolution, and Organismal Biology, 251 Bessey Hall, Ames, IA 50011; 2Nanjing Agricultural University, College of Resources and Environmental Sciences, Nanjing 210095, China; 3University of Georgia, Department of Crop and Soil Science, Athens, GA 30602.

The abundance of short-range-ordered (SRO) iron (Fe) and aluminum (Al) phases, estimated using oxalate-extractable metals (Feo and Alo), is often the strongest predictor of soil organic carbon (SOC) concentrations in humid ecosystems. However, the relative roles of Fe vs. Al in mediating this relationship remain poorly understood. Here, we synthesize several recent case studies spanning continental- to nano-scales to explore relationships among Fe, Al, and SOC. Using a continental-scale dataset of >2,500 soil samples from National Ecological Observatory Network (NEON) sites, a random forest model showed that Alo was a consistently stronger predictor of soil C than Feo. However, the relationships were nonlinear and differentially sensitive to climate. The response of SOC to increasing metal concentrations began to saturate at approximately 5 mg g⁻¹ for both Alo and Feo. A positive relationship between Alo and SOC was maintained across broad gradients of temperature and precipitation. In contrast, Feo-SOC relationships were strongest in cold, humid ecosystems and decreased with increasing temperature and moisture deficit. In a subset of these NEON samples, we found that Alo showed a strong relationship with the molecular composition of SOC measured using ¹³C NMR. Here, Alo was the best predictor of the contribution of lignin to SOC, whereas Feo had no significant relationship with any SOC molecular component. Rather, crystalline Fe phases (estimated as dithionite- minus oxalate-extractable Fe) were positively related to carbohydrate relative abundance. To further explore interactions among SOC molecules, Fe, and Al, we conducted a laboratory incubation where an Oxisol rich in SRO phases was amended with plant litter and ¹³C-labeled lignin and exposed to pretreatments varying in oxygen availability (0–12 days of anoxia). After 10 months, half of the added lignin was associated with the mineral soil fraction. Longer anoxic pre-treatments led to greater association of lignin-derived C with Fe, measured by nanoscale secondary ion mass spectrometry (NanoSIMS), likely due to co-precipitation following Fe(II) oxidation. However, further examination showed that Al:Fe ratios were even greater in lignin-enriched microsites. Based on these collective findings, we propose tentative hypotheses to motivate further study: 1) The differential climate sensitivity of Fe-C vs. Al-C relationships over broad spatial scales is influenced by the vulnerability of Fe-associated SOC to reductive dissolution in warm, wet environments. 2) Turnover of SRO Fe-associated SOC is faster than SRO Al-associated SOC. 3) Fe-associated SOC is not intrinsically stable but requires other biogeochemical mechanisms (e.g. aggregation, mineral substitution) to increase persistence.
THE PHYLLOSILICATE-DOMINATED MINERALOGY OF ASTEROID (101955) BENNU

V. E. Hamilton¹, A. A. Simon², H. H. Kaplan¹, P. R. Christensen³, D. C. Reuter², R. D. Hanna⁴, and D. S. Lauretta⁵

¹Southwest Research Institute, 1050 Walnut St. #300, Boulder, CO 80302; ²Goddard Space Flight Center, Greenbelt MD 20771; ³School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287; ⁴University of Texas, Austin, TX 78712; ⁵Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721.

NASA’s Origins, Spectral Interpretation, Resource Identification, Regolith–Explorer (OSIRIS-REx) spacecraft carries two spectrometers for the characterization of asteroid (101955) Bennu. OVIRS, the visible and near infrared spectrometer, and OTES, the thermal emission spectrometer, measure Bennu’s mineralogy, chemistry, and temperature.

Early in the mission, both spectrometers observed strong evidence for the presence of hydrated minerals on the asteroid’s surface [1]. One of the most prominent spectral features observed by OVIRS is a ~2.7-µm hydration band whose position (2.74 µm ±0.01) is most consistent with relatively magnesian phyllosilicates in CI and low petrologic subtype CM carbonaceous chondrites [1, 2]. This feature is present in all spectra observed to date and the band position has not yet been observed to vary within the uncertainty of the measurements. OTES reveals spectral absorption features attributable primarily to diagnostic phyllosilicate stretching and bending modes [1]. There are spectral differences attributable to particle size variations in the ~1250 - 830 cm⁻¹ (~8 - 12 µm) region but the lower wavenumber region (<~550 cm⁻¹ or >~18 µm) exhibits a spectral shape that does not vary with particle size and reveals phyllosilicates to be volumetrically dominant, as is the case for CI and lower petrologic subtype CM chondrites. By comparison with a wide range of CI and CM meteorite spectra having known modal mineralogies, we can infer that the surface of Bennu is likely comprised of ≥85-90 vol.% phyllosilicates.

The CI chondrites are the most aqueously altered carbonaceous chondrites known (>90 vol.% phyllosilicate) and CM group chondrites exhibit varying degrees of aqueous alteration that are typified by mineralogies containing ~55 - 90 vol.% phyllosilicates [3]. With progressive alteration, phyllosilicate compositions evolve from relatively iron-rich (e.g., cronstedtite) to relatively magnesian (serpentines and saponite) and these may be poorly crystalline. The spectral features observed by OVIRS and OTES constrain both the chemistry and the fractional abundance of phyllosilicates on Bennu to among the most altered compositions in our meteorite collections. The returned sample will therefore meet the mission objective of returning hydrated (and organic-rich) material from the early solar system.

PHYSICOCHEMICAL AND GEOTECHNICAL EVALUATION OF LIME TREATED FLUID FINE TAILINGS

Narain Hariharan¹, Nikolas Romaniuk¹, Michael J. Tate¹, Jesse Fox¹ and Dallas N. Little²

¹Graymont, 585 Southridge Circle, Sandy, UT 84070 ²Texas A&M University, Department of Civil Engineering, College Station, TX 77843.

Dewatering the clays present in the Canada’s oil sand fluid fine tailings (FFTs) beyond the liquid limit and reclaiming the tailing solids as a geomechanically stable stackable material requires the use of chemical additives capable of modifying the chemistry of the clays. Towards this end, in this study, two oil sands FFTs, FFT 1 and FFT 2, having a solids content of 25 to 30 % by mass were dewatered using a decanter centrifuge and pressure filtration processes respectively after treatment with a hydrated lime (calcium hydroxide) slurry to achieve solid cakes with solids concentrations ranging between 55 to 70 %. The primary focus of this work was to understand the nature and sequence of chemical reactions taking place between lime and the FFT minerals and to assess the associated physical effects by evaluating basic geotechnical properties.

First, a physicochemical evaluation of FFT 1 after lime treatment was conducted using analytical experiments including pH, cation exchange capacity (CEC), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The mineralogical composition of FFT G predominantly comprised kaolinite, illite and quartz. Comparison of the initial (Day 0) CEC, MBI and XRD patterns of the untreated and hydrated lime treated FFT centrifuge cakes indicates that the mineralogy of the source FFT was retained in the cake fraction after lime treatment while there was poor clay capture in the untreated cake. The XRD patterns further illustrate the formation of calcite in the lime treated FFT cakes at elevated pH due to a combination of the depletion of carbonates and bicarbonates and carbonation of the excess unreacted lime. Calcite in the lime treated cakes existed both as a separate phase and was deposited on the surface of kaolinites which was illustrated through SEM images. The formation of calcite was accompanied by an intensity reduction in the kaolinite peak as pH increased, in XRD patterns recorded 28 days after lime treatment. Further, elemental phase mapping of the SEM patterns showed the coexistence of Ca, Al and Si on the surface of the kaolinites leading to the possibility of calcite cementing the kaolinite particles. Adding lime to increase the pH of the FFTs above 12.0 enhances the solubility of the aluminates and silicates present in the clay minerals resulting in the formation of pozzolanic products which was illustrated using SEM.

To supplement the physicochemical effects observed, the impact of lime slurry on the immediate and long-term (first 6 months) geotechnical properties of FFT 2 were evaluated by measuring the changes in Atterberg limits, clay content and undrained shear strength of the pressure filter cakes. At a dosage of 1 % of the wet mass of the FFT, hydrated lime increased the plastic limit (PL) of the cakes and produced peak shear strengths more than 20 kPa at less than 65 % solids content within 1 day and over 100 kPa at 70 % solids content within 28 days after treatment. In summary, by increasing the pH of the FFTs unlike other coagulant and flocculant treatments, hydrated lime addition facilitates improved dewatering and reclamation characteristics of the FFTs by enhancing initial capture of clays within the cake followed by suppressing the clay activity and increasing long-term cake strength through pozzolanic reactions.
CURATION OF MARTIAN PHYLOSILICATES – DEVELOPING STRATEGIES FOR A UNIQUE ASTROMATERIAL COLLECTION

Andrea D. Harrington¹, Michael T. Thorpe², and Elizabeth B. Rampe¹.

¹ NASA Johnson Space Center, Houston, TX 77058; ² NPP at NASA JSC
*corresponding author: Andrea.D.Harrington@NASA.gov

The launch of NASA’s Mars 2020 mission kicks off the first stage of an international three-part Mars Sample Return (MSR) campaign, anticipated to return martian samples to Earth in 2031. One of the major intricacies of MSR is that Mars is classified as a restricted body, since it is considered by scientific opinion to be “of significant interest to the process of chemical evolution and/or the origin of life” by NASA’s Office of Planetary Protection. While this classification requires the implementation of an array of safety precautions to protect Earth from a possible biohazard (e.g. utilization of a highly specialized BSL-4+ containment facility), the anticipated presence of clays and hydrated minerals may require unique handling and storage conditions not currently utilized for current curation collections.

The majority of NASA’s pristine astromaterial collections are stored under ultra-pure and ultra-dry nitrogen, with a subset stored frozen, in helium, or under vacuum. Due to the nature of the samples and the environments in which they were collected (e.g. lunar, asteroidal, solar-winds), the use of these reducing/anoxic environments are preferential. Currently, due to an array of factors, this dry nitrogen environment is the benchmark for Mars sample handling and storage. However, given what is known about the martian surface, should other environments be considered?

The martian surface environment and geologic history is fundamentally different from Earth’s. The atmosphere is primarily composed of CO₂ and a low surface pressure (~6 mbar) allows for oxidizing conditions to prevail. The contemporary climate of Mars is exceedingly cold (~ -63°C), hyperarid, and aeolian reworking dominates the landscape. However, the sedimentary rock record of Mars reveals a vastly different history and because Mars lacks plate tectonics, ancient sedimentary rocks remain exposed on the surface. Phyllosilicates on Mars are concentrated in these ancient terrains (~3.5-4 Ga old), ultimately providing clues to aqueous environments that predate the sedimentary record of Earth. Orbital and in-situ measurements indicate that smectite is the most common clay mineral, but chlorite, serpentine, and other phyllosilicate phases have been identified from orbit. In-situ X-ray diffraction analyses by the Chemistry and Mineralogy (CheMin) instrument on the Mars Science Laboratory mission in Gale crater demonstrate that smectite present in ancient mudstone samples are generally collapsed and display a 10 Å basal spacing. Other hydrated phases exist on the martian surface (e.g., gypsum, anhydrite, and a hydrated X-ray amorphous component) that might also require special environments for curation.

As with other astromaterial collections, it is likely that these samples will be subdivided and stored in different environments. It is important to highlight the array possible environments early so proper studies can be performed to inform material restrictions, as well as sample handling and storage processes.
Uranium contamination in drinking water is an ongoing crisis for citizens of the Navajo Nation. This problem can be mitigated with locally produced clay pellets known to abate uranium, but parameters that effect the robustness of these pellets must be understood before they are utilized. It is known that chloride salt solutions affect the zeta potential and liquid limit of clays, but there is little study on how these solutions alter the robustness of a clay, especially following heat-treatment. This is surprising given how cations affect clay platelet coordination, such as potassium in illite clays. To better understand this effect, chloride salt solutions were mixed into two clays, a standard sodium-bentonite clay (SWy-1) and a locally sourced illite-smectite clay, at specific weight ratios during the pellet fabrication process. The chloride salt solutions used were LiCl, NaCl, and KCl with each at a concentration of 0.8M. The robustness of each set of pellets was quantified by the maximum compressive force (MCF) measured during unconfined compression testing. The addition of NaCl had little to no effect on the pellet robustness; the bentonite pellets maintained a MCF of 700±100 ftlb (n=15) while the illite-smectite pellets’ MCF slightly decreased from 2300±200 ftlb (n=15) to 2000±300 ftlb (n=15). The addition of the other chloride salts, however, has preliminarily shown to increase pellet robustness. The bentonite pellets’ MCF increased to 900±100 ftlb (n=5) when using LiCl and 1300±300 ftlb (n=5) when using KCl. This finding suggests that externally added cations can have a significant effect on heat-treated pellet robustness.
NANOSCALE MINERAL TRANSFORMATIONS CONTRIBUTE TO HYDROCARBON MOBILIZATION AND TRANSPORT DURING STIMULATION OF UNCONVENTIONAL RESERVOIRS

Ryan J. Herz-Thyhsen*1, 2, Quin R. S. Miller3, Gernot Rother4, John P. Kaszuba2–5, Thomas Ashley2, Ken Littrell6

1Enerplus Resources Corporation (USA), Denver, CO; 2Department of Geology and Geophysics, University of Wyoming, Laramie, WY; 3Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA; 4Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN; 5School of Energy Resources, University of Wyoming, Laramie, WY; 6Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, TN.

Hydraulic fracturing allows for production of hydrocarbons from low-permeability, organic-rich formations that harbor oil and gas within abundant nanoporosity. Although the exact mechanisms of fluid storage, release, and transport remain unclear, an evolving body of literature has highlighted the important role injected fluids play in inducing physicochemical changes to formation rocks. Understanding the evolution of pore networks during mineral reactivity in low-permeability rocks is crucial for understanding and optimizing efficient and sustainable recovery of resources hydraulic fracturing activities, helping establish the US as a net energy exporter.

In order to provide insight into the mechanisms listed above, we conducted a series of hydrothermal experiments in which low-permeability clay-rich sandstone from Wyoming’s Powder River Basin was reacted with a hydraulic fracturing at subsurface conditions. We used time-resolved aqueous geochemical analyses and electron microscopy to demonstrate fluid-rock interaction induced dissolution of calcite cement and clay minerals (illite and chlorite). We leveraged DOE user facility resources and synergistic National Laboratory expertise to illuminate how the nanoscale pore-network architecture was influenced by geochemical and mineralogic transformations. We analyzed unreacted and reacted rocks with small-angle neutron scattering in conjunction with high-pressure mercury intrusion to assess changes in pores with ~1-1400 nm diameters. These analyses revealed alteration to the pore-matrix interface resulted in reduced internal surface area and interfacial roughness, along with a 5- to 10-fold increase in permeability. These collective findings strongly suggest that mineral transformations enhance hydrocarbon mobilization and transport through low-permeability rocks. These insights have broad potential to enhance production in many other basins by informing stimulation strategies, including tailoring of injection fluid compositions.
NUCLEATION, GROWTH, AND IMPLICATIONS OF NANO-MANGANESE OXIDES VIA NANO-IRON OXIDE CATALYSIS

Michael F. Hochella, Jr.*

Department of Geosciences, Virginia Tech, Blacksburg, VA., 24061.

The secondary mineral nucleation and growth of manganese oxides in soils and sediments are thought to be among the most important inorganic scavengers of aqueous trace metals in contaminated sites around the world. These manganese oxides exhibit this dominant sorptive behavior despite the fact that they are much less abundant than iron oxides. In addition, because the resulting manganese oxides are typically one-, two-, and three-dimensional nanoparticles, their role is most often overlooked or unnoticed, sometimes despite careful macroscopic analysis. Even when microscopic analysis is used, they are often missed or discounted. Furthermore, many manganese oxides, which come in a remarkable variety of compositions and atomic structures, some of which are likely yet to be discovered and characterized, provide reactive sorptive sites internal to their atomic structures, often between sheets (like many clays) and within a great variety of tunnel structures. Therefore, these types of studies and knowledge go beyond academic curiosity, and into the realm of effective contaminant immobilization and clean-up strategies.

We have determined over the years that common and abundant iron oxides (hematite, goethite, ferrihydrite, magnetite, and likely many others) provide highly active catalytic surfaces for rapid abiotic nucleation of manganese oxides in oxygenated water in the laboratory1-4, and that analogues of these laboratory studies can be found in natural soils and sediments in the oxic zone.5-8 In the most detailed laboratory study to date using nanohematite3, in 48 hours of reaction with 10^3 M aqueous Mn^{2+}, manganite MnO(OH) nanowires were formed by way of nanowires of manganite-polymorphs groutite and feitknechtite. Within 168 hours of reaction, it was apparent that manganite nanowire surfaces were hausmannite, a mixed valence state Mn oxide (Mn^{2+}Mn^{3+}O_{2}) to a depth of roughly 2 nm. These experiments show how intricate these reactions can be where thermodynamic and kinetic aspects are dependent on surface sorption complexation details and semiconducting heterogeneous redox processes, as well as phase stability in heterogeneous and nano-dominant systems such as these. This complexity will inevitably be key in natural systems as well.

Hydrothermal synthesis of pollucite below 100°C for Cs immobilization

Seokju Hong¹, and Wooyong Um¹,*

¹Division of Advanced Nuclear Engineering (DANE), Pohang University of Science and Technology (POSTECH), Pohang, South Korea, 37673

Since radioactive Cs-137 was the most problematic radionuclide in the Fukushima nuclear accident, many researchers have developed various types of sorbents that can selectively remove the Cs ion. In addition, there were many researches about immobilization (or fixation) of Cs into final solid phase or waste form. Recently, pollucite (CsAlSi₂O₆) became a promising material for the final storage, because pollucite has an aluminosilicate structure that can hold Cs well.

However, the most disadvantageous thing in pollucite synthesis is that we need to use a stainless-steel pressure vessel at temperatures around 180–200 °C. Furthermore, even some researchers suggest that the threshold temperature for pollucite synthesis is 160°C, however this process still needs to use stainless-steel vessels.

Thus, in this study, a new hydrothermal synthesis using natural zeolite (clinoptilolite) at reduced temperature below 100 °C was developed. In addition, pollucite could be synthesized using a simple Teflon bottle, not a stainless steel pressure vessel, which can treat larger amounts of radioactive liquid waste than a stainless steel pressure vessel used.

A new hydrothermal synthesis condition was based on the desilication mechanism. When the solution pH was increased during the hydrothermal synthesis, Si was released from zeolite dissolution and at the same time, zeolite reacted with Cs in solution, creating a new mineral, pollucite. Other conditions such as Cs concentration, solution volume, and the amount of natural zeolite were also optimized to synthesize pollucite below 100 °C successfully, which can be used for immobilization of Cs from radioactive waste streams.

There are three major results in our study. First, pollucite can be synthesized below 100 °C by increasing the pH. In the high pH solution, natural zeolite (clinoptilolite, Si/Al ratio: ~4) released the Si and turned into pollucite (Si/Al ratio: ~2). Second, the amount of natural zeolite and the particle size of natural zeolites are important factors in determining the crystal phase. When the amount of zeolite is small (< 1g/10mL) or the size of zeolite particles (< 1mm diameter) is large, Cs-exchanged nepheline ((Cs, Na)₃Al₃Si₅O₁₂) or Cs/Na cancrinite ((Cs, Na)₆Al₆Si₆O₂₄) was also formed. Third, pollucite was primarily formed, although the concentration of other alkaline metal ions (Na⁺, K⁺, etc.) is higher than Cs⁺. In the case of Na⁺, it was found that pollucite was primarily formed even if the concentration of Na⁺ was 100 times higher than the concentration of Cs⁺.
Environmental End States Considerations for the Hanford Site

Nicolas J. Huerta¹ and Vicky L. Freedman¹

¹Pacific Northwest National Laboratory

Cleanup of the nuclear legacy at the Hanford site represents one of the most expensive and complex environmental remediation efforts in human history. This grand challenge must be conducted in a safe and efficient manner that is technically sound, responsive to stakeholder needs, and compliant with regulations.

The Tri-Party Agreement describes how regulators and the Department of Energy (DOE) are cooperating to cleanup Hanford radioactive and other wastes in a way that is compliant with laws and regulations. As part of this effort, the DOE issued a Record of Decision in 1999 to develop a Land Use Plan for the Hanford Site. The Hanford Site Cleanup Completion Framework was completed in 2013 to identify an Anticipated Future Land Use within defined areas of the Hanford Site. In conformance with this framework, cleanup is conducted according to milestones, which are dates by which DOE commits to plan and carry out its cleanup work at the sites. Remediation objectives will ultimately be guided by a selected site condition once remediation is complete, and includes the protection of human health and environment, the future site use, and stakeholder expectations. These conditions after remediation comprise the site “end state.”

This presentation describes how a risk-based approach can be used to organize cleanup, inform end state determination, and provide information that supports stakeholder evaluation of planned activities. Specifically, a risk-based approach seeks to balance safe operations, efficient resource use, and prioritization for distinct interim phases of the remedy process based on the best benefit for risk reduction. Further, application of associated performance metrics can be used to manage cleanup progress towards end state objectives.
TECTONIC SETTING OF EXPLOSIVE VOLCANIC ERUPTIONS IN THE UPPER ORDOVICIAN OF THE SIBERIAN PLATFORM

W.D. Huff1, A.V. Dronov2

1Department of Geology, University of Cincinnati, OH 45221-0013, USA.
2Geological Institute, Russian Academy of Sciences. Pyzhevsky per.7, 119017, Moscow, Russia.

In recent years 8 K-bentonite beds have been discovered in the Upper Ordovician of the Tungus basin on the Siberian Platform. All the beds were identified in the outcrops of the Baksian, Dolborian and Burian regional stages, which correspond roughly to the Upper Sandbian, Katian and probably lowermost Hirnantian Global Stages. The 4 lowermost beds from the Baksian and Dolborian Regional Stages were studied in detail. They are represented by thin beds (1-2 cm) of soapy light gray or yellowish plastic clays and usually easily identifiable in the outcrops. The beds were traced in the outcrops over a distance of more than 60 km along the Podkamennaya Tunguska River valley.

All K-bentonite beds have been found within the Upper Ordovician cool-water carbonate succession. The four lowermost K-bentonite beds, which were sampled, have been studied by powder X-ray diffraction and scanning electron microscopy together with energy dispersive X-ray analysis. The low percent of smectite in mixed-layer phases reflects a high degree of burial metamorphism since the time of their origin. The K-bentonites provide evidence of intensive explosive volcanism on or near the western margin of the Siberian craton in Late Ordovician time.

The K-bentonite beds from the Baksian and Dolborian regional stages (Katian) of the southwestern part of the Tungus basin in Siberia are thus derived from the alteration of volcanic ash falls. All four beds contain volcanogenic euhedral zircon and apatite phenocrysts. Zircon crystals from the uppermost K-bentonite bed within the Baksian regional stage provide a 206Pb/238U age of 450.58±0.27 Ma. The timing of volcanism is surprisingly close to the period of volcanic activity of the Taconic arc near the eastern margin of Laurentia. The Yenisei arc had its continuation along the western continental margin of Siberia and both of them constitute a single Taconic-Yenisei volcanic arc. Field studies of the Upper Ordovician succession along the Moyero River in the vicinity of the Anabar shield demonstrate an absence of K-bentonite beds along the eastern margin (in present day orientation) of the Siberian Platform. This contradicts popular paleogeographic interpretations and points to the position of a subduction zone along the western but not the eastern margin of the Siberian paleocontinent at this time.
Unconventional reservoirs are highly complex systems in which pressure, stress, fluid transport, and chemistry are intimately intertwined. This complexity continues to frustrate attempts to capture and predict responses to stimulation and production based on traditional and more simplified mechanics and modeling approaches. A multi-faceted approach that combines knowledge at several different spatial scales and that integrates the major chemical, mechanical, and fluid dynamics is needed to develop comprehensive simulations of highly complex unconventional oil shale systems. The DOE Fossil Energy-sponsored Hydraulic Fracturing Test Site (HFTS) field laboratory in the Permian Basin (Wolfcamp Formation) has provided a wealth of field data, creating an excellent opportunity to integrate geochemistry, geomechanics, geophysics, fluid flow, reservoir simulation, and reactive transport modeling into a project with an overall goal of linking microscale transformations of the shale to the reservoir scale. The HFTS data comprise of a full set of geophysical and tracer observations, slant cores taken through the stimulated rock volume, a characterization of propagation fractures, information on the reactivation of pre-existing natural fractures, and distribution of proppant in the subsurface. Besides the supplied field data, we describe early results from a multi-scale modeling and experimental effort to investigate the mechanical and hydrologic/geochemical response of the Wolfcamp shale to injection and production. Micro-chemical and micro-mechanical laboratory tests probe from the shale matrix, to the fracture surface, and into the fracture space as well which in turn supplies highly sought-after data for fluid flow/reservoir modeling. The end goal of this collaborative project is to apply experimental studies to micro- and reservoir-scale simulations for validation and predictive capabilities of unconventional stimulation and production. This endeavor is being carried out by four of DOE’s national laboratories: Lawrence Berkeley National Laboratory (LBNL), Lawrence Livermore National Laboratory (LLNL), National Energy Technology Laboratory (NETL), and SLAC National Accelerator Laboratory.
IMPACT OF GEOCHEMISTRY ON UNCONVENTIONAL SHALE EFFICIENCY AND MINERAL SCALE PRODUCTION: CLAY-RICH VERSUS CARBONATE-RICH SHALES

Adam D. Jew*1, Eleanor Spielman-Sun1, Qingyun Li1,2, Jihui Ding2, Asli Gundogar2, Tiziana Vanorio2, Anthony Clark2, Gordon E. Brown, Jr.1,2, and John R. Bargar1

1SLAC National Accelerator Laboratory, Stanford Synchrotron Radiation Lightsource, Menlo Park, CA, 94025; 2Stanford University, School of Earth, Energy, & Environmental Sciences, Stanford, CA 94305.

Unconventional oil/gas shale production has led to US energy independence and is a major contributing factor to the reduction in CO2 emissions over the past decade. In spite of these successes, unconventional stimulation practices remain highly inefficient. Current injection practices stimulate chemical reactions that damage fracture surfaces and the shale matrix, reducing permeability through mineral precipitation. A multi-faceted approach to understanding chemical drivers regarding permeability changes (increase/decrease) is needed to develop new practices that can mitigate mineral scaling and manipulate porosity in situ, thus tailoring the shale altered zone to enhance flow/production. Our group is investigating shale-hydraulic fracture fluid geochemical interactions in various shale plays across the US to develop conceptual and quantitative process knowledge that can be used to mitigate these challenges.

Producing shale plays encompass clay-rich (> 25 wt.%) and carbonate-rich (> 20 wt.%) lithologies. Most unconventional stimulation process initiate with large pH variations (initially -0.3 to 10) that result from injection of an acid spearhead. We have conducted experiments using shale samples from various plays using their respective fracture fluids. By using a variety of laboratory- and synchrotron-based analysis techniques in conjunction with reactive transport modeling, we have identified primary mineral scaling phases along with important chemical parameters (pH, O2, ionic strength, dissolved organics) controlling their stability and growth kinetics. Insights provided by these studies have enabled us to advance unconventional mineral scale control through incremental changes to fluid formulations.

Besides mitigating new mineral scale formation, it is important to tailor the altered shale zone to maximize flow. To best determine flow in shales, we are applying in situ CT imaging of shale during core flooding with acidic hydraulic fracture fluids. By injecting cores with Kr pre- and post-reaction we are monitoring porosity/permeability and primary flow paths via contrast CT imaging. These experiments have shown significant alterations to permeability and flow paths due to reaction which aids in developing new techniques/formulations to maximize flow. This work is being complemented by application of acoustic methods to measure porosity changes during reaction with acidic stimulation fluids. Overall porosity changes are readily identifiable via changes in P- and S-wave velocities in reacted shales which have shown promising results for field-scale use. By combining in situ analysis techniques with microscale manipulation of the shale there is the potential to increase overall production in wells lessening environmental impacts.
INVESTIGATION OF AGGREGATION AND PARTICLE SIZE ANALYSIS OF ILLITE

Tao Jiang

1University of Massachusetts Amherst, Department of Civil and Environmental Engineering, Amherst, MA 01002

Owing to their small sizes and chemically active surface, clay minerals can expectedly undergo intensive interactions (aggregation) in natural aqueous conditions (i.e., rivers, estuaries and oceans) with various types of suspended particulate matter (e.g., fine-grained cohesive sediments, organic matter, microorganisms) which are closely affected by the shear rate at varying hydrodynamic flow conditions (e.g., laminar flow, transitional flow, turbulent flow). It is well established that the aggregation of clay minerals plays an important role in many engineering practice (e.g., solid/liquid separation in water treatment) by forming larger-sized aggregates (size range: 200~500 μm) which settle relatively faster to the bottom of natural waters due to their large sizes and fractal structure, and the settled aggregates composed of meso/micro aggregates (combination of clay minerals and polluted materials) can therefore be separated from the bottom bed. While there have been numerous research conducted on the particle size analysis of kaolinite and smectite (two common clay minerals abundant in natural environment) affected by different factors (salinity, pH, hydrodynamic factors, biochemical flocculants) and preparation of corresponding macroaggregates, similar studies have rarely been conducted on the illite (a non-swelling clay mineral also abundant in nature), which is essentially due to their relatively higher negative layer charge and alkaline properties in aqueous environments, significantly hindering the particle-to-particle interactions for forming clay aggregates. Therefore, although illite can aggregate under specific conditions (e.g., adding salt to decrease repulsive double layer thickness of illite primary particles), pH adjustment for forming large-sized illite aggregates is necessary.

In this study, samples of the illite (IMt-1) purchased from the U.S. Clay Minerals Society (CMS) were used. A simple method was developed for preparing illite aggregates (i.e., subjecting illite-salt suspensions values to swing-action shaking). After shaking, a small portion of suspension containing different sizes of clay particles was firstly absorbed into a culture disk, and then placed under a microscope for imaging (Figure 1), followed by particle size analysis of the adsorbed suspensions (Figure 2) with the aid of Image J, an open-sourced image processing software. Four salinity levels (0,5,10, 35 ppt), three pH (pH= 8.61, 4.51, 2.25) and several hydrodynamic conditions (i.e., different shearing rate and shaking durations) were applied for investigation.
Figure 1. Microscopic images captured at two resolutions showing the formed illite aggregates (prepared in a suspension with salinity of 35 ppt at pH = 2.25)

Figure 2. PSDs of illite under saline environment at (a) pH = 8.62, (b) pH = 4.51 and (c) pH = 2.25
Rate coefficients used in simulations of experimentally-observed transport behaviors of nanoparticles and microplastics (colloids) in environmental granular media currently lack quantitative linkage to fundamental physicochemical characteristics. Quantitative linkage is herein demonstrated for: i) colloids ranging from nano- to micro-scale; in two field-based granular media of contrasting grain size: i) natural fine sand at the column scale; and ii) streambed-equilibrated commercial pea gravel at the field scale. Continuum-scale rate coefficients were linked to nanoscale interactions via mechanistic pore scale colloid trajectory simulations that predicted and defined fast- and slow-attaching subpopulations, as well as non-attaching subpopulations that either remained in the near surface pore water or that reentrained to bulk pore water. These subfractions of the classic collector efficiency were upscaled to continuum-scale rate coefficients that produced experimentally-observed colloid breakthrough-elution concentration histories and non-exponential colloid distributions from source. The simulations explained transition from hyperexponential to nonmonotonic colloid distributions from source as driven by longer near-surface colloid residence times before attachment due to relatively strong secondary minimum interaction and weak diffusion for microscale colloids. The assumption that the fast-attaching colloid subpopulation was depleted by attachment to grain surfaces captured the experimentally-observed direct scaling with granular media grain size of the distances across which non-exponential colloid distribution from source occurred. Three parameters were fit: i) fractional coverage by nanoscale heterogeneity; ii) efficiency of return to near surface domain; and iii) characteristic velocity for scaling transfer to near surface pore water, motivating future experiments to independently quantify these parameters.
Efficacy of Fired Natural Clays for the Sequestration of Aqueous Uranium and Lead

Jeremy Jones, Moticha Franklin, Antonio Lara

New Mexico State University, Department of Chemistry and Biochemistry, Las Cruces, NM 88003

Two of the most dangerous heavy metal contaminates found in drinking water are lead and uranium, both of which cause serious detrimental life threatening effects. Modern technologies that combat these toxins in water are generally expensive and difficult to maintain. Most people affected by this problem do not have the means to implement these types of technologies. Clays offer an appropriate solution due to their cation exchange capabilities, but when clays become wet, they are difficult to manage. Alternatively, solid phase fired clay pellets are easy to manage, implement, maintain, and are cost effective. The main objective of this study is to determine the efficacy of fired clay pellets for the abatement of uranium and lead in aqueous solutions. Two clays were chosen, a clay from New Mexico and the reference clay from Arizona. Each fired clay material has been exposed separately and simultaneously to 250 ppb aqueous solution of uranium and lead for seven days. To keep the chemical sorption potential similar between exposures, each metal contributes 125 ppb to the solution in the simultaneous exposure. All samples were tested in triplicate and agitated for the duration of experiment to minimize concentration gradient potential. The supernatant of the exposed samples was analyzed with inductively coupled plasma – mass spectrometry. All samples exposed to the clay pellets exhibited concentrations below the EPA MCL, 30 ppb for uranium and 15 ppb for lead. Based on this analysis, it can be determined that both clay materials provide an efficacious method in the removal of aqueous uranium and lead. Given the inherent chemical and physical properties of the clays and their transformation to pellet form, they are a unique material that enables the removal of heavy metal cations from water. Fired clay pellets offer an appropriate alternative to modern technologies for the remediation of drinking water contaminated with uranium and lead.
Changes in Clay Mineral Assemblages of Legacy Sediments in the Calhoun Critical Zone Observatory, SC: Evidence for Anthropogenic Landscape Change

Bear Jordan$^1$

$^1$University of Georgia, Department of Geology, Athens, GA 30601.

The Critical Zone Observatory (CZO) is a National Science Foundation program whose goal is to develop a model of how physical, biological and chemical processes interact within the “living skin” of the Earth. Specifically, the Calhoun CZO examines landscape degradation as a result of agricultural processes. Calhoun, SC was historically farmed which led to extensive erosion and the production of legacy sediments, or sediments eroded as a result of post-European settlement farming practices. An organic-rich paleosol was identified within the Calhoun CZO at Old Rays Tributary that had been subsequently buried by legacy sediments. This paleosol defined the surface between pre-legacy sediments and the legacy sediments themselves. The present study hypothesised that the respective mineral assemblages in the depositional sequence would vary across this boundary. Using X-ray powder diffraction with internal zincite and external corundum standards, descriptive mineralogies across the depth profile were produced. Results indicate that pre-legacy sediments carry a signature of amphibole and discrete micas while legacy sediments carry a signature of increased kaolin group minerals and degraded micas (i.e. clays). These findings support the hypothesis and draw into question the provenance of the two sediment groups. A possible explanation for the higher clay content of the legacy sediments is from erosion of interfluvial B-horizon material adjacent to the floodplain. The abundance of primary minerals (amphibole and mica) in the pre-legacy sediments may also reflect an allochthonous deposition due to backwater flood events.
Iodine (I⁻ and IO₃⁻) Sequestration and Removal by CoAl and NiAl Layered Double Hydroxides

Jaehyuk Kang¹*, Tatiana G. Levitskaia², and Wooyong Um¹

¹Division of Advanced Nuclear Engineering, Pohang University of Science and Technology, Pohang-si, Gyeongsangbuk-do, 37673, South Korea; ²Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA, 99354, USA.

*Jaehyukkang@postech.ac.kr

The iodine species (I⁻ and IO₃⁻) released from nuclear power plant (NPP) operation and/or severe nuclear accidents poses a risk to human health and the environment due to high environmental mobility and toxicity. Layered double hydroxides (LDHs) were investigated as a potential remedial approach that can remove the iodine species from radioactive waste solution, because the LDHs showed high anion exchange capacity, reconstruction/memory effect, and redox reaction [1]. The main objective of this study is to synthesize the LDHs using various cations, estimate the iodine removal efficiencies, and study/understand the removal mechanism of iodine species under various aqueous conditions. In LDHs synthesis, respective 7.5 or 2.5 mmol M²⁺ nitrate (Co²⁺ or Ni²⁺) and 3.0 or 1.0 mmol M³⁺ nitrate (Al³⁺) were mixed in 50 mL of deionized water (DIW) using hydrothermal reaction method [2]. The pH of mixed solution was adjusted to 8 at room temperature. After 3 days with vigorously stirring for aging, the mixed solution was transferred into a Teflon lined autoclave vessel, and reacted at 110 °C for 3 days. The resultant slurry was filtered, washed with DIW, and dried at room temperature. Subsequently, iodine species (I⁻ and IO₃⁻) equilibrium sorption, kinetics of sorption, isothermal sorption, and desorption experiments were carried out to estimate the iodine removal efficiencies with various solid to solution ratios (g L⁻¹) of 1 to 50. The materials before and after sorption test were then characterized using x-ray diffraction, scanning electron microscopy with energy dispersive x-ray, Fourier transform infrared spectroscopy, and x-ray photoelectron spectroscopy.

Both I⁻ and IO₃⁻ were efficiently removed by the synthesized CoAl (1.53 and 2.04 mmol g⁻¹ for I⁻ and IO₃⁻ sorption capacities, respectively) and NiAl (1.70 and 1.78 mmol g⁻¹ for I⁻ and IO₃⁻ sorption capacities, respectively) LDHs. In addition, the NO₃⁻ was released during both I⁻ and IO₃⁻ sorption on both CoAl and NiAl materials. The characterization results suggest that the main iodine removal mechanism is the anion exchange between iodine species and NO₃⁻ in the interlayer of LDHs.

Acknowledgments
This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP: Ministry of Science, ICT and Future Planning) (No. NRF 2016R1D1A1B02013310) and the Deep Vadose Zone – Applied Field Research Initiative at Pacific Northwest National Laboratory. The work in part was conducted at Pacific Northwest National Laboratory (PNNL) operated by Battelle for the U.S. Department of Energy under Contract DE-AC05-76RL01830.

References
Impact of interlayer cation composition on smectite $\delta^2$H

Nadine J. Kanik$^{1,2}$, Fred J. Longstaffe$^1$, and Arkadiusz Derkowski$^2$

$^1$The University of Western Ontario, Department of Earth Sciences, Ontario, N6A 5B7, Canada
$^2$Institute of Geological Sciences, Polish Academy of Sciences, Krakow, PL-31002, Poland

The interlayer cation composition and associated hydration enthalpy can potentially affect the $\delta^2$H of smectites and other expandable clay minerals. These complexities arise from the presence of strongly bound adsorbed water. It constitutes a potential additional source of hydrogen when attempting to measure the isotopic composition of structural OH groups. To approach this problem, we have measured the $\delta^2$H of different cation-saturated, dried forms of six Clay Minerals Society Source Clay smectites. A modified protocol for sample drying and on-line High Temperature Conversion Elemental Analysis (TCEA) Continuous Flow-Isotope Ratio Mass Spectrometry (CF-IRMS) was used to make the isotopic measurements. Thermogravimetric analysis (TGA) gave information on smectite hydration characteristics.

The hydration properties associated with different cation saturations clearly affected the measured $\delta^2$H (Figure 1). The stronger the hydration enthalpy of the interlayer cation (Ca$^{2+}$>Na$^+$>K$^+$), the higher the residual (after degassing) adsorbed water content. Higher hydration enthalpy led to poorer accuracy and reproducibility of $\delta^2$H for any given smectite (Figure 2). The contribution of strongly-bound water was measured by TGA as the mass loss between 220-1000°C in excess of that from dehydroxylation (Ca-smectite>Na-smectite>K-smectite). Among all drying conditions and interlayer cation forms, drying at 220°C for 4 or 24 hours for K-saturated smectites resulted in the lowest contribution of adsorbed water to the hydrogen pool. This protocol produced the most accurate and reproducible $\delta^2$H for smectite hydroxyl hydrogen. Notwithstanding potential rehydration during the short sample loading interval (<2 min), the TCEA method provided the lowest measurement error and most accurate values for hydroxyl $\delta^2$H. This method also facilitated greater sample throughput than possible using classical methods.

Acknowledgements: Partial funding provided by the Nuclear Waste Management Organization.
Radioiodine (I-129) is consistently among the top three risk drivers at radionuclide waste disposal sites in the United States. This risk stems from its long half-life (16M years), high inventory (fission yield is 0.7%), high perceived mobility in the environment (as anionic solutes), and high toxicity (as a thyroid seeker). A field study is underway to quantify biogeochemical processes controlling I-129 transport in the terrestrial environment at an I-129 contaminant plume on the Savannah River Site in South Carolina. Aquifer iodine speciation (iodide, iodate or organo-iodine) was shown to greatly impact transport. Iodine species distribution varied in a manner consistent with changes in pH and dissolved organic carbon concentrations along the flow path from the disposal source-term (97% iodide, 3% iodate) to the wetlands located 0.7 km downstream (30% iodide, 30% iodate and 35% organo-iodine). Furthermore, the aquifer I-129 was significantly re-concentrated in the wetland, reaching levels as much as 1000 times drinking water limits. In the wetlands, the I-129 was strongly bound to the sediment, almost entirely by covalent bonds to aromatic moieties of the sediment organic matter. Over the last 20 years, the I-129 aqueous concentrations in the wetlands have been generally increasing, suggesting that the tail end of the contaminant plume has not travelled past the wetland, and that the wetland is acting to attenuate I-129 mobility. Extrapolating this data to the future provided initial estimates of when the contaminant plume may reach below drinking water limits (1 pCi/L) without imposing any remedial action.
URANIUM HOT-SPOTS IN WETLANDS LOCATED 2, 3, AND 8 KILOMETERS DOWNSTREAM FROM A FUEL FABRICATION FACILITY

Daniel I. Kaplan¹, Kimberly A. Roberts¹, Maxim I. Boyanov², Kenneth M. Kemner², Edward O’Loughlin², Connor J. Parker², Brian A. Powell¹,², John C. Seaman³, Ronald Smith⁴, Pamela Weisenhorn²

¹Savannah River National Laboratory, Aiken, SC 29808; ²Argonne National Laboratory, Lemont, IL 60439; Savannah River Ecology Laboratory, University of Georgia, Aiken, SC 29801; Savannah River Nuclear Solutions, Aiken, SC 29808.

Recent aerial and walk-over gamma mapping has identified three uranium hot spot located 2, 3, and 8 km downstream from a former fuel fabrication facility on the Savannah River Site, South Carolina. These distances greatly exceed previously reported distances travelled by large amounts of actinides and contradicts present understanding and modeling that predicts uranium transport of <50m. Studies were undertaken to identify important hydro-biogeochemical processes responsible for the uranium immobilization in these three wetland locations and to identify how the released uranium moves such far distances. Of the 44,500 kg of uranium released into the wetlands during the 1960s, 70% and 14% was immobilized in the hot spots located 2-km (10.6 ha) and 3-km (17.1 ha) downstream, respectively. An estimate of the uranium mass in the 8-km hotspot (~8 ha) has not been completed. In situ distribution coefficients ($K_d = C_{solid}/C_{liquid}$) were determined in six soils recovered from the hot spots. Soil uranium concentrations were as high as 14,099 mg/kg (background ~2 mg/kg). Compared to (ad)sorption $K_d$ values (200 - 600 mL/g), these desorption $K_d$ values were generally much greater (170 to 6493 mL/g). Sequential extraction data indicated that the uranium was strongly associated to the soil, i.e., it could not be extracted with dilute acetic acid (0.44 M CH₃COOH + 0.1 M Ca(NO₃)₂). Contrary to expectation, there was not an enrichment of uranium in the clay or silt fractions compared to the total soil. SEM/EDX measurements of the soils revealed the presence of hot particles containing percent levels of uranium. Suspended solids in the stream, including iron and organic matter rich flocs, had uranium concentrations hundreds of times greater than background levels. Measurements of filtered (<0.45 µm) stream water has consistently been <30 µg/L uranium. Finally, analysis of topographic maps indicated that these hot spots were located in reaches along the stream where flow was slow and the stream broadened. These observations have led us to hypothesize that a large fraction of the stream uranium avoided immobilization by the strongly binding wetland sediment by being associated with suspended solids that remained mobile until they reached the slow-moving, low-energy portions of the stream, where they settled out of suspension.
Application of correlative Raman microscopy and micro-indentation for proppant shale rock interaction: a Caney shale case study.

Allan Katende and Mileva Radonjic, Oklahoma State University (OSU), Stillwater, OK, USA.

A key feature of shale reservoirs is their low level of permeability. As a means of producing these reservoirs in a cost-effective manner, there is a requirement to create hydraulic fractures with highest level of conductivity, but these fractures are subsequently filled with high amounts of fracture fluid chemicals during hydraulic fracturing. Unfortunately, production from shale is impacted by the formation of damage that results from clay swelling. Fracturing fluid composition, formation brine salinity, and rock mineralogy all contribute to swelling-induced conductivity damage. The goal of this work is to develop insights into the proppant embedment that results from the mineral composition of the shale following instrumented indentation and Raman spectroscopy technique. The Caney Shale is an organic-rich, often calcareous mudrock. Many studies have examined the impact that clay has on different kinds of shale productivity but there is currently no data reported on Caney in relation to horizontal drilling; all reported data is on vertical wells and in Caney formations that is shallow, compared to an emerging play that is at double the depth. However, there remains a lack of understanding of the mechanisms involved. While many scholars have investigated the influence that clay has on fracture conductivity, the combination of the use of indentation techniques with Raman spectroscopy as a means of comprehending shale well production is an area that is in need of further consideration because it is a non-invasive that can enable researchers look at a fractured wall in post API test and no drying of a sample is required. Indentation tests were performed on a micro level on drilled rock core specimens as a means of determining the mechanical composition of bulk phases of these multiphase materials. The outcomes of the micro-indentation revealed that the bulk mechanical properties of the shale sample were higher overall. The reduced hardness and elastic modulus were comparable to those measured previously on neighbouring formations. The creep effect impacts the maximum penetration depth and the modulus of elasticity of the shale sample. The variation in mechanical properties can be attributed to the changes in the mineralogical composition and microstructures. We believe that this method can provide an understanding into trends and help connect to field performance that would enable more comprehensive completions and avoid fracture plugging and loss of production. By identifying insights into the composition matrix of the shale and the impact this has on its mechanical properties, we propose that it may be possible to adjust fracturing fluid composition such that it is precisely tailored to the mineral composition for the Caney Shale. This can potentially avoid proppant embedment and increase the production of stimulated shale volume.

Key words: Hydraulic fracture, Clay Swelling, Proppant embedment, Proppant deformation, Fracture conductivity.
Incorporation of Iodate in Calcium Carbonate at Variable pH and Si Concentrations

Yelena P. Katsenovich1*, Rocio Trimino Gort (DOE Fellow)1, Ravi Gudavalli1, Nikolla P. Qafoku2, Jim Szecsody2, Vicky Freedman2, Leonel Lagos1

1Applied Research Center, Florida International University, 10555 W. Flagler Street, Miami, Florida 33174; 2Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99354.

Radioiodine (129I) releases to the subsurface at the U.S. Department of Energy (DOE) Hanford Site in Washington State have resulted in large dilute plumes that cover an area of over 50 km2 [1, 2]. The most concentrated 129I plume is associated with the 200 West Area in the 200-UP-1 operable unit (OU), where 129I concentrations are approximately one order of magnitude higher than the drinking water standard. Speciation measurements showed that groundwater iodine at the Hanford Site exists mainly as IO3-, followed by organo-iodine and iodide with averages of 76%, 22% and 2%, respectively [3]. The radioactive iodine 129I is toxic to human and wildlife and accumulates in the thyroid.

Calcium carbonate minerals are abundant in nature and exist primarily as amorphous calcium carbonate, calcite, aragonite and vaterite, with calcite being the most thermodynamically stable form under ambient conditions and vaterite the least stable. Sequestration of iodate with calcite has been considered as a potential in situ treatment approach to immobilize 129I [4, 5]. Silicon is the most common element in minerals and under waste induced alkaline conditions, the dissolution of quartz and aluminosilicates can increase pore water concentrations of silicate species that may affect the formation of calcium carbonate phases [6]. However, there are limited data on how environmental conditions, specifically pH and porewater silicon concentrations, affect iodate incorporation into calcium carbonate.

The focus of this study is to investigate the effect of pH ranging from 6.5 to 9 on IO3- co-precipitation with calcium carbonate in the presence and absence of silicon. Data show that iodate incorporation into calcium carbonate phases was pH dependent and favored at pH of 6.5 and 20 mM of Si. Iodate uptake by adsorption was lower relative to the co-precipitation reaction. At higher pH, less iodate was incorporated into and adsorbed onto calcium carbonate precipitates. The presence of silicate during precipitation of calcium carbonate inhibited the transformations of vaterite into calcite and contributed to the prolong existence of vaterite. Its highest percentage was measured when conditions were ideal for the maximum removal of iodine. In the presence of Si, X-ray diffraction analysis detected a formation of calcium iodate solid phase, lauterite [Ca(IO3)2]. SEM-EDS elemental maps further confirmed the strong association of iodine with Ca, which is a component of formed calcium carbonate solids, and to a lesser extent with Si.

Figure 1. Vaterite spheroids and rhombohedral calcite crystals doped with IO3- at pH 6.5 in the presence of 20 mM Si.

About the effect of reactive silica on the bentonite performance at interfaces

Stephan Kaufhold*1, Reiner Dohrmann1,2, and Kristian Ufer1

1 Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Stilleweg 2, 30655 Hannover, Germany; 2 Landesamt für Bergbau, Energie und Geologie (LBEG), Stilleweg 2, 30655 Hannover, Germany.

Bentonites are candidate materials for sealing of high-level radioactive waste. To date few different bentonites were intensively studied for this new field of application despite the fact that bentonite properties vary from one deposit to another. They may vary with respect to the type and amount of accessory minerals, chemical composition, charge and charge distribution of the smectites, microstructure (relative arrangement of clay and accessory particles), and type of exchangeable cation (amongst others). These parameters may affect the performance of bentonite barriers and hence have to be studied empirically. Recently one important parameter could be identified in lab experiments which determines the performance of bentonites both at the bentonite-iron and bentonite-cement interface (Kaufhold et al., 2019a; Kaufhold et al., 2019b). Kaufhold et al. (2015) proved higher corrosivity of bentonites dominated by low charged smectites and that corrosion products varied from magnetite to a Fe-silicate. Both findings could not be explained in 2015. Systematic corrosion experiments performed since then, however, proved that the structural Fe of low charged smectites is more readily reduced by hydrogen (formed by anaerobic corrosion) than that of high charged smectites. This means that low charged smectites are more readily destabilized upon reduction by hydrogen hence providing silica which is available for formation of the corrosion products. Short term corrosion tests based on electron microscopic inspection confirmed that bentonites containing natural reactive silica (opal-A and/or opal-CT present in the starting materials in the corrosion experiments) led to production of Fe-silicates while magnetite was found in case of bentonites without naturally present reactive silica. In conclusion, silica is a chemical sink for the Fe2+ liberated by anaerobic corrosion. In the case of the cement-bentonite interface, however, naturally present reactive silica was found to buffer the smectite alteration caused by the high pH-values of the cement pore water. Silica reacts with CaO forming Ca-silicate which reduces the pH and hence leads to a lower extent of smectite alteration. Reactive silica, which can be measured e.g. by alkaline chemical extraction using either soda or sodium hydroxide, is an important component of barrier bentonites either determining the reaction pathways or even buffering alteration reactions.

Contaminants can incorporate in minerals as a result of \textit{in situ} remediation processes, interactions with local minerals following release from waste forms (WF), or secondary phase formation during WF alteration/aging. These phenomena have a significant impact on the safety and efficiency of remediation strategies and waste disposal operations. Yet, our understanding of the fundamental mechanisms that control contaminant incorporation in minerals remains poor. For example, the charge compensation schemes that allow for aliovalent substitution are rarely known. This knowledge gap represents a clear impediment to the development of predictive models of contaminant incorporation.

Extended X-ray absorption fine structure spectroscopy (EXAFS) would be ideally suited to determine the local, atomic-level structure around contaminants in minerals, however, interpretation of EXAFS data is remarkably challenging due to the high degree of static disorder usually associated with contaminant incorporation. A solution is to use spectra calculated from atomic trajectories generated by \textit{ab initio} molecular dynamics (AIMD) simulations as standards in linear combination fits to measured spectra.

In this presentation, we will review several success stories in which this AIMD-EXAFS approach was used to resolve the nature, proportion, and structure of the multiple coordination environments around contaminant incorporated in key mineral phases. Specifically, we will present how the AIMD-EXAFS approach shed light on iodate and chromate incorporation in calcite as a potential sequestration pathway. The ability of calcite to incorporate many types of contaminants (toxic metals, actinides, radioactive oxyanions, etc.) will also be discussed. We will also present insights gained from the AIMD-EXAFS approach into the interactions of uranium with a local iron oxyhydroxide phase. Finally, the incorporation of Tc in ettringite will serve as an example of how the AIMD-EXAFS approach can help determining the fate of contaminants in aging cementitious WFs.
MOLECULAR-SCALE CONTROLS ON HETEROGENEOUS NUCLEATION AND GROWTH AT MINERAL-WATER INTERFACES


Pacific Northwest National Laboratory, Richland, WA 99354

Current geochemical modeling paradigms for reactive fluid flow often rely solely on bulk thermodynamics. However, this approach overlooks the vastly different outcomes that can result when heterogeneous nucleation and growth pathways become kinetically favored and coating phases develop that control the chemistry of the aqueous phase. This presentation will use the formation of metal carbonates and hydroxides on carbonate substrates as a model system to shed light on the effects of properties such as solubility, interfacial energy, cation ionic radius, and water exchange rate on heterogeneous nucleation and growth of coatings at mineral-water interfaces.

Specifically, evidence from atomic force microscopy, X-ray pair distribution function analysis, and ab initio molecular dynamics simulation revealed that the heterogeneous growth of a (Cd,Ca)CO₃ solid solution on CaCO₃ (low lattice misfit) followed a non-classical pathway, whereby amorphous precursor particles formed in solution, deposited on the surface, and then underwent an epitaxy-mediated phase transformation (Fig. 1).

X-ray photoelectron spectroscopy (XPS), transmission electron microscopy, and energy-dispersive X-ray spectroscopy showed than cation intermixing can reduce the nominal lattice misfit, which enabled the formation of a thick epitaxial coating in the case of MnCO₃ growth on CaCO₃ (high lattice misfit). In contrast, epitaxial coatings with high lattice misfits could not be grown on MgCO₃ as the slow kinetics of water exchange around Mg²⁺ prevented it from participating in cation intermixing (Fig. 2).

Finally, XPS and scanning electron microscopy were employed to probe how a mineral substrate with favorable lattice registry can influence the competitive growth of CoCO₃ and Co(OH)₂ and extend the range of conditions in which one phase is formed over the other.

Fig. 1. Heterogeneous mineral nucleation can follow a non-classical pathway like that found in homogenous aqueous conditions.

Fig. 2. Cd-rich nanoparticles precipitate on MgCO₃ whereas (Mn,Ca)CO₃ film forms on CaCO₃.
MOLECULAR SIMULATION OF INTERFACIAL WATER STRUCTURE AND EFFECTS ON PARTICLE ATTACHMENT

Sebastien N. Kerisit*1, Elias Nakouzi1, and James J. De Yoreo1

1Pacific Northwest National Laboratory, Richland, WA 99354.

Oriented attachment (OA) of nanoparticles is an important and common crystallization pathway. Efforts to isolate and quantify the interparticle forces that underlie OA have only recently been initiated, and the role played by the interfacial solvent structure in the confined region between nanocrystal surfaces in enabling and controlling OA remains an open question.

This presentation will feature classical molecular dynamics (MD) simulations performed to compute the free energy landscape of nanoparticles approaching mineral substrates in both vacuum and pure water. Periclase (MgO), muscovite (KA1Si3O10(OH)2), and pyrophyllite (Al2Si4O10(OH)2) nanoparticles exposing the (100), (001), and (001) surfaces, respectively, were brought to contact with substrates exposing the same surfaces. These mineral surfaces were selected to investigate a range of hydrophilicities (periclase > muscovite > pyrophyllite). The MD simulations revealed that the interfacial water structure created free energy minima for nanoparticle approach that corresponded to integer numbers of intervening water layers (Fig. 1). The depth of the free energy minima and the free energy barriers between minima correlated positively with the hydrophilicity of the mineral surface. While the range of solvent-mediated interactions was predicted to be short (a few intervening water layers at most for MgO), the free energy barriers were calculated to be large (fraction of an eV per nm²), and the effect of misalignment diminished rapidly with the number of intervening water layers. The results help explain the formation of mesocrystals and the observed ability of nanoparticles to rotate before attachment while in a long-lived solvent-separated state.

Recent developments in atomic force microscopy (AFM), specifically 3D fast force mapping, are enabling direct measurements of interfacial water structure with sub-nanometer resolution. These developments have the potential to transform our understanding of the role interfacial water structure plays in OA of nanoparticles. However, it is not known whether chemical interactions between AFM tips and mineral substrates can influence the measurements. This presentation will also feature MD simulations of model amorphous silica tips approaching boehmite (AlOOH) and muscovite substrates. MD simulation results on the nature and extent of the amorphous silica tip-substrate interactions and on the effects of the tips on the interfacial water structure will be presented.
MODIFICATION IN SMECTITE STRUCTURE THROUGH PILLARING AND CATION SATURATION FOR AFLATOXIN ADSORPTION

Ahmad Khan*1,2, Mohammad S. Akhtar1, Saba Akbar1,2, Ana L. Barrientos-Velázquez2 and Youjun Deng2

1Institute of Soil Science, PMAS Arid Agriculture University Rawalpindi, Punjab, 46300, Pakistan; 2Department of Soil and Crop Sciences, Texas A&M, Texas, 77843-2474, USA

Smectite adsorbs aflatoxin and is used as toxin binder in animal feed. A modification that enhances its effectiveness in adsorption process will be beneficial. Smectite selectivity for aflatoxin against pepsin in gastric fluid needs further investigation. Smectite was pillared with polycations and, in a separate experiment, saturated with different cations and assessed for in vitro aflatoxin adsorption in aqueous suspension and synthetic gastric fluid.

A well crystalline smectite from Bhimber, Pakistan with 37 GR as reference were washed overnight with Al and Al/Fe solution where active metal ratio was 5 % and total metal concentration was 0.6 mol L⁻¹. Interstitial ions were washed and the suspension was dried at 60 °C and a portion was calcined at 500 °C for 2 h. Separately, the clay was washed three times with 0.5 M solutions of Ca, Mg and Zn and 1 M of Li followed by washing with distilled deionized water and air dried. A portion was heated at 200 °C and 400 °C for 2 h. All the modified clays were analyzed with X-ray diffraction and treated with 4 mg L⁻¹ aflatoxin solution in water and in simulated gastric fluid while shaking overnight at 37 °C. Solution aflatoxin was measured, and the difference was considered as the amount adsorbed.

The Al and Al/Fe pillaring caused expansion of the smectites to 18 Å that was stable after calcination as determined by X-Ray diffraction. Mg and Zn saturation had 15 Å peak at 200 °C which collapsed at 400 °C. For Li the 14.6 Å peak collapsed at 200 °C while in case of Ca 15 Å peak was stable up to 400 °C. The Al pillaring increased aflatoxin adsorption to 90.4 g kg⁻¹ compared to 54.5 g kg⁻¹ in non-pillared clay. In simulated gastric fluid, aflatoxin adsorption reduced similarly with and without pillaring. With calcination of pillared clays aflatoxin adsorption reduced to the level of 20 g kg⁻¹ but the un-pillared calcinated Na-saturated smectite adsorbed 120 g kg⁻¹. Without heat treatment effect the smectite with divalent cations adsorbed more aflatoxin than smectite with monovalent Li at the exchange sites in water. Among the divalent cations Ca saturated smectite had the highest adsorption of 83 g kg⁻¹ followed by 74 g kg⁻¹ and 67 g kg⁻¹ in Zn and Mg saturated clays, respectively. With the heat treatments Ca saturation highest adsorption was at 400 °C and with Zn, Mg and Li the highest adsorption was at 200 °C. Compared with water, in gastric fluid aflatoxin adsorption increased with Li and decreased with divalent cations saturation. Pepsin addition in gastric fluid increased aflatoxin adsorption irrespective of cation saturation in unheated clays. Heat treatment effect with different cations saturation on aflatoxin adsorption in water and gastric fluid was significantly different in divalent and monovalent cations saturation. Zn-saturated smectite adsorbed highest aflatoxin in gastric fluid with pepsin followed by Mg- and Ca-saturated clays. Abrupt decline in aflatoxin adsorption after heating at 400 °C in Li, Zn and Mg exchanged smectite was associated with structure degeneration. In gastric fluid pepsin interference reduced aflatoxin adsorption.

Pillaring in smectite can enhance the aflatoxin adsorption in aqueous conditions but may not improve selectivity for aflatoxin over pepsin. Cation exchanged smectites with heat effect may improve selectivity for aflatoxin over pepsin and enhance efficacy of smectite as feed additive.
Simultaneous Removal of Both Cesium and Iodate using Prussian Blue Functionalized Layered Double Hydroxides (PB-LDH)

Jueun Kim¹, Jaehyuk Kang¹, Wooyong Um¹,²

¹Division of Advanced Nuclear Engineering, POSTECH, 77, Cheongam-ro, Nam-gu, Pohang, Korea; ²Division of Environmental Science & Engineering, POSTECH, 77, Cheongam-ro, Nam-gu, Pohang, Korea

Prussian blue (PB) known as ferric hexacyanoferrate has a high removal efficiency for Cs⁺, because its channel size is similar to Cs⁺ ion. In addition, layered double hydroxides (LDHs) show high iodate removal performance using ion-exchange, redox reaction, and reconstruction effects. However, studies have rarely done for removing both Cs and I radionuclides at the same time. Based on the advantages of both PB and LDHs, in this study, we synthesized the LDHs functionalized by PB to enhance the removal efficiencies of both Cs and I radionuclides.

CoCr LDHs were synthesized in 4:1 molar ratio by coprecipitation method. About 0.80 mol/L CoCl₂ and 0.20 mol/L CrCl₃ were dispersed in deionized water (DIW) and the pH was adjusted to 12 by adding 2.0M NaOH before being aged in room temperature for 12 hrs. After black colored slurry was centrifuged at 3000 rpm for 10 mins, washed several times with DIW, and dried at 110 °C oven. To functionalize PB on the LDH surfaces, both CoCr LDH (2.714 g) and FeCl₃ (0.648 g) were simultaneously dissolved in 15 mL of DIW, and this mixed solution was vigorously stirred for 1h. Subsequently K₄[Fe(CN)₆] (1.267 g) was dispersed in 5 mL of DIW and slowly added into the mixed solution. After that, all mixtures were centrifuged, washed with DIW for several times, and dried at 100 °C.

The sorption experiments were conducted to estimate sorption capacity of PB-LDH. Three different sorbents, PB, CoCr LDHs, PB-LDH (0.01 g each) was dissolved in 10 mL of 5 ppm solutions (CsIO₃, CsCl, and NaIO₃, respectively), and the samples were reacted on the shaker at 130 rpm for 3 d. After reaction, the supernatants were filtered with 0.45-μm syringe filter and analyzed by inductively coupled plasma-mass spectrometer (ICP-MS, NexION 300D) to determine the concentration of Cs and IO₃⁻ ions. All sorption experiments were prepared in triplicate.

<table>
<thead>
<tr>
<th>Removal efficiency [%]</th>
<th>CsIO₃</th>
<th>Cs⁺</th>
<th>NaIO₃</th>
<th>IO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB</td>
<td>99.8</td>
<td>0.00</td>
<td>99.3</td>
<td>6.86</td>
</tr>
<tr>
<td>CoCr LDHs</td>
<td>0.266</td>
<td>92.6</td>
<td>2.36</td>
<td>92.8</td>
</tr>
<tr>
<td>PB-LDH</td>
<td>99.7</td>
<td>89.8</td>
<td>99.7</td>
<td>88.6</td>
</tr>
</tbody>
</table>

The PB-LDH sorbent showed the high removal efficiency both Cs⁺ and IO₃⁻ (99.7% and 88.6%, respectively) in the individual solutions compared to other sorbents (PB and CoCr LDHs). In addition, the PB-LDH showed the similar removal efficiency of Cs⁺ and IO₃⁻ (99.7% and 89.8%, respectively) in the mixed solution. This PB-LDH could become a promising sorbent for simultaneous removal of both Cs⁺ and IO₃⁻, reducing operation cost.
FORMATION OF CHLORITE DURING EARLY DIAGENESIS IN RECENT SEDIMENTS OF GDAŃSK BAY (BALTIC SEA)

Marta Kisiel*,1, Michał Skiba1, Artur Kuligiewicz2, Magdalena Makiel1, Mateusz Damrat3, Katarzyna Maj-Szeliga1, Marek Zajączkowski4

1Jagiellonian University, Institute of Geological Sciences, Department of Mineralogy, Petrology and Geochemistry, 3a Gronostajowa St., 30-387 Kraków, Poland (*m.kisiel@doctoral.uj.edu.pl); 2Polish Academy of Sciences, Institute of Geological Sciences, 1 Senacka St., 31-002 Kraków, Poland; 3Polish Geological Institute - National Research Institute, 4 Rakowiecka St., 00-975 Warsaw, Poland; 4Institute of Oceanology Polish Academy of Sciences, 55 Powstańców Warszawy St., 81-712, Sopot Poland

The aim of the present study was to recognize early diagenetic transformations of clay minerals likely taking place in brackish environment of Gdańsk Bay (Baltic Sea). Vistula River loads and sediments of Vistula prodelta (collected from seafloor and from two cores located within the Gdansk Bay) were studied. pH was determined for 1:1 sediment-water slurry. Clay fraction was separated using a procedure given by Jackson (1969). X-ray diffraction patterns were collected for oriented mounts of Na+-, K+-, and Li+- saturated samples. Layer charge locations in swelling clays were determined by Green-Kelly test (Lim and Jackson, 1986). The charge values were measured using O-D method (Kuligiewicz et al., 2015). Relative contents of major cations in studied clays were analyzed using SEM-EDS. pH values for Vistula loads and the seafloor sediments were 6.7-8.42, whereas in the cores it decreased down to 2.5. Dioctahedral montmorillonite, mica and kaolinite were main constituents of the clay fractions from Vistula loads. Traces of chlorite and hydroxyinterlayerd minerals (HIM) were also identified. The seafloor sediments contained montmorillonite, mica, kaolinite, and HIM. Clay fractions from the cores were significantly depleted in montmorillonite and enriched in chlorite relative to the clays from the seafloor and the Vistula loads. Layer charges of swelling clays in all studied samples ranged from 0.46 to 0.56 per formula unit which indicated that the clay fractions were dominated by high-charge smectites. Clays from the prodelta samples were enrichment in MgO and K2O relative to the clays separated from the loads. There was a strong, positive correlation between MgO content in clay fractions and salinity of the water. K2O content showed strong, positive correlation only with depth of the samples in one of the cores. Selective adsorption of magnesium and the hydroxylation in interlayer spaces of smectite are likely main reactions leading to formation of chlorite at the expanse of high-charge smectite in the Gdańsk Bay sediments. Formation of illite in outer prodelta sediments was also likely to take place.

Acknowledgments: This study was financed by National Science Centre, Poland [grant number: UMO-2016/23/N/ST10/01388].

Clay Mineralogy of the Tomanova Formation – deposits of periodic swamps and lakes developed on river flood plains during Upper Triassic

Marta Kisiel¹, Michał Skiba*,¹ Piotr Jaglarz¹, Beata Żymelka¹, Katarzyna Maj-Szeliga¹, Roksana Woźniak¹, Magdalena Makiel¹.

¹Institute of Geological Sciences, Jagiellonian University, 30-387 Kraków, Gronostajowa 3a, Poland

*michal.skiba@uj.edu.pl.

The aim of the present work was to study clay mineralogy of the so called Tomanova Formation a ~65m thick complex of inland fresh water sediments of upper Triassic age located within a sedimentary cover of a crystalline core of the Tatra Mountains. Despite the fact that in general the sedimentary cover underwent high degree of diagenesis, as indicated by a lack of smectite and presence of illite and chlorite, the Tomanova formation was expected to serve as a kind of time capsule preserving the primary clay mineralogy. This was expected because of to the fact that the formation was buildup of finely grained sediments mainly which likely, before sedimentation, were subjected to strong/intensive chemical weathering within the alimentation area. As such the sediments were expected to contain only Al-Si minerals.

Samples used in the present study were collected from outcrop located within Czerwone Żlebki in the Tomanova Valley in the Polish Part of the Tatra Mountains. Four layers rich in clays were selected for detailed mineralogical study. Both bulk samples and the clay fractions were analyzed using XRD, FTIR and chemical methods. Layer charge of swelling clays separated from the samples were measured using O-D method described/proposed recently by Kuligiewicz et al. (2015).

Al studied samples contained dioctahedral vermiculite with some admixtures of kaolinite and quartz. Measured mean layer negative charge absolute values for the vermiculites were in the range 0.64-0.76.

Obtained results indicated that the Tomanova Formation indeed served as a kind of sealed time-capsule which protected primary dioctahedral vermiculite from diagenetic changes despite the high degree of diagenesis within the entire sedimentary cover of the Tatra crystalline core. This finding is of great importance because in general dioctahedral vermiculite is regarded to be a metastable and a very reactive phase which occurrence is limited to soils and young fresh water sediments. According to the authors of this paper knowledge this is a first case reporting occurrence of dioctahedral vermiculite in sedimentary rocks. What is more the results clearly show that formation of dioctahedral vermiculite deposits is possible even within strongly diagenetically altered geologic formations. This is important because dioctahedral vermiculite has a potential to serve as a molecular sieve for radiocesium immobilization.

Acknowledgments: This study was financed by National Science Centre, Poland [grant number: UMO-2016/23/B/ST10/02000].

References
COSIA’s Clay Challenge

Brad Komishke¹ and Lucas Barr²

¹Teck Resources Limited, Teck Energy Department, Calgary, Alberta, T2G 1A6; ²Canada’s Oil Sands Innovation Alliance, Tailings Environmental Priority Area, Calgary, Alberta, T2P 3R7.

Canada’s Oil Sands Innovation Alliance (COSIA) accelerates the pace of environmental performance improvement in Canada’s oil sands through collaborative action and innovation. Fluid Tailings (FT) inventory has consistently increased since the start of oil sands production in 1968. There was close to 1.2 Bm3 of legacy fluid fine tailings in 2017. Fluid Tailings are a liquid suspension of oil sands fines (<44µm) in water; which is a by-product of the bitumen extraction process. Approximately 218 km² of active tailings structures and ponds (89 km² of open tailings pond - water area) exist and need to be reclaimed. Clay in suspension is the primary culprit for FT inventory.

The COSIA Tailings Environmental Priority Area Steering Committee is seeking leading-edge technologies to explore the bulk and surface attributes of oil sands clay minerals to effect a beneficial behavioral change in the tailings.

COSIA members
Granulated and Functionalized Halloysite for Anions Adsorption

Anna Koteja*1, Paulina Maziarz1, Agnieszka Sołińska1 and Jakub Matusik1

1AGH University of Science and Technology, Mickiewicza 30 30-059 Krakow, Poland.

The anionic contaminants are commonly present in the industrial and mining wastewaters as well as in the agricultural effluents. These compounds, when exceed the critical loads, may pose a threat to the natural environment. Thus, the companies are constantly seeking for the most convenient and cost-effective technologies for their removal. The fixed-bed adsorption processes are often proposed and applied in the tech-scale remediation of polluted waters. The key factor that determines the efficiency of the process is the type of adsorbent. In this work, a surfactant modified halloysite was used for the enhanced anions adsorption.

Raw halloysite (H) from Dunino deposit (Poland) was first granulated and then the granules were modified with hexadecyltrimethylammonium bromide (HDTMA) surfactant. The aqueous solution of HDTMA was passed through a bed filled with granulated halloysite. The materials were analyzed before and after the adsorption process with the means of XRD, FTIR, and CHN elemental analysis. Adsorption of As(V), P(V), S(VI), Cr(VI), V(V), W(V), Mo(IV), on both the raw H and the modified H-HDTMA adsorbents, was performed in a laboratory fixed-bed column apparatus. The constant parameters in all experiments were: the anion initial concentration $C_{in} = 1$ mmol/L, the initial solution pH$_{in} = 6$, and the solution flow rate $Q = 2$ ml/min. The column diameter was 2.5 cm and the bed depth was equal to 2.5 cm (10 g) and 5.0 cm (20 g). Anion concentration in the effluent was measured with the UV-Vis spectroscopy, AAS or ICP methods. The granulation process influenced the structure of the raw halloysite. The XRD patterns showed a relative decrease of the peaks related to the halloysite structure, also in the FTIR spectra the bands related to structural OH groups and the Si-O framework decreased in intensity and broadened. Moreover, an increased amount of water was detected. On the other hand, the HDTMA modification did not further alter the mineral structure. The surfactant presence was confirmed by CH$_2$ stretching bands in the 3100-2800 cm$^{-1}$ region of the FTIR spectra. The amount of HDTMA immobilized on the H surface was equal to ~4.2 wt. %. The column studies showed that the anions adsorption was significantly improved due to the HDTMA modification. The bed adsorption capacity (mmol/kg) was calculated basing on the breakthrough curves (breakthrough time * $Q * C_{in}$/adsorbent mass). For the raw halloysite the bed capacity ranged from 0.5 mmol/kg (for W(V)) to 9.3 mmol/kg (for Mo(IV) and V(V)), while in the case of H-HDTMA it ranged from 16.5 mmol/kg (for S(VI)) to 77.0 mmol/kg (for W(V)). The most significant improvement of the adsorption capacity, due to the HDTMA modification, was observed for tungsten (from 0.5 to 77.0 mmol/kg) and for vanadium (from 9.3 to 54.3 mmol/kg). The complex mechanisms responsible for anions uptake were investigated through analysis of solid samples recovered after experiments.

Acknowledgement: This research was funded by the National Centre for Research and Development (Poland), grant number TANGO2/340790/NCBR/2017.
ORGANIC-MINERAL INTERACTIONS AT THE MOLECULAR LEVEL: IMPACTS AND RESEARCH NEEDS

Prof. James D. Kubicki
Dept. of Geological Sciences, The University of Texas at El Paso (jdkubicki@utep.edu)

Interactions of natural organic matter with mineral and mineraloid surfaces are critical in the environment. Global processes such as C cycling and climate change are heavily impacted by this chemistry. Soil stability and quality depend upon bonding of organic compounds to inorganic substrates which is a major factor in agricultural productivity. Furthermore, the health impacts of mineral aerosols are functions of the surface chemistry of the inhaled particulate matter.

When considering C cycling and climate change, one needs to consider that soil organic matter and biota contain approximately four times the C as found in land plants globally. The loss of this organic matter and conversion to CO₂ adds to the atmospheric concentration, and more importantly, depletes soils of organic matter critical to water retention and soil health. Thus, as temperatures and droughts increase, many soils are simultaneously losing their resiliency to support plants in the new climatic conditions. The seminal paper of Torn et al. (1997) demonstrated that mineraloids in soils are particularly useful for slowing the organic C turnover rate, so understanding this organic-inorganic interface is imperative.

Another relationship to understanding climate change is the role that aerosols play in the Earth’s radiation balance and precipitation. Minerals with surficial layers of organic matter may have dramatically different optical properties with respect to reflecting and absorbing visible light and/or retaining IR radiation. Because aerosols act as cloud condensation nuclei, the surficial properties for water adsorption onto these particles are central to predicting precipitation patterns. Certainly whether a mineral is hydrophilic or hydrophobic will be affected by the presence of adsorbed organic matter. Given that aerosol effects and precipitation prediction are two of the largest uncertainties in current climate models, increasing our understanding and decreasing the uncertainties is desirable.

The human health impacts of aerosols is of increasing concern. Mineral dusts are a significant component of the overall global aerosol burden, especially in arid regions such as the U.S. Southwest, the Sahel, the Middle East and China. The direct impacts of particular matter on lung health have been studied for decades, but the role of organic coatings has not been a major focus. Additionally, new research is demonstrating indirect health impacts such as the role of Pb in obesity. Because ingested minerals can be a source of elements such as Pb, As and Hg, the organic coatings on these minerals may impact the bioavailability and risk associated with this environmental stressor.

This talk will discuss these issues and research employing spectroscopic methods combined with computational chemistry to determine the mechanisms organic compound adsorption onto several minerals. These results can be used to model rates of desorption/degradation as well as optical properties. Research needs for the coming decade will be addressed as we move to model and predict natural processes accounting for their complexity, varying spatial and temporal scales and wide variety of environmental factors.

ACTIVATION ENERGY OF SMECTITE REHYDROXYLATION

Artur Kuligiewicz*1, Arkadiusz Derkowski1

1Institute of Geological Sciences, Polish Academy of Sciences, ul. Senacka 1, 31-002 Krakow, Poland

Kinetic studies on clay-water interactions provide a valuable insight into the structure of water adsorbed on the clay mineral surfaces. Accurate estimation of kinetic parameters, such as activation energy (Ea) of a clay mineral-water interactions allow predicting behavior of clays at elevated temperatures. We compare performance of various kinetic models in modeling smectite rehydroxylation (RX) reaction based on theoretical and experimental data.

Ea of solid state process can be calculated based on the following kinetic equation:

\[ g(\alpha) = k(T) t, \]

where \( g(\alpha) \) is the reaction model, \( \alpha \) is the extent of conversion, \( k \) is reaction rate constant (dependent on temperature) and \( t \) is time. Ea can be calculated form \( k \) using Arrhenius equation, if the value of \( k \) is determined at various temperatures. Commonly \( k \) is determined from fitting \( g(\alpha) \) to data comprising the same time for each temperature program used. We propose a new approach to calculate Ea using a model fitting-methods, which involves fitting data covering the same extent of conversion (\( \alpha \)), instead of the same time.

Ea values calculated with the proposed approach were constant irrespectively of the applied reaction model, even if only a limited range of \( \alpha \) is used and were equal to Ea used to generate theoretical data.

A set of thermogravimetric (TG) experiments was performed on a pure smectite reference samples SWy-3 (cis-vacant) and SCa-3 (trans-vacant) by connecting a humidity generator to the TG analyzer. In contrast to the time-based calculation, the Ea values for RX reaction obtained with the new approach for different reaction models were almost constant, which confirms the results of theoretical tests (Fig. 1).

ACKNOWLEDGEMENTS:
This study was financed by the Polish National Science Centre grant OPUS13 25/B/ST10/01675.
QUANTIFICATION OF AEROSOL PARTICLES GENERATED THROUGH RAINDROP IMPACTION

Gourihar Kulkarni*, Susannah Burrows, and Swarup China

Pacific Northwest National Laboratory, Richland, WA 99354

Rain droplet impact on soil surfaces generates particles (aerosols) that affect atmospheric radiation and the formation of liquid and ice clouds. Various sources of aerosols exist, but one major contributor is a soil dust. Recently, the mechanism of aerosol release through droplet impact on soil surfaces was reported, but the atmosphere significance of such aerosols was not explored. In this project, we designed an experimental setup that includes a raindrop tower to allow water droplets to fall at terminal velocity and a Laser Aerosol Spectrometer to measure the number particle concentration as a function of size. High speed imaging was also used to visualize the release of particles post-impact, validating these measurements. Experiments were performed with 5 mm raindrops on 9 soil classes. Water droplets were released at the top of the tower in varying time intervals and allowed to impact the soil surface. The first drop impaction generated a high concentration of fine soil particles with size ranges falling in the ‘scavenging gap’ window implying these particles will be suspended in the atmosphere. Subsequent drops produced less particles due to the existing moisture concentration in the soil. These observations have implications toward total aerosol emissions and may explain why certain soil-based diseases, microbes, and other chemicals, such as petrichor, spread after a rainfall.
Micropollutants (MPs), such as pharmaceuticals, personal care products, steroid hormones, industrial chemicals, pesticides etc., create significant challenges for water and wastewater treatment processes due to their low concentrations and high structural diversity. In the following study, clay-iron-organic composites were designed as sorbent-catalysts to adsorb and oxidize trace-organics from water. A clay-iron oxide framework was modified with organic polymers designed to enhance adsorption of a wide range of MPs while the clay-iron backbone serves both as mechanical support and as a catalyst for Fenton-like oxidation (destruction) of the adsorbed pollutants. The modifying polymers are based on cyclodextrin molecules cross-linked with an aromatic fluorine-rich molecule, decafluorobiphenyl, to enhance adsorption of common problematic pollutants. The composites were characterized using BET, XRD and FTIR. The composites exhibit high adsorption capacity for several micropollutants; such as perfluorooctanoic acid (flame retardant), bisphenol A (endocrine disruptor) and carbamazepine (pharmaceutical). In parallel, the iron-oxide/clay framework exhibited high catalytic behavior-activating both hydrogen peroxide and persulfate efficiently. The cyclodextrine toroid trap the pollutants near the oxidant activation site (similar to an enzyme’s active site), consequently, the micropollutants are effectively removed and destroyed by these novel composite materials. This highly efficient adsorbent-catalyst platform is a promising technology that may be implemented as a tertiary treatment for wastewater either as a stand-alone treatment step or as part of an active barrier in soil-aquifer treatments.
Illite is a primary autigenic and alloigenic clay mineral in sedimentary rocks. Distribution and transport of this mineral substantially affects permeability and, therefore, oil/gas extraction and CO₂ sequestration from/in reservoirs. Illite makes up to 90% of fillings in rock pores in form of nano- to micro-scale particle aggregates that are electrostatically attached to each other. Change of pore water conditions, e.g., after fluid injection or changes of geological settings may result in changes of charge and particle mobilization. At natural conditions, particles commonly preserve growth and dissolution morphologies that affect their charge and aggregation properties. Surface sites at crystal defect sites, such as atomic steps, possess acidity different from sites at atomically flat faces [1]. In aqueous environments characterized by a variety of pH and saturation states, heterogeneous surface charge distribution can be expected. We employ Kinetic Monte Carlo approach to investigate illite nanoparticle dissolution morphologies and corresponding spatial distribution of surface charge at different pH conditions. For that purpose, we readapt our previous KMC model developed for dioctahedral mica (Figure 1) dissolution studies [2] for illite nanoparticle structure and morphology. We vary shape, size and amount of lattice defects to access their influence onto charge properties. The latter ones are quantified as charge maps as well as surface $\zeta$-potentials. The results are compared to experimental observations.

Figure 1. Kinetic Monte Carlo modelling of muscovite dissolution and experimental measurements. From Left to right: Atomistic KMC model where different probabilities are assigned to different surface sites, simulated pitted muscovite surface, pitted surface topography measured by using Atomic Force Microscopy.

References:

Iron oxides, hematite and magnetite are ubiquitous minerals in Earth’s surface and subsurface. These minerals can be commonly found as coatings of mineral grains or rock-forming minerals in assemblages such as laterites or iron banded formations. Iron oxide minerals have distinct adsorptive properties towards toxic metals [1], particularly for arsenic extraction from drinking water [2]. Morphology and size of nano- and micro-particles generally depend on the growth conditions. Nano- and microtopography of naturally occurring iron oxide particles is defined by stable crystal faces, atomic and macrosteps that are formed during crystal growth and dissolution. Dissolution mechanisms of iron oxides constitute an interesting and unsolved problem due to coupled dissolution and Fe$^{3+}$/Fe$^{2+}$ electron transfer reactions [3].

We employ Kinetic Monte Carlo (KMC) simulations to decipher nano-scale dissolution and As adsorption mechanisms for hematite particles. As we have demonstrated in our previous studies, ion adsorption on mineral surfaces preferentially occurs at structural defects, e.g., atomic steps and etch pits [4]. The central focus of the present study is on the relationship between nanoparticle morphology, distribution of atomic steps and As adsorption mechanisms. The validation of the model is based on complementary Atomic Force Microscopy and Vertical Scanning Interferometry studies of dissolving hematite surfaces and their characterization for potential adsorption sites.

References:

As the detection of recalcitrant pharmaceutical molecules in fresh waters increases, multiple scientific questions rise regarding their fate and transport from domestic or hospital wastewater effluents to the environment, and how to prevent these scenarios. Water treatment plant and soil were both considered in this work as two determining compartments where clay can play a major role on the pollutant transfer. We will present how the implication of clay minerals on the pollutant fate in natural system can inspire new application for remediation in water treatment.

In soil, the transfer of pollutant carried by water through the pore network is mainly driven by the affinity of the pollutant for the soil constituents. Here we used flow-through percolation column to study the role of soil particulate matter on the mobility and fate of three pharmaceuticals, ofloxacin, ibuprofen and carbamazepine. Controlling the physical chemistry of the percolating solution enabled us to tune the eluviation of the finer clay fraction from the porous medium, and to estimate its contribution in the colloidal vectorisation of the pollutants. The injected pharmaceuticals underwent a 25-35% higher mobility through the soil under conditions that favored clay dispersion (i.e. lower ionic concentration) and transport.

Such affinity of clay for pharmaceuticals was exploited to design new a depolluting material. In water treatment, eliminating the most recalcitrant molecules often requires a quaternary refining treatment where a sorbent material is used. Here, a silica-clay nanocomposite was synthesized as an alternative to conventional adsorbent material (e.g. activated carbon), in order to improve both operating cost and environmental sustainability. Efficiency in removing 5 pharmaceuticals was evaluated in a real groundwater. The nanocomposite made of 95% smectite and 5% SiO₂ NPs exhibited the highest efficiency for pollutant removal. This was related to the lower apparent density and high surface area of the composite material when compared to pure clay. Moreover, after its use in suspension for water treatment, the material could be easily recovered from solution by sedimentation due to a stable aggregated state.

These studies are of interest in the current context of increasing water scarcity in regions most impacted by global climate change. An alternative management of freshwater resources comes with increasing the reuse of treated wastewater in a shortening water usage cycle. This implies an increasing concern of recalcitrant pollutant in both treatment and reuse steps, where local clay materials have a role to play.
Smectite (swelling) clays are charged, layered, nanoporous minerals that can effectively inhibit the subsurface transport of chemical contaminants and radionuclides. However, coupled changes to local water activity, aqueous major ion composition, and stress state can alter clay structure, driving water adsorption/desorption and ion exchange reactions that make clay permeability difficult to predict. At clay bulk densities typical of subsurface applications (~1400-2000 kg m\(^{-3}\)), clays exist primarily in crystalline swelling states, where individual interlayer nanopores contain discrete water contents (especially 0-, 1-, 2-, and 3-water layer states). While bulk clay water content varies smoothly in response to perturbations due to coexistence of these layer states, the physiochemical properties (e.g. bulk density, structure, and dynamics) of interlayer nanopore water are distinct from bulk aqueous solution due to the interplay between hydrogen bonding with structural hydroxyl and siloxane groups and counterion solvation. Here we present complementary experimental and classical molecular simulation data that inform a thermodynamic model used to predict crystalline swelling states as a function of water and ion activities and applied stress. Simultaneous small-, mid-, and wide-angle X-ray scattering (SAXS/MAXS/WAXS) data were obtained for paired low- (e.g. suspended; 50 kg m\(^{-3}\)) and high- (e.g. compacted, 1600 kg m\(^{-3}\)) dry bulk density Wyoming montmorillonite (Wy MMT) equilibrated in mixed NaCl-KCl aqueous solutions. The coexistence of layer states was determined at each density for identical equilibrium aqueous compositions. The thermodynamic model was parameterized based on experimental data to predict clay microstructure and swelling pressure as a function of water and ion activities and applied stress. To evaluate the structural and energetic underpinnings of the observed thermodynamic behavior, we performed a series of classical molecular simulations employing a new cis-vacant structure that realistically reproduces the interlayer structure of Wy MMT. These simulation results illustrate that mixtures of layer states (e.g. 2-water layer hydrate mixed with 3-water layer hydrates in a single tactoid) exhibit near perfect regular solution behavior with excess free energies of mixing significantly in excess of the free energy difference between swelling states. Together these results support the use of a thermodynamic approach to predict bulk clay microstructure and swelling pressure in the subsurface, although further work is required to predict the unexpected dynamic couplings between bulk water content and stress that arise from rapid perturbations to water activity and composition.
Searching for a “reactive” ferrihydrite phase during Fe(II)-catalyzed ferrihydrite transformation using Mössbauer Spectroscopy

Drew E. Latta*1, Kevin M. Rosso2, and Michelle M. Scherer1

1The University of Iowa, Dept. of Civil & Environmental Engineering, Iowa City, IA 52242; 2Pacific Northwest National Laboratory, Physical Sciences Division, Richland, WA, 99352.

The presence of Fe(II) has been shown to transform ferrihydrite, a poorly crystalline iron oxide mineral, to more stable and crystalline polymorphs much faster than when Fe(II) is not present. Ferrihydrite transformation to less soluble and more stable minerals (e.g., goethite, magnetite, and, rarely, hematite) significantly influences iron biogeochemical cycling and has important implications for release of toxic metals to groundwater, availability of soil carbon to microbial respiration, and interpretation of the ancient rock record.

Despite clear evidence that ferrihydrite transformation is influenced by Fe(II):Fe(III) ratios,1-2 anions,3 and other metals,4 a detailed mechanistic understanding of the process remains elusive. There are, however, several intriguing data sets that support the hypothesis that transformation of ferrihydrite to more stable minerals proceeds through a “reactive” ferrihydrite phase, presumably formed at the surface of the recrystallizing ferrihydrite.2,5

To explore whether there is any spectroscopic evidence for a reactive ferrihydrite phase forming during Fe(II)-catalyzed recrystallization, we conducted selective isotope experiments with 57Fe Mössbauer spectroscopy. Specifically, we conducted experiments with Mössbauer-visible naturally-abundant Naferrihydrite (2.2% 57Fe) reacted with 56Fe(II) in parallel with identical experiments conducted with Mössbauer-invisible 56ferrihydrite reacted with 57Fe(II). These isotope specific parallel experiments provide a detailed spectroscopic view of both the bulk ferrihydrite particles and the newly-formed 57Fe(III) at the ferrihydrite surface and will enable us to evaluate whether we can isolate a spectroscopic signature for reactive ferrihydrite. Our work will provide a mechanistic insights into the initial steps of ferrihydrite transformation to more crystalline minerals in the presence of Fe(II).

RIVER CORRIDOR WASTE SITES: PNNL’S CONTRIBUTIONS TO ADDRESS REMEDIATION CHALLENGES

Amanda Lawter*, James Szecsody, and Rob Mackley

Pacific Northwest National Laboratory, Richland, WA 99352

The Hanford Site River Corridor contains multiple former waste sites that are at various stages of characterization and remediation. Remediation of these waste sites is a priority in order to prevent future migration of contamination from the vadose zone to groundwater and the Columbia River. This presentation will discuss the current state of waste sites along the river corridor, the conceptual model for migration of contamination from vadose zone to groundwater, and the unique challenges at these sites caused by the proximity of the Columbia River. PNNL’s technical role in the past, present, and/or future remediation efforts at select waste sites will be highlighted.
Using synchrotron radiation powder diffraction and X-ray/Neutron pair distribution function to refine kaolinite structure.

Seungyeol Lee*1,2,3, and Huifang Xu3

1USRA Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, TX 77058, USA (slee2@lpi.usra.edu); 2ARES, NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, USA; 3Department of Geoscience, University of Wisconsin–Madison, Madison, WI 53706, USA.

Kaolinite, Al₂Si₂O₅(OH)₄, is the most common clay mineral which forms from chemical weathering of aluminum silicate minerals (e.g., feldspar). The kaolinite plays significant roles in the geological process (e.g., weathering and adsorption of trace elements) and industrial applications (papers, ceramics, and medicines). Due to the characteristics of fine-grained crystals of the kaolinite phase, applying the single-crystal XRD technique has been challenged to determine the crystal structure of kaolinite.¹ We used synchrotron high-resolution XRD and X-ray/Neutron PDF methods to provide a detailed structure of kaolinite including average and local structure information.

Rietveld refinement from the synchrotron XRD pattern provides the high quality of the average structure of triclinic kaolinite with the space group C1 symmetry. The refined unit cell parameters are a = 5.1546(9) Å, b = 8.9425(11) Å, c = 7.4033(15) Å, with $R_{wp} = 5.57\%$. The kaolinite structure from Rietveld refinement agrees well with the previously published kaolinite structures.²,³ The PDF refinement of synchrotron X-ray and neutron PDF provides high-quality structure parameters including anisotropic atomic displacement parameters (ADP). Both X-ray and neutron PDF refinement are not sensitive to determine the H position and thermal factors. The unit-cell parameters and bond distances of non-hydrogen structure of kaolinite from X-ray/Neutron PDF refinement show good agreement with synchrotron XRD and previous kaolinite structures.²,³ Both atom positions and shape of ellipsoids from the X-ray and neutron PDF refinement are very similar. The anisotropic ellipsoid shapes of OH atoms are different from those of O atoms due to the H atoms. The anisotropic ellipsoid shapes of O atoms are in the planes perpendicular to Si–Si axes in the tetrahedral sheet of corner-sharing SiO₄ tetrahedra. In conclusion, synchrotron powder XRD is useful to determine the average structure including unit-cell parameters, fractional atomic coordinates, occupancies, and isotropic atomic displacement parameters. X-ray/Neutron PDF methods are sensitive to study the local structure with ADP. The method can be useful to characterize clay minerals that are not suitable for single-crystal XRD.

Exploring potential origins of life on Earth and Mars by determining ribose stability in mixtures of borate-bearing clays

Shelbie A. Legett¹, Chris M. Yeager¹, Patrick J. Gasda¹, Matthew A. Nellessen², Laura J. Crosse², Eric J. Peterson², Nina L. Lanza¹, Adriana L. Reyes-Newell¹, Dorothea M. Delapp¹, Andrea Labouriau¹, Roger C. Wiens¹, Samuel M. Clegg¹, Debarati Das³

¹Los Alamos National Laboratory, Bikini Atoll Road, Los Alamos, NM 87545; ²University of New Mexico, Department of Earth & Planetary Sciences, Albuquerque, NM 87131; ³McGill University, Department of Earth & Planetary Sciences, Montreal, Quebec, Canada.
*slegett@lanl.gov

Ribose, boron, and clay minerals have all been recognized as possible major players in the origins of life on early Earth. Ribose is a prebiotic molecule necessary for RNA development. However, because ribose quickly degrades in water, it must be stabilized before it can form the more complex molecules needed for early life. Boron is one possible answer to this problem as complexation with borates has been shown to considerably slow the degradation and promote the phosphorylation (needed to create nucleotides for RNA) of ribose in solution [1,2,3]. Yet, boron is highly mobile in aqueous solutions, thus a concentrating mechanism is required for this element to play a role in riboside formation under prebiotic conditions. On early Earth, boron (as a trace element) likely weathered out of major minerals before concentrating and sorbing to available clay minerals in groundwater [3,4,5]; while on Mars, boron was recently found in a similarly clay-rich, lacustrine environment [6]. Because of this, we hypothesize that clays could function as a borate-concentrating scaffold for ribose stabilization and phosphorylation.

The goals of this study are to define the stability of ribose in solution with borate-bearing clays, analyze the products of ribose-borate-clay reactions, determine the structure of any clay-sorbed ribose-borate complexes, and compare the results for Earth- and Mars-relevant clays under various conditions. Because the bulk compositions of Earth and Mars differ (predominately granitic vs basaltic), we use distinct clays to represent each planet. Earth-relevant clays include Ca-montmorillonite and kaolinite, and Mars-relevant clays include saponite and nontronite. We hypothesize that we will see higher concentrations of boron-ribose complexes sorbed to the Mars-relevant clays due to the affinity of both boron and nucleotides for Fe-Mg-rich swelling clays [4,7]. To test this hypothesis, borate-bearing clays are mixed with ribose in aqueous solutions containing various dissolved ions, at pH 8-11, at temperatures from 25-80°C, and under air or nitrogen atmospheres. Samples of the solution are taken at various intervals over 24 hours to be analyzed by GC-HRMS, and the final clay products are analyzed via XRD and solid-state, high-resolution magic angle spinning ¹H, ¹³C, and ¹¹B NMR. The results of this study will lead to a better understanding of prebiotic reactions on early Earth and will give us new insight into how to best search for signs of life on Mars with the Perseverance rover and future sample return missions.

VISUALIZING ALUMINUM IONS, CLUSTERS, AND CRystallINE FILMS AT THE MICA-WATER INTERFACE WITH IN-SITU AFM

Benjamin A. Legg*1,2, James J. De Yoreo1,2

1University of Washington, Materials Science & Engineering Department, Seattle, WA 98195.
2Pacific Northwest National Laboratory, Physical Sciences Division, Richland, WA 99354;

Mineral-water interfaces can drive complex chemical processes, including local changes in ion concentration and speciation, the formation of molecular clusters, and the nucleation of new phases. High speed atomic force microscopy (AFM) provides a powerful tool for visualizing these phenomena. Here, we apply in-situ AFM to study the behavior of aluminum ions at a mica-water interface. We demonstrate the ability to image individual hydrolyzed aluminum ions and track the assembly of these ions into aluminum hydroxide clusters. Complementary streaming potential measurements allow us to build surface speciation models for aluminum at the mica water interface. Our results show that the mica-water interface dramatically increases the local concentration of aluminum ions and drives their speciation toward more hydrolyzed states. Only the doubly-hydrolyzed species Al(OH)2+ appears to be visible with AFM. It seems that less hydrolyzed species cannot be observed due to their higher mobility. Dynamically fluctuating aluminum hydroxide clusters subsequently form from hydrolyzed aluminum species that are concentrated at the interface, and this leads to the formation of epitaxial gibbsite films. However, the process of gibbsite formation at the interface is dramatically different than in the bulk solution. Electrostatic forces at the interface appear to modify the energetics of aluminum adsorption and stabilize high partial coverages. This modifies the energetics of cluster formation and leads to a barrier-free process of crystal growth. The resulting crystalline film maintains a network of nanometer-scale gaps, which may help preserve charge neutrality.
Forgotten minnesotaite as relevant Fe(II)-bearing- and H₂-releasing phyllosilicate

Małgorzata Lempart¹, Arkadiusz Derkowski¹ and Artur Błachowski²

¹ Polish Academy of Sciences, Institute of Geological Sciences, Senacka 1, 31 002 Krakow, Poland
² Pedagogical University, Institute of Physics, Podchorazych 2, 30 084 Krakow, Poland

Minnesotaite that is often incorrectly described as a ferrous analogue of talc, contains Fe(II) substituting for Mg in the octahedral positions, associated with a complex structure resulting in a superlattice and triclinic geometry (Guggenheim and Bailey 1982). Due to the highest Fe(II) content and uniformity of chemical composition, 2:1 layered minnesotaite is the most appropriate reference material to test redox reactions of Fe(II)-rich phyllosilicates. In contrast to a widely accepted model of oxidation by incorporation of oxygen, Fe(II) oxidation of phyllosilicates is driven by dehydrogenation reaction, processing as follows: Fe²⁺ + OH⁻ → Fe³⁺ + O₂⁻ + ½ H₂↑ (Lempart et al. 2020).

In this study, minnesotaite (115274 sample from The Smithsonian Museum repository, Fe²⁺2.6Mg₀.4 Si₄O₁₀(OH)₂) was thermally treated in order to trace its structural changes under conditions closely reflecting an anaerobic and aerobic geological environment. The mass loss (corresponding mainly to H₂O(+) evolution) and volatiles evolving during heating was tested by coupling thermogravimetry (TG) with a quadrupole mass spectrometry (MS) using fast ramp heating experiments (20°C/min rate) up to 1000 °C, under dry nitrogen and synthetic air gas atmosphere. Diffuse reflectance infrared Fourier transform spectrometer equipped with a thermal chamber (thermo-DRIFT) was applied to study structural transformation in situ. Fe(III)/Fe(II) ratio was determined using the Mössbauer spectroscopy measurements (in 300K and 80K).

Minnesotaite heated in N₂ gas released simultaneously H₂O and H₂ between 600 and 750 °C, associated with dehydroxylation and oxidative dehydrogenation, respectively (Fig. 1). Due to dehydrogenation resulting in H₂ release, the TG-measured mass loss originating from dehydroxylation was reduced by 7% in respect to the theoretical full occupancy of OH groups. The reduction of OH groups available for dehydroxylation corresponded quantitatively to the oxidation of 20% of Fe(II) that formed magnetite in the experiment’s final product (at 1000 °C) (Fig. 1). Out of two populations of Fe(II) determined by Mössbauer measurements (cis- and trans- OH Fe(II)), only one trans-octahedral site of Fe(II) was sensitive to oxidation, whereas the other cis-site was not altered by heating. Heating under oxidizing gas atmosphere caused a complete oxidation of structural Fe(II) and the formation of excess H₂O in the carrier gas not reflected by mass loss change on TG curve. Hydrogen evolving near 560 °C immediately combined with external oxygen to form water at the mineral surface according to reaction: 4(Fe²⁺ + OH⁻) + O₂ → 4(Fe³⁺ + O₂⁻) + 2H₂O↑. Thermo-DRIFT measurements performed to correspond to the TG-MS experiments allowed observing the selective decrease of the OH stretching bands located at: 3652, 3634, 3621, and 3602 cm⁻¹ originating from the OH coordination with Fe(II) and Mg. However, the order of bands decomposition resulted in unexpected observations, showing that the 3Fe²⁺-OH band is not the most sensitive to oxidative dehydrogenation. Concluding, we found that the oxidation of minnesotaite is driven by dehydrogenation under inert as well as under oxidizing conditions and both the conditions result in hydrogen release.

Acknowledgments: We are very grateful to The Smithsonian National Museum of Natural History for the minnesotaite sample (115274).

ON THE DIRECT RADIATIVE AND BIOGEOCHEMICAL IMPACTS OF MINERALOGY DUST: A COMPARISON OF THE CLAY- AND SILT-SIZED SOURCE CATEGORIES IN THE SOIL

Longlei Li*1, Douglas S. Hamilton1, Natalie M. Mahowald1, Maria Gonçalves Ageitos2,18, Almut Arneth3, Yves Balkanski4, Tami C. Bond5, Ken S. Carslaw6, Paul Ginoux7, Robert O. Green8, Stijn Hantson9, Akinori Ito10, Olga Kalashnikova8, Jed O. Kaplan11, Martina Klose2, Jasper F. Kok12, Keith Lindsay13, Ron L. Miller14, Lars Nieradzik15, Vincenzo Obiso2,14, David Paynter7, Carlos Pérez García-Pando2,19, Sagar D. Rathod16, Rachel A. Scanza17, and David R. Thompson8

1Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, NY, United States; 2Earth Sciences Department, Barcelona Supercomputing Center, Barcelona, Spain; 3Institute of Meteorology and Climate Research/Atmospheric Environmental Research, Karlsruhe Institute of Technology, Garmisch-Partenkirchen, Germany; 4Laboratoire des Sciences du Climat et de l’Environnement, UMR 8212 CEA-CNRS-UVSQ-UPSaclay, Gif-sur-Yvette Cedex, France; 5Department of Mechanical Engineering, Colorado State University, Fort Collins, CO, USA; 6School of Earth and Environment, University of Leeds, Leeds, UK; 7Geophysical Fluid Dynamics Laboratory, Princeton, NJ, United States; 8Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA; 9Geospatial Data Solutions Center, University of California, Irvine, CA, USA; 10Yokohama Institute for Earth Sciences, JAMSTEC, Yokohama, Japan; 11Department of Earth Sciences, The University of Hong Kong, Hong Kong; 12Atmospheric and Oceanic Sciences, University of California, Los Angeles, CA, United States; 13National Center for Atmospheric Research, Boulder, CO, USA; 14NASA Goddard Institute for Space Studies, New York, NY, United States; 15Institute for Physical Geography and Ecosystem Sciences, Lund University, Lund, Sweden; 16Department of Atmospheric Science, Colorado State University, Fort Collins, CO, USA; 17Atmospheric Sciences and Global Change Division, Pacific Northwest National Laboratory, Richland, WA, USA; 18ICREA, Passeig Lluís Companys 23, 08010 Barcelona, Spain; 19Department of Project and Construction Engineering, Technical University of Catalonia, Terrassa, Spain

Mineral dust is a complex aerosol which consists of multiple mineralogical constituents. The high degree of spatiotemporal variation in composition, atmospheric abundance, and physiochemical properties of dust aerosol presents challenges in accurately estimating the impact of dust on climate and biogeochemical cycles. This presentation reviews two of the latest science on the dust DRE uncertainty quantification in the present climate and the impact of atmospheric dust iron on ocean biogeochemical cycles. Most of the previous studies have primarily focused on providing models with more accurately measured complex refractive index (CRI) for a single “bulk” dust offline. Here, we treat dust as a mixture of common minerals and compute the CRI online. There are several advantages of doing this. For example, the treatment incorporates the regional variation of the dust components into the dust DRE estimate; it also takes the advantage that the imaginary CRI for individual mineral is better measured than for the mixture. Our modeling study reveals a large uncertainty in the current dust DRE estimate due to the fractional abundance of iron-oxides in the soil, especially those falling into the clay-sized mineral category. In addition to directly perturbing the Earth’s energy balance, deposition of the atmospheric soluble iron from dust into the ocean provides a new source of critical nutrients for phytoplankton, modifying net primary production, nitrogen fixation, and carbon export. We compare regional differences in this dust iron flux from clay- and silt-sized categories and highlight regions which are most sensitive to including mineralogical composition information.
EVALUATION OF DEWATERING AND STABILIZING BAXITE RESIDUE BY CONTROLLING PH, DOUBLE LAYER THICKNESS, AND SURFACE HYDROPHOBICITY AS WELL AS CEMENTING METHODS

Chiawei Lin, Ana L. Barrientos Velazquez, Youjun Deng, Julie A. Howe

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

Refining bauxite raw ore to aluminum hydroxides (gibbsite or bayerite) for metallic aluminum production through the Bayer process has generated roughly 120 million tonnes of waste globally. Conventionally, these wastes, known as “bauxite residue,” are stored in a disposal impoundment. Various attempts have been made to utilize bauxite residues, including uses in building construction, and as catalysts, coatings, and pigments. However, this is minimal compared to over 4 billion inventories that have been accumulating. Therefore, it is critical to develop a more efficient method to increase the storage capacity of the pond/lagoon storage facilities. The high-water holding capacity, high alkalinity, and fine particle size of the iron oxides and aluminum (oxy)hydroxides of the bauxite residues are limitations to dewatering and forming stable aggregates.

A few methods are used to reduce the water content or to neutralize the alkalinity of the bauxite residues. To increase the solid content prior to deposition, slurry is thickened by vacuum or high-pressure filtration. For alkalinity neutralization, addition of seawater, strong acids, gypsum, and carbon dioxide have been proposed. It is noteworthy that most research focuses on the “fresh” residue rather than the residue at the disposal area. Few studies have evaluated the potential to improve the existing disposal pond capacity. The first objective of this study is to explore the effectiveness of the following four approaches in dewatering and stabilizing bauxite residue wastes: 1) reducing pH, 2) reducing the thickness of diffuse double layer with polyvalent cations, 3) enhancing surface hydrophobicity with surfactants and polymers, and 4) enhancing particle cementation with phosphate. The second objective is to determine mechanisms of dewatering and stabilization of residues by monitoring the mineralogical, surface, and chemical changes of the bauxite residues.

Preliminary results showed the successful neutralization of alkalinity using calcium and magnesium, which formed hydrotalcite and carbonate minerals. However, the effect of pH in improving the settling performance was minor. Although no obvious difference in the settling volume was observed, adding polyacrylamide significantly accelerated flocculation. Adding calcium or magnesium with the polymer appeared to have synergetic effects. Particle size analysis indicated that a major portion of the “wet” bauxite residue aggregates was smaller than 10 µm. Bauxite residue solidified into cement-like structures when dried. These preliminary results suggest that varying pH, changing ionic strength, and changing surface polarity did affect the double layer thickness of the minerals in the residue, but had little effect on packing of the flocs and water holding capacity of the wet residue, which implied that micropores persisted in the treatments.
THE ROLE OF WATER IN ANELASTICITY OF CLAY MATERIALS

Harrison Lisabeth and Brian Bonner

Energy Geoscience Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., Berkeley, CA 94720

Clay materials have extremely small pores, weak frictional strength and unique surface characteristics, which lead to complex interactions with pore fluids. The dynamics of these fluids is fundamental to the anelastic dissipation of energy in clay-rich materials. Study of the anelastic properties of clays can provide insight into these dynamics and points towards fluid control of phenomena such as dispersion and strain-dependent stiffness and attenuation. We present some initial results from an experimental study of the anelastic properties of clay-rich materials as a function of frequency and strain. Observations of anelastic effects in the seismic frequency band for soft rock containing clay and sandy cohesive sediments show important energy losses controlled by the presence of water. Nanoindentation of montmorillonite demonstrates hysteretic damping, also dependent on water. Conventional thinking based on poroelastic effects is inadequate to explain the results. First principle calculations from the literature suggest that atomic scale motions of water molecules may be dissipative. In addition, dynamic changes in clay structure to externally applied strain suggest a whole new class of possible dissipation mechanisms. We discuss these results in the context of future opportunities to use anelastic spectroscopy to investigate the dynamics of water in clay-rich materials.
RARE EARTH ELEMENTS EXTRACTION FROM GEOTHERMAL BRINE USING MAGNETIC NANOFLUIDS

Jian Liu*, Michael A. Sinnwell, Paul F. Martin, Praveen K. Thallapally, and B. Peter McGrail

Pacific Northwest National Laboratory, Richland, WA 99352, USA.

Extracting rare earth elements (REE) from geothermal brines is a very challenging problem due to the low concentrations of these elements and engineering challenges with traditional chemical separations methods involving packed sorbent beds or membranes that would impede large volumetric flow rates of geothermal fluids transitioning through the geothermal power plant. We are demonstrating a simple and highly cost-effective nanofluid-based method for extracting REE from low-temperature geothermal brines. Core-shell composite nanoparticles are produced that contain a magnetic iron oxide core surrounded by a shell made of metal-organic framework (MOF) sorbent functionalized with chelating ligands selective for the rare earth elements. By introducing the magnetic nanoparticles at low concentration (≈0.05 wt%) into the geothermal brine, rare earth ions will be captured by a very high concentration of chelating sites on the nanoparticles during a short residence time. The magnetic nanoparticles are then effectively separated out with an electromagnet and standard extraction methods are then applied to strip the rare earth metals from the nanoparticles, which are then recycled back to the geothermal power plant. The results of a study on the operating parameter matrix for the magnetic separator showed that it is possible to achieve a high (>99%) magnetic particle retention rate under appropriate combinations of magnetic power and liquid flow rate. We have also shown that it is possible to maintain the REE adsorption capacity of the magnetic particles after over 500 h continuous cycling. In a case study, the internal return rate (IRR) of using the magnetic nanofluid extraction technology to separate Eu from a Salton Sea geothermal brine was estimated to be over 18%, which indicates promising economic feasibility.
INTEGRATED *IN OPERANDO* IR, EIS, XRD, AND NMR INSTRUMENTATION FOR STUDYING SUPERCritical FLUID-CLAY INTERACTIONS

John S. Loring¹, Geoffrey M. Bowers², James R. Kirkpatrick³, Chris J. Thompson¹, Hardeep S. Mehta⁴, Herbert T. Schaeff, Paul F. Martin¹, David W. Hoyt⁴, and Eric D. Walter⁴

¹Pacific Northwest National Laboratory, Richland WA 99352
²Department of Chemistry and Biochemistry, St. Mary’s College of Maryland, St. Mary’s City, MD 20686
³Department of Chemistry, Michigan State University, East Lansing, MI, 4882
⁴The Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory, Richland WA 99352

A fundamental understanding of expandable clay behavior in in variably hydrated supercritical mixtures of CO₂ and CH₄ is important for optimizing CO₂ enhanced gas recovery from tight shale formations. Wet supercritical CO₂-clay interactions also influence the physical and mechanical properties of shale caprocks that are typically used as seals in geologic carbon storage operations. This workshop covers PNNL’s in operando infrared (IR), electrical impedance spectroscopy (EIS), X-ray diffraction (XRD), and magic angle spinning nuclear magnetic resonance (MAS-NMR) capabilities for studying supercritical fluid-clay interactions. IR quantifies and provides molecular-scale detail about intercalated H₂O, CO₂, and CH₄ using a high-pressure cell that is designed for titrating H₂O to target relative humidities and that is equipped with both transmission and attenuated total reflection optics. Newly developed EIS monitors charge carrier (e.g., interlayer cation) diffusivity and uses a high-pressure impedance electrode that mounts within the IR titration cell. XRD quantifies clay basal spacing using a high-pressure cell comprised of X-ray transparent beryllium, and MAS-NMR measures interlayer cation, H₂O, CO₂, and CH₄ speciation and dynamics using a high-pressure zirconium rotor. The XRD and MAS-NMR cells are flow-through and are installed in a fluid circulation system that utilizes an IR spectrometer with transmission optics in the flow path for measuring fluid composition. We will detail key aspects of the instrumentation, experimental protocol, and data analysis, for each capability, and we will provide examples of how their results are integrated to provide a full understanding of clay response in humidified supercritical fluids.
A focused view of an incipient fungal-mineral interaction and its putative weathering product

Rebecca A. Lybrand1*, Paul Schroeder2, Dragos Zaharescu3, and Odeta Qafoku4

1Oregon State University, Corvallis, OR 97330; 2University of Georgia, Athens, GA 30602; 3University of Wisconsin- Green Bay, Green Bay, WI 54311; 4Pacific Northwest National Laboratory, Richland, WA 99354

Fungi play a fundamental role in regulating the biogeochemical cycling of nutrients derived from soil minerals and rocks as demonstrated by the ubiquitous distribution of fungal-generated tunnels, pits, and etch patterns on mineral surfaces. Questions remain on understanding how the identity and surface properties of mineral grains (a fundamental weathering scale unit) change under interactions with abiotic and biotic factors operating at the micro- to nanoscale. Here, our objective was to assess the potential pathways for the formation of secondary iron precipitates observed on a pyroxene grain surface colonized by fungal hyphae. Our study focused on a pyroxene mineral sample retrieved as part of a larger in-soil mesh bag experiment where granular basalt (250-53 µm) was deployed in a humid, hardwood forest (Calhoun Critical Zone Observatory, South Carolina) for three years. We also demonstrate the application of a coupled microscopy approach to examine mineral signatures of abiotic or biotic processes, including weathering features, i.e., dissolution tunnels and secondary mineral formation, identified near a fungal-mineral interface. We employed scanning electron microscopy to determine surface elemental distribution and to probe features at the microscale. Transmission electron microscopy (TEM) was used to examine a fungal-mineral interface that presented putative evidence for biomineral formation. Our results indicate that the secondary mineral phase is magnetite as confirmed through TEM diffraction patterns. The secondary precipitates occurred along the fungal-mineral contact, both on the mineral surface and in the near-surface of the grain (up to 20 microns depth). We hypothesize that the magnetite may represents a secondary weathering product produced by the fungi that precipitated both on the mineral surface and in microfractures of the pyroxene grain.

<table>
<thead>
<tr>
<th>SEM-EDS →</th>
<th>TEM → Provides a cross-sectional view of same site where secondary mineral formation was detected. Diffraction patterns confirm magnetite as the secondary mineral phase.</th>
</tr>
</thead>
</table>

**Figure 1.** A two-dimensional presentation of secondary Fe-rich precipitates detected using SEM (left) and a three-dimensional cross-section of the same interface obtained with TEM. The diffraction pattern confirmed the formation of magnetite as the secondary mineral phase (right). Abbreviations in the figure include Scanning Electron Microscopy- Energy Dispersive Spectroscopy (SEM-EDS) and Transmission Electron Microscopy (TEM).
WEATHERING OF GLAUCONITE IN SOILS OF TEMPERATE CLIMATE

Magdalena Makiel*1, Michał Skiba1, Katarzyna Maj-Szeliga1, Marta Kisiel1, Artur Błachowski2 and Wojciech Szymański3

1Institute of Geological Sciences, Jagiellonian University, 30-387 Kraków, Gronostajowa 3a, Poland; 2Institute of Physics, Pedagogical University, 30-084 Kraków, Podchorążych 2, Poland 3Institute of Geography and Spatial Management, Jagiellonian University, 30-387 Kraków, Gronostajowa 7, Poland

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

The aim of the present research was to investigate the processes of glauconite weathering in soils of temperate climate. Five soil profiles developed on glauconite-bearing rocks from southeastern Poland were selected for investigations. Basic physical and chemical properties of bulk soil samples (<2 mm) such as color, texture, pH, carbonates, and soil organic carbon contents were determined. Clay fractions (<2 µm and <0.2 µm) and green pellets were separated using centrifuge and neodymium magnet, respectively, after application of Na-acetate buffer treatment. Bulk soils, obtained clays, and pellets were analyzed using X-ray diffractometry (XRD). Selected clays and pellets were also analyzed using Fourier-transform infrared spectroscopy (FTIR), Mössbauer spectroscopy (MS), and energy-dispersive spectroscopy (EDS). Thin sections were prepared from undisturbed soil material from selected horizons, and observed under optical microscope.

The pH conditions of the studied soils varied from 4.3 to 8.6. Three of the soils were acidic and two of the soils were alkaline. Glauconite pellets from the lowermost horizon of each profile showed very similar chemical composition, however the Fe(II) constituted from 4% to 13% of the total Fe. Glauconite weathering products were observed mostly in clay fractions, which contained, except for glauconite, also rich in smectite glauconite-smectite mixed layered minerals, kaolinite, and Fe-oxides and oxyhydroxides, such as goethite, lepidocrocite or hematite. MS results, indicated a presence of FeOOH nano-minerals. FTIR spectra showed that among the weathering products the Al-rich clay minerals dominated. No significant differences in the weathering effects were observed between soils having different pH. Content of Fe(II) in primary glauconite did not seem to influence the weathering processes either. The weathering was likely affected by soil properties varying in time and space, such as water activity and related red-ox conditions.

Acknowledgements:
This study was financed by the National Science Centre, Poland [grant number: UMO-2016/23/B/ST10/02000]
Hanford Central Plateau Groundwater: Strategies and Implementation for Cleanup and Monitoring

Adam R. Mangel¹, Judy R. Robinson¹, Inci Demirkanli¹, and Mike Truex¹
¹Pacific Northwest National Laboratory, Richland, WA 99354.

The Central Plateau on the Hanford Site has been the location for processing and waste management activities since 1945. Nearly a century later, it is the focal point of a concerted environmental remediation effort championed by the Department of Energy (DOE).

Groundwater resources on the Central Plateau represent a vector for contamination to leave the site, threatening public resources including the Columbia River. In order to protect groundwater, the public, and the surrounding environment from exposure to radiological and chemical contamination, remediation efforts are focused on (1) shrinking the portion of the Central Plateau that will require continued management, (2) defining consistent and comprehensive cleanup approaches that favor large scale remedies rather than a site-by-site approach that can result in fragmentation and (3) long-term stewardship of biological, natural and cultural resources.

PNNL has played an integral role in the on-going evolution of monitoring and remediation strategies. This has been through the development of spatial-analysis tools and conceptual site models using state-of-the-art numerical modeling codes which predictively evaluate contaminant attenuation and transport. Geophysical monitoring has also been used for site characterization and to monitor remediation amendments, providing a non-invasive and cost-effective complement to traditionally acquired soil and/or borehole groundwater samples. This talk will detail the evolution of groundwater remediation on the Central Plateau focusing on PNNL involvement, and communicate fundamental institutional knowledge required for continued remediation efforts.

Figure 1.2: Source of groundwater contamination on the Hanford Site (from DOE-RL-2007-20)
Mycotoxins are complex organic compounds produced due to metabolic processes by filamentous fungi of different genera. Currently there are about 300 known metabolites that have adverse effects on living organisms. Most hazardous mycotoxins pose serious danger even at very low concentration and have been reported to be highly toxic and carcinogenic. Therefore decontamination strategies were developed and new low-cost approaches are constantly proposed and tested. The use of bentonite adsorbents in animal diet is capable of reducing toxins bioavailability. However some mycotoxins like fumonisin FB1 (FB1) can form anionic species which excludes the use of negatively charged clays or lowers their efficiency. Layered double hydroxides (LDH) are used as adsorbents, supports for catalysts and drug carriers. They are built of positively charged brucite-like layers containing both divalent and trivalent cations. The layer charge is balanced by exchangeable anions in contrast to cations present in clay structures. Thus in theory they can be perfect candidates to adsorb FB1. However the fundamental research on the use of LDH for mycotoxins removal is scarce and incomplete. The presented study was designed to explore the affinity of chemically different LDH structures to the FB1. Several LDH materials (Mg/Al and Mg/Fe) with differing layer charge were synthesized by co-precipitation both from metal nitrates and chlorides. The adsorption experiments showed a clearly higher adsorption capacity for the Mg/Al LDH samples (0.08-0.14 mol/kg) as compared to the Mg/Fe LDH samples (0.04-0.08 mol/kg). Not much difference in removal efficiency was observed between chloride and nitrate intercalated LDH samples. However, a visible trend of increasing adsorption capacity along with higher Mg/Al ratio (lower layer charge) was noticed. The highest capacity corresponded to the FB1 content of ~11.5% wt. The kinetic experiment revealed fast adsorption with equilibrium achieved in the first 1-2 minutes. This suggested surface adsorption confirmed by XRD, which excluded FB1 intercalation as no interlayer expansion was observed. For all the materials a visibly higher adsorption was found for pH in the range of 4-5. The reason for that seems to be connected with several factors suggested by FTIR results. These include: (i) the ability of FB1 to form anionic species due to partial deprotonation of carboxyl groups, (ii) the appropriate conformation of the FB1 molecules which do not form clusters, (iii) lower carbonate content of LDH due to lower pH and its lower charge density. The strong interaction of FB1 and LDH surface was confirmed by XPS technique for the samples equilibrated at different pH values. In particular the most significant distortion of brucite-like layer was observed at pH 5. It was attested by broadening and splitting of bands in the Mg2s, Al2p and O1s spectra. The research confirmed a high affinity and selectivity of LDH structures towards anionic forms of FB1 mycotoxin.

Acknowledgement: This research was funded by the AGH University of Science and Technology, grant number 16.16.140.315. The research was conducted by Jakub Matusik at the Texas A&M University (College Station, TX, USA) thanks to support from Fulbright Scholar Program – Senior Award (2019/2020).
Kaolin particles coated with zero-valent iron – competitive adsorption of Pb/Cd, regeneration and reuse possibilities

Paulina Maziarz*1
pmaziarz@agh.edu.pl

Jakub Matusik1
jmatusik@agh.edu.pl

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

The issue regarding zero-valent iron (Fe0) nanoparticles arouses great interest due to their perspective use as adsorbents of inorganic ions which is of environmental importance. Recently, the research was focused on the synthesis of layered mineral-Fe0 composites in order to improve chemical stability of obtained composites and prevent Fe0 particles agglomeration. This modification allows to obtain composites that exhibit outstanding adsorption properties which facilitates their application in wastewater treatment.

For a study, naturally occurring halloysite, from Polish deposit Dunino (south-west Poland) was used as support for Fe0 particles. Earlier studies, revealed that Dunino mineral sample is composed of both dehydrated halloysite and kaolinite in proportions 59:41². The halloysite-Fe0 (H-Fe0) composites were synthesized following the borohydride reduction method¹. As a source of Fe³⁺, the FeCl₃·6H₂O was used. In the experiments for multi-element solutions, the Pb(II) and Cd(II) concentrations were 0.5 mmol/L and 1.0 mol/L. The experiments were carried out for composites dosage of 2 g/L and 5 g/L. The Pb and Cd concentrations were analyzed using Inductively Coupled Plasma Optical Emission Spectrometry. The reusability and chemical stability of composites was evaluated in subsequent adsorption-desorption cycles, using two methods: (1) desorption with 0.1 mol/L HCl and (2) combination of (1) followed by materials regeneration with NaBH₄. Additionally, the experiment with granular halloysite impregnated with Fe0 particles in a fixed bed column system for competitive Pb/Cd removal was also carried out.

The successful synthesis of the composite was confirmed by XRD patterns. Apart from the peak at 7.20 Å characteristic for kaolin minerals a peak at 2.03 Å, assigned to Fe0 particles was found. The SEM and STEM images revealed tubular and plate like particles of kaolin minerals doped with Fe0 nanospheres. The Fe0 formed characteristic chain-like structures. The size of single nanoparticle was approximately 60 nm. The competitive adsorption experiments revealed higher Pb(II) removal in comparison to Cd(II). The reusability studies showed that desorption method (1) led to a significant decrease of adsorption capacity in the subsequent adsorption steps. In turn, the application of re-reduction of iron allowed to maintain a high adsorption efficiency of Pb(II) as well as Cd(II). The removal efficiency was equal to ~100% and 90% after 3 adsorption steps, respectively. Moreover, the experiment also indicated high chemical stability of the composites during adsorption as well as desorption steps. The XPS analysis enabled to confirm that Pb(II) and Cd(II) were removed by chemisorption on iron oxy/hydroxide shell covering the Fe0 particles, since only peaks attributed to Pb-O and Cd-O were observed. The application of granular halloysite impregnated with Fe0 particles in a fixed bed column system and competitive adsorption also showed high efficiency of the studied composite. However, the results revealed more efficient removal of Pb(II) in comparison to Cd(II), which was in agreement with batch studies.

The experiments with multi-element solution revealed high adsorption capacity of the studied H-Fe0 composites toward Pb(II) and Cd(II). The research also allowed to develop an effective method of the HFe0 composites regeneration, using re-reduction of iron with NaBH₄, after each adsorption-desorption cycle. Moreover the results of column adsorption studies together with high sorption efficiency, the regeneration and re-use studies indicate promising possibility of H-Fe0 composites application in multi-contaminated wastewaters treatment.

Iron oxides and organic acids -both amino and non-amino - are very common in the environment. Their presence and interactions are essential in predicting the movement of elements central to the regulation of life, climate and environmental quality. The physical and chemical properties of iron oxides, as well as carboxylic acids, vary in the natural environment. Therefore, to predict the current and future environmental responses to anthropogenic alteration to Earth it’s important to capture the impacts of these variations in the environment. This study looks at how the presence of amino acids as zwitterion influences the interaction with different iron oxides minerals compared to their non-amino counterparts. To understand these interactions, we study the sorption behavior of two non-amino carboxylic acids; acetate (C$_2$H$_3$O$_2$Na.3H$_2$O) and propionate (C$_3$H$_5$NaO$_2$) and two amino acids; glycine (C$_2$H$_4$NNaO$_2$) and L-alanine (C$_3$H$_7$NO$_2$) onto the surface of synthetic ferrihydrite and hematite under pH conditions between 3 and 12. Our results show significant differences in the quantity sorbed, as well as the kinetics of these reactions. For instance, the amount of non-amino acids increases with increasing pH on the iron oxides but different rates. In contrast, for the amino acids, the amount of L-alanine sorbed onto hematite decreases sharply with the increase in pH while glycine decreases more gradually with an increase in pH. My presentation will discuss the links between surface properties of iron oxides, speciation of non-amino versus amino carboxylic acids and observed sorption dynamics.
BASIN-SPECIFIC OIL AND GAS RESEARCH STRATEGY: INCREASE ULTIMATE RECOVERY AND OPERATIONAL EFFICIENCY

Elena S. Melchert*

United States Department of Energy, Upstream Oil & Gas Research, Washington DC 20585.

Update of Department of Energy (DOE) onshore research portfolio and recent advances in improving recovery of oil and gas from unconventional (shale) resources including activities related to produced water. Briefly describe new technology for increasing ultimate recovery, focusing on field sites, fundamental shale studies, and data-driven approaches, including technologies, particularly sensing and data analytics approaches, sponsored by DOE.
FACTORs REGULATING THE FORMATION OF SYNTHETIC IMOGOLITE NANOPARTICLES

F. Marc Michel*1, McNeill Bauer1, Clément Levard2

1Department of Geosciences, Virginia Tech, Blacksburg VA 24061 USA, 2CNRS-CEREGE, Aix-Marseille University, Aix-en-Provence, France

Imogolite and proto-imogolite are nanosized aluminosilicates with high potential value in industrial and technological applications, however it remains unclear what factors control their formation and abundance in nature and in the lab. This work investigated the complex system of physical and chemical conditions that influence the formation of these nanominerals. Samples were synthesized and analyzed by powder x-ray diffraction, in situ and ex situ small angle x-ray scattering, and high-resolution transmission electron microscopy. Multivariate regression analysis combined with linear combination fitting of pXRD patterns was used to model the influence of different synthesis conditions including concentration, hydrolysis ratio and rate, and Al:Si elemental ratio on the particle size of the initial precipitate and on the phase abundances of the final products. The developed models described how increasing Al:Si ratio, particle size, and hydrolysis ratio increased the proportion of imogolite produced, while increasing the concentration of starting reagents decreased the final proportion. The model confidences were >99%, and explained 86 to 98% of the data variance. It was determined from the models that hydrolysis ratio was the strongest control on the final phase composition. The models also were able to consistently predict experimentally derived results from other studies. Additional electron imaging and chemical analysis revealed that imogolite grows by the attachment end-to-end of imogolite precursors "labeled" with germanium. These results demonstrated the ability to use this approach to understand complex geochemical systems with competing influences, as well as provided insight into the formation of imogolite and its nonclassical growth into well-formed nanotubes.
Exploring pore network evolution processes in unconventional reservoirs with neutron scattering

Quin R. S. Miller a*, Ryan J. Herz-Thyhsen b†, Gernot Rother c, H. Todd Schaef a, and John P. Kaszuba b,d

a Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington, USA. b Department of Geology and Geophysics, University of Wyoming, Laramie, Wyoming, USA. c Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA. d School of Energy Resources, University of Wyoming, Laramie, Wyoming, USA. † Current affiliation is Enerplus, Denver, Colorado, USA.

The global energy landscape is changing rapidly due to production of hydrocarbons from low permeability formations via horizontal drilling and reservoir stimulation with hydraulic fracturing fluids. Understanding the evolution of nanoscale pore and fracture networks in these environments is crucial for maximizing sustainable hydrocarbon extraction and promoting America’s energy security. The abundant nanoporosity in these rocks is important to understand as it exerts strong controls on reservoir connectivity, provides ample reactive surface area, and hosts nanoconfined fluid-rock interfaces with emergent size-dependent behavior. In concert with other experimental approaches, we utilized small angle neutron scattering (SANS) to quantify how pore network architecture characteristics, including internal specific surface area, porosity, pore size distribution, and connected pore fraction, change after reaction with hydraulic fracturing fluids. This presentation will detail SANS analysis of the connectivity and anisotropic nature of Woodford Shale, and reveal a newly-delineated mechanism of hydrocarbon release and mobilization. Some of these SANS results are based on basin-specific samples from multiple stacked reservoirs in the Powder River Basin, WY. Lastly, we will discuss how coupling SANS with aqueous geochemistry analyses highlights the potential for monitoring downhole physicochemical processes via tracking produced fluid chemistry.
NANOSCALE FORCES AND NONLINEAR TRANSPORT BEHAVIORS OF GEOCOLLOIDS UNDER NANOCONFINEMENT

Yuanzhong Zhang, Rundong Huang, Xuanlin Du, Sang Bum Kim, and Younjin Min*

Department of Chemical and Environmental Engineering, University of California, Riverside

It is known that geocolloids play a major role on the transport and distribution of energy-related contaminants (e.g. naphthalene and cesium etc.) in environment. However, there are many fundamental questions to be answered pertaining to their transport processes and molecular interactions at the nano- and micro-length scales, that are closely related to corresponding relaxation dynamics of colloidal suspension.

Here, monodisperse silica nanoparticles with the radius of ~50 nm were synthesized and selected as model geocolloids. The Surface Forces Apparatus (SFA) was used to measure collective surface forces arising between confining mica surfaces (i.e. model geosurfaces) across colloidal dispersions of silica nanoparticles at varying degrees of confinement as well as dispersant conditions. In the presence of silica nanoparticles in the presence of monovalent ions (10 and 100 mM KCl), the measured forces were purely repulsive on approach and separation; the repulsive forces were long-ranged starting from about up to 500 nm contrasting to the case without silica nanoparticles where the onset of repulsion was less than 10 nm. When silica nanoparticles were dispersed in pure water, the magnitude of onset of repulsion remains constant irrespective of concentration of silica nanoparticles, giving rise to the adhesive instabilities (jumps-out) due to the osmotic pressure effect during separation. When silica nanoparticles were confined to a gap of several colloidal diameters between mica surfaces, a dramatic increase in viscosity of 2-3 orders of magnitude from the bulk was observed, which can be described by the density distribution function and potential mean force characteristics of intermolecular interactions in fluids. Our results provide a picture of the complex colloidal dynamics and interactions between geosurfaces across geocolloidal suspensions, highlighting the impact of nanoconfinement and colloidal stability manipulated by salts.
**Surface Induced Ni(II) Precipitation at the Palygorskite-Solution Interface Revealed by EXAFS, HRTEM, and DRS**

Xinxin Mo¹, Matthew G. Siebecker², Wenxian Gou¹, Wei Li¹*

¹ School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China
² Department of Plant and Soil Science, Texas Tech University, Lubbock, Texas 79409, United States

Sorption reactions at the mineral/water interface control the fate and transport of trace metals in aqueous geochemical environments. However, a good understanding of the structure-reactivity relationship at mineral/water interface is still not clearly established. While extensive studies have focused on layered structure clay minerals, we chose a chain-type clay mineral (palygorskite) as the adsorbent and investigated the mechanisms of Ni uptake with a combination of macroscopic batch studies, transmission electron microscopy (TEM), diffuse reflectance spectroscopy (DRS), and extended X-ray absorption fine structure (EXAFS) spectroscopy. The results demonstrated that below pH 6, the sorption was dominated by outer-sphere and inner-sphere surface complexation. Above pH 7.5, the EXAFS data suggested the formation of α-Ni(OH)₂ type of precipitate, in agreement with its linear type sorption isotherm. A special finding is that the precipitates can form at a very low Ni concentration (~ 0.07 mM), with the sorption density of Γ=0.09 μmol m⁻², which corresponds to a 0.3% monolayer coverage for palygorskite. In contrast, at this low level of Ni concentration, surface precipitates have not form with γ-Al₂O₃. We assume that Ni can be directly induced to precipitate on palygorskite surface (we call it “continuous nucleation”), differing from the traditional adsorption-to-polymerization process on γ-Al₂O₃ surface (we call it “staged nucleation”) (Fig.1).

We further tested the role of mineral surface in the Ni precipitates formation. It was revealed that linear shape isotherm was also observed for Ni sorption on sepiolite, a clay with similar structure and chemical composition of palygorskite, indicating a similar reactivity of the both chain-structure phyllosilicates. The findings not only improved the current understanding of metal sequestration at the mineral/water interfaces, but also provided new insights into the surface reactivity of clay minerals.

![Conceptual diagrams of metal precipitation processes on mineral surfaces](image)

*Fig. 1 Conceptual diagrams of metal precipitation processes on mineral surfaces: (A) The traditional way to view surface precipitation, called “Staged nucleation model”, and (B) the new view we proposed in this study, called “Continuous nucleation model”.*
Control of the structure and dynamics of water by clay nanotubes

Geoffrey Monet, Erwan Paineau*, Gilberto Teobaldi, Stéphane Rols, and Pascale Launois*

Laboratoire de Physique des Solides, CNRS, Université Paris Saclay, Orsay, France; STFC, Didcot, UK & Beijing Computational Science Research Centre, China; Institut Laue-Langevin, Grenoble, France

The physics of the new states of water in nanoconfinement is apprehended in terms of the distortion and/or frustration of its hydrogen-bond network. The case of confined water molecules, which are not linked together by hydrogen bonds, also makes it possible to study the original properties of water [1], but only a few realizations of such configurations can be found in the literature.

Here, we present a joint experimental and simulation study of the structure and the dynamics of the water layer at the inner surface of geo-inspired imogolite clay nanotubes [2], namely single-walled alumino-germanate nanotubes. Results of density functional theory molecular dynamics (DFT-MD) simulations and inelastic neutron scattering uncover an unprecedented structuring of the nano-confined water. Water molecules form a two-dimensional triangular pattern on the inner cylindrical surface of the nanotube. They share three hydrogen bonds with the germanol groups of the nanotube, and they are not linked to each other. The dynamics of water molecules is measured and simulated to be markedly different from that of bulk water. We also find that water impacts the dynamics of the nanotube. Finally, analysis of the temperature dependence of the measured density of states from 10K to 300K allowed us to evidence a remarkable harmonic character of water dynamics on the whole temperature range.

FT-MD atomic density colormap showing hydroxyl groups at the inner surface of the nanotube and water molecules of the adsorbed layer (one of them is encircled in purple). Oxygen and hydrogen densities are shown in red and pink, respectively. The horizontal axis corresponds to the curvilinear coordinate along the nanotube circumference and the z axis is the nanotube axis.

[2] G. Monet et al., article under review
The synthesis of antibacterial minerals to combat antibiotic resistance

Keith D. Morrison

Nuclear and Chemical Sciences Division, Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

Antibiotics changed the world. They allowed for the widespread control of bacterial infections, which had been the leading cause of death. However, the overuse of traditional antibiotics in humans and animals had resulted in the emergence of stronger, more potent bacterial strains that are no longer treatable with conventional antibiotics. Developing new antibacterial treatments is vital to preventing the future spread of infectious diseases and the erosion of advances in human health and food sustainability over the last century. A resurgence of inquiry into alternative antibacterial mechanisms has emerged as human pathogens have evolved antibiotic resistance. Documented use of reduced metal-rich clays in healing necrotizing fasciitis led to renewed interest in ancient uses of minerals for healing wounds. However, natural samples are too variable to provide an antibacterial material with consistent properties for clinical/commercial settings. If such minerals are to play a role in combatting antibiotic resistant bacteria then there is a need to improve on their bactericidal efficacy and consistency. We have synthesized Mg, Al and Fe smectite-Fe sulfide mineral assemblages that can effectively kill pathogenic bacteria (both antibiotic susceptible and resistant). These synthetic minerals mimic their natural counterparts by providing the sustained release of Fe$^{2+}$ and hydrogen peroxide while lowering solution pH. Understanding the geochemical and mineralogical processes that regulate antibacterial activity, and learning how to optimize them will help to usher in the medical application of new mineral-based antimicrobials.
OVERVIEW OF THE HANFORD SITE’S CLEANUP MISSION

Katherine A. Muller*, Christopher E. Bagwell, Michael J. Truex, and Mark B. Triplett

Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99354

From 1943 through the late 1980’s, the Hanford Site produced plutonium for national defense. Production and separations activities generated significant quantities of radioactive and chemical waste that pose a potential threat to human and environmental health. In 1989 the Hanford Site mission transitioned from nuclear production to waste management and environmental cleanup when the U.S. Department of Energy, Washington State Department of Ecology, and U.S. Environmental Protection Agency signed a comprehensive cleanup and compliance agreement known as the Tri-party agreement. The Tri-party agreement set the framework for the Hanford Cleanup by establishing legal responsibilities, defining and prioritizing cleanup actions (CERCLA and RCRA), and setting enforceable milestones for cleanup compliance. The overarching goals of the Hanford cleanup are to protect the Columbia River, consolidate waste and provide long-term stewardship to protect human and environmental health as well as protecting Hanford’s cultural, historical and ecological resources into the future. To achieve these goals, cleanup actions have focused on three major components: The River Corridor, Central Plateau, and tank waste - each having unique challenges and compliance drivers. This seminar will detail the regulatory framework under which the Hanford cleanup operates, outline the overall approach to cleanup, discuss the multiple cleanup missions and prioritization, and highlight some of the technical challenges.
THERMODYNAMICS OF HYDROTALCITE FORMATION AND ADSORPTION

Alexandra Navrotsky

Center for Materials of the Universe, Arizona State University, Tempe, AZ

Hydrotalcites or layered double hydroxides (LDH) are important phases in aluminum-rich aqueous environments. We have studied their thermodynamics of formation using high temperature solution calorimetric techniques. Their enthalpies and entropies of formation from binary oxides, water, and the anion-forming constituents are generally similar to those of a mixture of binary constituents. The interlayer anion is more important than the cation in determining phase stability. The carbonate LDHs are predicted to be less soluble than those containing nitrates or halides. The energetics of CO2 sorption on two MgAl LDHs of different compositions has been measured by gas adsorption calorimetry, showing rather strong bonding, especially at low coverage. These thermochemical data form the basis for calculating LDH dissolution, the trapping of heavy metal cations, and other geochemical applications.
BORON ADSORPTION ONTO CLAY MINERALS: IMPLICATIONS FOR MARTIAN GROUNDWATER GEOCHEMISTRY

M. A. Nellessen¹, L. Crossey¹, P. Gasda², E. Peterson¹, N. Lanza², A. Reyes-Newell², D. Delapp², C. Yeager², A. Labouriau², R. C. Wiens², S. Clegg², S. Legett², D. Das³,

¹University of New Mexico, ²Los Alamos National Laboratory, ³McGill University.

It is hypothesized that boron may be vital for prebiotic processes to occur on Earth, and possibly on Mars. Ribose is remarkably labile in solution. However, borate-ribose complexes are stable in water and could, thus, represent a key precursor in RNA formation on the early Earth. The results from the NASA Curiosity rover, currently exploring Gale crater, Mars, suggest Gale was once host to a lacustrine environment as evidenced by its layered deposits of phyllosilicate-rich sandstones and mudstones. These deposits have experienced extensive diagenetic modification including the formation of Ca sulfate veins. Often, 100s ppm of boron have been found within these veins. This discovery of boron in veins opens the possibility for life to have developed independently on Mars. The goal of this project is to shed light on borate behavior in the Martian groundwater by testing the amount of borate adsorption to Mars-like and common terrestrial clay minerals as a function of pH and borate concentration. Martian clays are more Fe and Mg rich as compared to Al, Ca, and K-rich common of terrestrial clays. It is unknown whether or not Fe/Mg clays are more efficient at adsorbing boron so this study hopes to address this question. We mixed borate solution to each clay varying the pH from 6 to 10 as well as varying borate concentration at pH 8. Clay samples were analyzed with Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES), Laser Induced Breakdown Spectroscopy (LIBS), and X-Ray Diffraction (XRD). Preliminary tests on two montmorillonite clays (A & B, Fig 1) at all pH values (200 ppm B) revealed some degree of sorption, though the expected 8-9 pH peak was not observed [1]. Instead, both clays exhibited the greatest sorption at pH 10, with a steady decrease with decreasing pH. This may be due to using different clays and concentrations of borate fluid. Our preliminary results show that varied concentration displayed a positive correlation between initial fluid concentration and adsorption. This is important for predicting whether clays on Mars should be boron-rich, if Gale lake was near-neutral, we could expect a low to no boron sorption, while if it was more alkaline, the sorption could be high, depending on the concentration of B in the lake or groundwater. This research found that while the two clay samples used in analysis did not follow expected trends, they still saw the most sorption in alkaline pH. Further experimental analysis will include repeating the procedure on Mars-analog clays to determine how Mars-like clays adsorb boron given varying pH, initial borate concentration, and ionic composition of the fluid matrix.

Figure 1: The montmorillonites displayed trends increasing with pH rather in comparison to results from [1] which peaked around pH 8

REDUCTION-DRIVEN MOBILIZATION OF CLAY MINERAL Fe

Anke Neumann*, Luiza Notini de Andrade, Drew E. Latta, W.A.P.J. Premaratne, and Michelle M. Scherer

1School of Engineering, Newcastle University, Newcastle upon Tyne, UK, anke.neumann@ncl.ac.uk; 2Department of Environmental Sciences, ETH Zurich, Switzerland; 3Department of Civil and Environmental Engineering, The University of Iowa, Iowa City, IA, USA; 4Department of Chemistry, University of Kelaniya, Kelaniya, Sri Lanka

Most clay minerals contain Fe in their structure, ranging from trace concentrations to up to 30 wt% in nontronites. Similar to other Fe minerals, also clay mineral Fe can be utilized by microbes as terminal electron acceptor for respiration, which consequently leads to the production of reduced clay mineral Fe (Fe(II)). In contrast to other Fe(III)-bearing minerals such as oxides or oxyhydroxides, clay mineral Fe(II) remains within the clay mineral structure, which is stabilized by the low solubility of its aluminosilicate framework. Hence, clay mineral Fe has traditionally been regarded as a renewable source of reduction equivalents, reversibly undergoing Fe reduction and re-oxidation. Indeed, this concept has been established experimentally for microbial reduction and using chemical reductants such as dithionite. However, some inconclusive results from microbial and chemical reduction experiments suggest that microbes and their activity (e.g. release of exudates) might contribute to solubilizing a small proportion of clay mineral Fe. Furthermore, clay mineral Fe reduction with the naturally relevant, abundant reductant Fe(II) results in similar clay mineral Fe reduction extents as microbial reduction and could thus be viewed as an idealized microbial Fe reduction process, yet without the additional complexities of microbial life and activity.

In this study, we applied this recently discovered process of clay mineral Fe reduction with aqueous Fe(II) to investigate the effect of Fe reduction for mobilizing Fe from the clay mineral structure during microbial Fe reduction. We prepared non-reduced, partly reduced, completely reduced, and reduced-reoxidized samples of Fe-rich clay minerals NAu-1 (20 wt% Fe) and NAu-2 (22 wt% Fe), using aqueous Fe(II) and the chemical dithionite as reductants. To estimate the 'mobile' Fe in the clay minerals, we developed and applied a sequential extraction procedure, which we complemented with Mössbauer spectroscopic characterization of extracted solids. We found negligible amounts of extractable Fe in non-reduced clay minerals, indicating that our extraction procedure does not sequester clay mineral Fe(III). In contrast, up to 20% of structural Fe(III) could be extracted in partly reduced clay minerals, suggesting that interfacial electron transfer mobilized a significant portion of structural Fe in clay minerals. Interestingly, the observed extent of mobilization was similar for partial reduction with Fe(II) and with dithionite, indicating that structural Fe mobilization is a function of structural Fe reduction. To test this hypothesis further, we used dithionite to reduce all structural Fe in clay minerals NAu-1 and NAu-2 and found that 80-95% of structural Fe could be extracted and only 3-13% were recovered in the HF digestion. Interestingly, re-oxidation of partly reduced clay minerals restored all clay mineral Fe(III) and its resistivity to the extraction procedure, consistent with the widely accepted concept of clay minerals undergoing reversible Fe reduction and re-oxidation. Similarly, fully dithionite-reduced and re-oxidized clay minerals contained also only exclusively Fe(III), yet a large proportion was mobilized in the sequential extraction and only half of the clay mineral structural Fe was recovered in the HF digestion. These results suggest that the significant structural changes imposed in Fe-rich clay minerals at high reduction extents render the re-oxidized structural Fe more labile than in the native clay mineral structure.

In summary, both wet-chemical extraction and Mössbauer spectra indicated (1) that clay mineral structural Fe(III) became increasingly mobilized during its reduction, whereas it was not accessible for sequential extraction before reaction with either aqueous Fe(II) or dithionite and (2) that high reduction extents led to a permanently increased susceptibility of structural Fe to mobilization.
References:
An In-depth Look at Methylene Blue Index Titration

Jason Ng*, Heather Kaminsky and Andrea Sedgwick.

Northern Alberta Institute of Technology, 10210 Princess Elizabeth Avenue, Edmonton, AB T5G 2R1

Clays and clay minerals dominate the behavior of oil sands fluid fine tailings (FFT) and influence tailings management processes. The clay activity of FFT is commonly determined using the methylene blue index (MBI), a titration test based on the amount of methylene blue dye adsorbed by the clays in a sample. As effective dispersion of clays is an important criterion for an accurate MBI, a full-factorial design of experiment (DOE) was conducted to systematically study the factors, including slurry amount, buffer volume, basic pH adjustment, sonication time, temperature and mixing speed during sonication, affecting clay dispersion process. Key parameters affecting the titration procedure and challenges associated with the visual halo endpoint determination method will also be discussed. This work will assist the development of an automated clay analyzer, which can provide repeatable MBI results in shortened analysis time for characterization of the clays in oil sands tailings.
FLOW EXPERIMENTS OF ORGANIC NANOMATERIALS INTERACTIONS WITH IRON (III) OXIDE SURFACES

Marie Aurore Niyitanga Manzi*1, Omar R. Harvey1

1Texas Christian University, Department of Geological Sciences, Fort Worth, TX 76129.

As engineered nanomaterials increasingly make their way into the environment through nanotechnology it is important to understand how they react in different conditions because they can lodge in places their bigger counterparts would not. Ultraviolet-visible spectroscopy was used to investigate the flow sorption and desorption reactions between four organic nanomaterials and iron (III) oxides. The nanomaterials used are two generations of Poly amido amine (PAMAM) dendrimer, PAMAM G4-OH and PAMAM G.35-COOH, and two variations of Nitrogen-doped Graphene Quantum dots (N-GQD), untreated N-GQD and ozone-treated N-GQD, and the iron oxides synthesized were ferrihydrite and hematite. As shown in figure 1 and 2 below, the quantity of PAMAM G3.5-COOH sorbed onto ferrihydrite and hematite varied as a function of pH. However, the other nanomaterials’ quantity sorbed (unt-NGQD, oz-NGQD, and PAMAM G4-OH) did not vary across all experimental pHs. My presentation is about how the characteristics of the nanomaterials and iron oxides affect the mechanism and kinetics of their sorption and desorption reactions across environmentally significant pH conditions (3-11).
Interaction of variable charge soils with bacteria: The important role bacteria play in maintaining a healthy soil

Jackson Nkoh Nkoh\textsuperscript{1,2},

nkohjackson@issas.ac.cn

Ren-Kou Xu\textsuperscript{1,2}

\textsuperscript{1}State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, P.O. Box 821, Nanjing, China

\textsuperscript{2}University of Chinese Academy of Sciences, Beijing 100049, China

The presence of rhizobacteria in soils is beneficial to plants as they protect them against pathogens, promote growth, decrease pollutant uptake, and increase soil fertility. It has been reported that bacteria adhesion on variable charge soils enhanced the surface negative charge and improved cation retention. However, little information exists about the relationship between bacterial adhesion, soil surface charge, and soil acidification. The adhesion of \textit{Pseudomonas fluorescens} on a clay (Ultisol-Liuzhou) and sandy Ultisol (Ultisol-Yingtan) was studied. The effect of bacterial adhesion on soil acidification, soluble and exchangeable base cations (Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Na\textsuperscript{+}, K\textsuperscript{+}), and chemical forms of Al was investigated after simulated acidification. Also, changes in the soil negative surface charge and surface functional groups of bacteria at different pH was studied by zeta potential and ATR-FTIR spectroscopic analyses. After interaction with bacteria, the zeta potentials of both soils became increasingly negative as soil pH was increased. The increase in the negative zeta potential of soil-bacteria composite was attributed to a charge transfer mechanism whereby a negative charge was transferred from the bacteria to the soil surface after specific adhesion of bacteria. After acidification, the pH of the bacteria-treated soils was higher than that of the untreated soils which suggested that bacterial adhesion induced an inhibitory effect on soil acidification. This observation was attributed to the protonation of oxygen-containing functional groups on the adhered bacterial surface which led to the formation of neutral molecular groups (e.g. COO\textsuperscript{-} to COOH), a reduction in the activity of H\textsuperscript{+}, and inhibition of acidification. The adhesion of bacteria had a positive effect on the soil effective cation exchange capacity (ECEC) and soluble/exchangeable base cations. The release of exchangeable base cations from bacteria-treated soil, and the decrease in soil ECEC and exchangeable base cations with decreasing pH confirmed that protonation of organic anions on adhered bacteria was mainly responsible for the inhibition of soil acidification. Additionally, the pH ameliorating effect of adhered bacteria inhibited the release of toxic Al\textsuperscript{3+} into soil solution and simultaneously enhanced the proportions of organically bound and sorbed hydroxyl Al. The increment in organically bound Al varied from 11.0-42.3% for sandy Ultisol and 7.9-40.6% for clay Ultisol, with a corresponding increment of 3.8-18.2% and 0.9-25.0% for sorbed hydroxyl Al respectively, as HNO\textsubscript{3} concentration was increased from 0-40 mmol kg\textsuperscript{-1}. Thus, bacterial adhesion to soil surfaces is important for enhancing soil negative surface charge, ameliorating soil pH, and improving soil pH buffering capacity.

\textbf{Keywords:} \textit{Pseudomonas fluorescens}, variable charge soils, aluminum toxicity, soil acidification, cation exchange capacity
MECHANISM OF INHOMOGENEOUS CONCENTRATION OF CS IN 2:1 CLAY MINERALS: SYSTEMATIC NUMERICAL STUDIES

M. Okumura*1, S. Kerisit2, I.C. Bourg3, L.N. Lammers4,5, T. Ikeda6, M. Sassi7, K.M. Rosso8, and M. Machida1

1Center for Computational Science & e-Systems, Japan Atomic Energy Agency, Japan ; 2Physical Sciences Division, Pacific Northwest National Laboratory, Washington, USA ; 3Department of Civil and Environmental Engineering, Princeton University, New Jersey, USA ; 4Department of Environmental Science, Policy, and Management, University of California Berkeley, California, USA ; 5Earth and Environmental Science Area, Lawrence Berkeley National Laboratory, California, USA ; 6Synchrotron Radiation Research Center, Quantum Beam Science Research Directorate (QuBS), National Institutes for Quantum and Radiological Science and Technology (QST), Hyogo, Japan.

Radiocesium was released into the environment due to the Fukushima Dai-ichi nuclear powerplant accident in 2011. Most of them were fall onto surface ground with rain. It has been known that radiocesium was retained for long time by clay minerals in surface soil. Therefore, the surface ground became a gamma ray emitter with long lifetime in Fukushima. Many residents needed to evacuate from their home to avoid additional dose originated from the radiocesium retained in the surface soil. In order to solve this situation and return them to their home, Japanese government has been performed large scale decontamination in Fukushima. Main technique of the decontamination was removal of surface soil. This method was very effective. The decontamination campaign succeeded because air dose rates in many residential areas were reduced below the limit given by Japanese government. Nowadays, many residents returned to their home. Another serious problem, however, arose, i.e., huge amount of waste soil contaminated by radiocesium, which is a by-product of the decontamination. Maximum amount of the waste soil was estimated at approximately 22,000,000 m³. The huge amount of waste soil imposes a heavy burden on the Japanese people, because long term storage of the waste soil requires costs of construction of extensive storage sites, ceaseless monitoring, and so on.

Batch and column experiments have played important roles on studies of adsorption behavior of cesium on clay minerals. They revealed that clay minerals have complex adsorption isotherm, which implied that there are several adsorption sites in them, i.e., radiocesium distributes inhomogeneously in the clay minerals. Many experimental results implied that these adsorption sites correspond to pars of the clay minerals. It is, however, difficult to observe the adsorption behavior on the adsorption sites directly even by recent advanced observation techniques. Because the adsorption is intrinsically atomic scale phenomenon, i.e., cesium ions adsorbed on sub-nanometer structures of the clay minerals. Numerical simulations have great advantage of studies on the microscopic structures. But there are no systematic microscopic numerical simulation studies about cesium adsorption on clay minerals.

We performed numerical simulations of cesium adsorption on clay minerals systematically [1]. Density functional theory and classical molecular dynamics were used for the simulations. We modeled expected adsorption sites shown in Fig. 1, i.e., basal surfaces, edges, frayed edges, hydrated interlayers, and interlayers. From the basal surface simulations, it was revealed that adsorption strength of cesium depends on not only layer charges but also their positions and local structures. The simulations of the edges revealed that the edges adsorb cesium selectively against sodium, which is consistent with experimental results. It was
shown that the frayed edges adsorb cesium selectively against potassium. The mechanism of the selective adsorption was also revealed. It is matching between ion diameter and the interlayer distance in the frayed edge, i.e., the interlayer distance is adjusted to potassium ion diameter when the interlayer is closed, but they fit the diameter of a cesium ion, which is larger than one of potassium, when the interlayer is opened by weathering. Possibilities of cesium migration into the interlayers was also shown.

Adsorption strengths among the adsorption sites were compared. Table 1 shows that the frayed edges are the strongest adsorption site [1]. This result supports the scenario that cesium ions migrate from the basal surfaces to the interlayers, and finally they are fixed by the interlayers. We discussed possibility of cesium move caused by nuclear decays of radiocesium, which is an unrecognized risk of long-term storage of the waste soil.

We can discuss a direction of development of volume reduction techniques based on the results. The results indicate that radiocesium is adsorbed in the deep interlayer of the clay minerals, which is difficult to be extract by ion exchange with competitive cations, e.g., potassium. Therefore, other methods destroying clay minerals themselves are promising. One of most promising candidates is heat treatment with salts [2].

![Microscopic models of the adsorption sites.](image-url)

Figure 1. Microscopic models of the adsorption sites.
Table 1. Adsorption energies of the adsorption sites.

<table>
<thead>
<tr>
<th>Adsorption sites</th>
<th>Basal surfaces</th>
<th>Edges</th>
<th>Hydrated interlayers</th>
<th>Frayed edges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption energy [kJ/mol]</td>
<td>0-0.5</td>
<td>-2</td>
<td>-4</td>
<td>-27</td>
</tr>
</tbody>
</table>

References
Analysis of X-ray Amorphous Phase Abundance and Composition in Basaltic Samples as Potential Amendments for Martian Soil Analogues

Aditi Pandey*1, Paul Schwab and Doug W. Ming2

1 Texas A&M University, 2474 TAMU College Station, TX, 77843, USA; 2 NASA, Johnson Space Center, Houston, TX, USA

X-ray amorphous phases in varying proportions have been inferred in all samples analyzed by the CheMin X-ray Diffractometer onboard the Mars Science Laboratory rover in Gale Crater, Mars. The origin of these phases on Mars is not apparent and conceptualizing the geochemical processes that led to the observed abundances and trends requires clues from terrestrial samples. However, quantification of amorphous phases is challenging, and typical X-ray diffraction analyses need to be supplemented with internal standards and fluorescence-based chemical mass balance calculations. Characterization of naturally occurring amorphous minerals on Earth will help to decipher planetary processes on Mars and will facilitate the synthesis of Martian soil analogues that are representative of the average Martian regolith including the amorphous phase. Characterization of an assortment of samples collected from cinder cones of Hawaii’s Mauna Kea volcano using a combination of X-ray diffraction (XRD), X-ray fluorescence (XRF), and alkaline extraction are reported here to test the potential of these materials to serve as amendments to currently available Martian soil simulants. Rietveld refinement of 20% corundum spiked samples and mass balance calculations from XRF were used to estimate amorphous abundances. X-ray diffraction abundances will be compared to measured values from alkaline extraction of amorphous silica quantified using visible spectrophotometry. The total content of amorphous materials in one of the Hawaiian samples was found to be 43.6% using the Rietveld refinement analysis (Figure 1). Alkaline-extracted amorphous silica measured from this sample was only 0.8-1.0%, suggesting a large fraction of the amorphous composition to be nanophase iron/aluminum oxides or aluminosilicates. The lack of amorphous silica in this poorly weathered volcanic basalt is consistent with the quantities of crystalline aluminosilicate minerals in Figure 1. Nanophase iron oxides are another major component of the amorphous materials on Mars, making this basaltic soil a good candidate amendment for many simulants.

Figure 1. Mineral composition calculated from Reitvel refinement analysis of a Hawaiian sample.
It is well documented that the major sorbents in soils are organic matter, silicate clays, and metal-oxyhydroxides. In particular, interactions between organic matter and fine-grained minerals, such as aluminum oxides, have been cited as important stabilizers of the humic matter in soils, which has large implications for the storage of anthropogenic carbon and pollutants (i.e., hydrophobic organic acids) in the environment (Keil and Mayer 2014). Utilizing simple organic acids containing functional groups present in humic compounds enhances understanding of metal-hydroxide and organic acid interactions at the mineral-water interface. The energetics of these interactions largely depend on the sorbate, the physico-chemical characteristics of the sorbent, and solution conditions (e.g. pH). Ongoing work in our lab, using flow-adsorption microcalorimetry (FAMC) to directly and systematically measure energy dynamics of sorption at the oxide-water interface indicated that adsorbed water onto boehmite and boehmite-bayerite mixed-phased samples increased binding energetics of acetate, propionate and butyrate at pH 5. The presentation will cover energy dynamics data collected for these mono-carboxylates and their respective di-carboxylate counterparts (oxalic acid, malonic acid, and succinic acid) binding onto a series of synthetized boehmites and bayerites. Focus will be placed on resolving effects of carboxylate carbon chain length, the number and acidity of carboxylates and aluminum oxide surface properties on binding dynamics.
CENTRAL PLATEAU TANKS

Carolyn I. Pearce*, Mark B. Triplett†, and Vicky L. Freedman

Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99354

At the Hanford Site, WA, USA, approximately 55 million gallons of waste are stored in 177 single shell tanks (SSTs) or double shell tanks (DSTs). Sixty-seven of Hanford’s SSTs are suspected to have released up to 1 million gallons of waste to the subsurface. Although all pumpable liquid has been transferred to DSTs as a form of interim stabilization, several million gallons of interstitial, drainable liquid remain in the 149 SSTs. Several methods have been employed to determine that a tank has leaked, or is leaking, waste to the environment, including: (i) in-tank monitoring of the waste surface level; (ii) ex-tank monitoring of moisture content and gamma signatures in dry wells; (iii) electrical resistivity tomography (ERT) to detect subsurface electrical conductivity associated with moisture content and conductive tank waste fluids, e.g. nitrates; and (iv) boreholes for geochemical characterization of soil beneath the tanks. These measurements, along with historical data from tank leak documents, tank waste transfer records and process flow sheets, have been used to compile an inventory of waste lost to the subsurface migrating through the vadose zone towards groundwater. It was thought that past tank leaks could not reach groundwater until the late 1990s, when cesium and technetium were detected just above groundwater beneath two tank farms. As a result, the Department of Energy did not have an adequate basis for making cleanup decisions because there was insufficient knowledge on contaminant movement through the vadose zone. Since then, much research has been conducted to identify the contribution of tank leaks to the 170 km² of Hanford groundwater that is contaminated above drinking water standards. SST Waste Management Areas have small but concentrated groundwater plumes that are associated with past releases from tanks or transfer systems and contain technetium-99, uranium, and chromium. Here, case studies of specific tank farms (WMA B-BX-BY and WMA C), describe both past and future actions to mitigate tank farms releases.
Formation of Fe(III)-bearing dioctahedral smectite on Mars

Tanya S. Peretyazhko¹, Arlaine Sanchez², SJ Ralston¹, Brad Sutter¹, Doug W. Ming³

¹Jacobs, NASA Johnson Space Center, Houston, TX, 77058, USA; ²University of Nevada, Las Vegas, 4505 S Maryland Pkwy, Las Vegas, NV 89154, USA ³NASA Johnson Space Center, Houston, TX, 77058, USA.

Trioctahedral Mg/Fe-saponite and dioctahedral Fe(III)-bearing nontronite have been identified by the instruments on surface of and in orbit around Mars. Martian smectite likely formed through aqueous weathering of basaltic crustal materials. Experimental studies demonstrated that saponite, but not nontronite, precipitated during alteration of Mars-analog basalt over a broad range of pH conditions (Peretyazhko et al 2018). The widespread occurrence of nontronite on Mars has been proposed to form through oxidation of Fe(II)-rich saponite (Chemtob et al 2017). Nontronite can form through oxidation of saponite prepared by a sol-gel method (Chemtob et al 2017), however, saponite prepared by alteration of Mars-analog basalt has not been oxidized to nontronite in laboratory experiments.

The objective of this study was to compare the formation of nontronite through oxidation of Fe(II)-rich saponite prepared by sol-gel and basalt alteration methods. For sol-gel synthesis, silicate gels with various proportions of Fe(II), Mg and Al were precipitated and then aged at 200 ºC for 14d (Chemtob et al 2017). For basalt-alteration synthesis, 250 mg of reduced Mars-analog basalt [Fe(III)/ΣFe = 0.12, ΣFe = Fe(II) + Fe(III)] was mixed with 10 mM FeCl₂/100 mM acetic acid solution and incubated at 200 ºC for 14d (Peretyazhko et al, 2018). The X-ray diffraction analysis confirmed saponite formation in all samples (d₀2₁ 4.57-4.62 Å, d₀₆₀ 1.53-1.54 Å).

Oxidation experiments were performed by reacting 2 g/l saponite suspensions with 0.2 wt% hydrogen peroxide (Chemtob et al 2017). Saponite formed by sol-gel method transformed into nontronite (d₀₂₁ 4.47-4.54 Å, d₀₆₀ 1.52 Å) after one week. Saponite formed by alteration of Mars-analog basalt remained trioctahedral saponite but became enriched in Fe(III) (d₀₂₁ 4.57 Å, d₀₆₀ 1.53 Å). The results indicate that starting material (basalt or gel) could affect saponite oxidation mechanism. Oxidation of saponite precipitated from the silicate gel caused structural reorganizations and nontronite formation while oxidation of saponite formed through basalt alteration only caused Fe(II) oxidation. Nontronite formation on Mars through saponite oxidation likely requires precipitation of Fe(II)-rich saponite through solution or gel and not via alteration of basalt. Alternatively, nontronite on Mars could form from oxidized Fe(III)-rich precursor basaltic material. Experiments will be performed to study nontronite formation from Mars-analog basalt simulant with variable Fe(III) content.

References:
Intercalation of uranyl peroxide nanoclusters into pillared layered double hydroxides

Samuel N. Perry*1, Stuart J. Mills2 and Peter C. Burns1,3

1Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, IN, 46556, USA; 2Geosciences, Museum Victoria, GPO Box 666, Melbourne, Victoria 3001, Australia; 3Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN, 46556, USA

During the Manhattan Project and ensuing Cold War, U was released into the subsurface at sites such as Hanford, WA both accidentally and deliberately, resulting in persistent contaminant plumes1. When exposed to H2O2 in alkaline aqueous solutions, U(VI) polyhedra self-assemble into large, hollow polyoxometalates (POMs) that can exceed 3 nm in diameter2. Due to their relatively large volumes, high solubility and persistence in aqueous solution, uranyl peroxide nanoclusters have generated considerable scientific and industrial interest for applications in nuclear fuel reprocessing3. Layered double hydroxides (LDHs) or hydrotalcites are a class of layered compounds composed of brucite-like, Mg(OH)2, cationic sheets charge balanced by an anionic interlayer4. Synthetic LDHs are the subject of much research due to their highly tailorable composition, high anion exchange capability and an interlayer that can expand up to 4 nm4. Intercalation of uranyl peroxide nanocluster macro-anions into LDHs could allow for novel applications in the fuel cycle and in sites of legacy U contamination (eg. Hanford, Oakridge National Laboratory) or nuclear disasters (eg. Fukushima Daichii).

Magnesium-aluminum layered double hydroxides were synthesized with organic anions propping the interlayer to various gallery heights (MgAl) and characterized with PXRD, ICP-OES and SEM. The LDHs were reacted with several uranyl peroxide nanocluster species, of which pyrophosphate-containing nanoclusters showed the greatest removal of ppm U from solution when reacting with MgAl. Measurements of the supernatant over time show that U is released into solution after several days of internment in the MgAl, suggesting pillared LDHs may offer a novel means of U waste remediation.

Surface characteristics of ancient glass analogues for long-term disposal of vitrified radioactive waste

A. Plymale*1, J. Wells1,2, C. Pearce1, C. Brislawn1, E. Graham1, T. Cheeke3, J. Allen4, S. Fansler1, B. Arey1, B. Matthews1, M. Bowden1, D. Saunders1, V. Danna1, J. Weaver5, R. Sjöblom6, J. McCloy7, E. Hjärthner-Holdar8, M. Englund8, E. Ogenhall8, D. Peeler1, and A. Kruger9

1PNNL, Richland, WA; 2OSU, Corvallis, OR, 3WSU, Tri-Cities, Richland, WA; 4EWU, Cheney, WA; 5NIST, Gaithersburg, MD; 6LUT, Luleå, Sweden; 7WSU, Pullman, WA; 8Arkeologerna, Uppsala, Sweden; 9US DOE, Office of River Protection, Richland, WA

Glass from a ~1500-year-old vitrified Swedish hillfort, Broborg, is a suitable analogue for radioactive waste immobilized in glass because it is: 1) of known composition, 2) from a known alteration environment, and 3) of known provenance. Characterization of the alteration layers on glass-rich samples from Broborg (Fig. 1) provides unique insight into millennial-scale natural processes that drive glass corrosion, including the role of microbes. The interaction of glass with aqueous solutions results in 1) dissolution, 2) formation of a porous layer from which soluble elements, e.g., Na, are released into solution while less soluble elements, e.g., Si and Al, are retained, and 3) subsequent precipitation of minerals, including phyllosilicates, on the glass surface. By identifying alteration phases formed on Broborg glass under ambient conditions and comparing them with those produced by laboratory-based accelerated aging tests, the effectiveness of short-term glass aging tests can be assessed. More accurate aging tests, in turn, could lead to improved radioactive waste loadings without compromising the long-term integrity of waste glass. Our results show that Broborg glass supports a microbial community of bacteria, fungi, and protists potentially involved in glass alteration. These organisms can exhibit biocorrosive properties, including silicate dissolution, extraction of essential elements, and secretion of geochemically reactive organic acids. However, long-term biofilms also possess a homeostatic function that could limit glass alteration.

Figure 1: Left: inner wall at Broborg. A) back and B) front image of vitrified material from Broborg (inset in B shows higher magnification image of glass). C) X-ray computed tomography image of cut surface and D) image of cut surface. E) and F), scanning electron microscopy of microbial colonization of glass surface.
Knowledge about the influence of nanoparticles (NPs) on environmental systems’ behavior is far from complete. Many Earth systems are affected by the presence of incidental NPs (INPs), which form in different environmental settings as a result of a variety of anthropogenic activities. These nanoparticles usually have high reactivity and may alter contaminant and nutrient mobility. Although processes are inherently local in nature, they may have temporally and spatially dynamic regional and global environmental impacts. Significant volumes of nuclear waste have been and are currently generated resulting in many contaminated sites around the globe. Nuclear wastes has the potential to alter soil and sediment chemically and mineralogically, by promoting mineral dissolution followed by the precipitation of a variety of INPs, which in turn, may affect metal and radionuclide fate and transport in different ways. Examples of INPs formation and contaminant associations are included in this presentation emphasizing their role in controlling and/or affecting contaminants' mobility.
ASSESSING THE ASSOCIATIONS OF ORGANIC MOLECULES WITH CLAY SIZE MINERALS

O. Qafoku¹, A. Andersen¹, L. Kovarik¹, M.E. Bowden¹, D.E. Perea¹, A. Dohnalkova¹, R. Kukkadapu¹

¹Pacific Northwest National Laboratory, 3335 Innovation Boulevard, Richland, WA 99354

Soils sequester and protect organic matter via strong organo-mineral associations. The capacity of soils to accumulate organic matter is typically estimated based on the strong correlation between organic C and soil’s surface area and clay content. It is thus predicted that organic compounds will bind strongly to the reactive sites of soil’s clay-sized minerals. To gather more insights into organo-mineral associations and assess the binding mechanisms of organic functional groups at mineral reactive sites, we used direct micron scale probing techniques coupled with molecular scale computer simulation.

We conducted experiments using two model minerals that are abundant in arid soils, natural illite and synthetic calcite with a < 2 µm particle size. Each mineral was reacted with a mixture of four organic molecules chosen to represent different classes of organic matter: lignin, proteins, lipids, and sugars. Microscopy and tomography direct techniques probed the reacted mineral surfaces from submicron to atomic scale. Molecular scale computer simulations were employed to elucidate the dynamic relationships between specific mineral surfaces, structures of organic compound, and their preferential surface accumulation.

Batch experiments data, collected with nuclear magnetic resonance spectroscopy, revealed significant adsorption of lipids, amino acids, and lignin by calcite (at pH 8) and less adsorption of the same organic moieties by illite (at pH 5). Microscopy techniques showed accumulation and strong association of polymerized organic molecules with calcite particles. In contrast, on reacted illite organic molecules appeared as an amorphous layer that accumulated below 100 nm thickness. The experimental data is in agreement with molecular simulations, which indicated that contingent on concentration, organic molecules may interact alone or in conjunction with each-other as they approach mineral surfaces. This characterization of model mineral-organic systems at submicron to nano size level can serve as a foundation towards mechanistic understandings of natural complex systems.
The influence of clay mineralogy on reservoir damage of carboniferous sandstone in Gulf of Suez rift basin, Egypt.

Ahmed. E. Radwan
radwanae@yahoo.com
Ahmed. Radwan *, Mohsen. M. Attia *

* Geology department, Faculty of science, Sohag university, Egypt.

Formation damage represents a challenge in the oil and gas industry, many studies conduct to understand formation damage mechanisms, but fewer studies were conducted for analysis the data to detect the source, causes and design of suitable treatment technique of formation damage for each well. Clay minerals have high impact in the formation damage studies. In this paper, an investigation had been done to quantify the reasons and mitigation of the formation damage problem in the Carboniferous Nubia sandstone reservoir within the Gulf of Suez area, where integration of the all available geological, reservoir and production data reviewed to make confident prognosis or diagnoses of formation damage and achieved a complete vision of the sources of formation damage and suggested solutions and treatments. Therefore, in assessing formation damage in the studied well, all aspects of the well data and its history were integrated in this study, including: core analysis, X-ray diffraction, mineralogy, water chemistry, reservoir geology, reservoir fluids, offset well production, production history, drilling history (including fluids used), cementing program, completion, perforation reports (including fluids used), workover history and stimulation history. Deep investigations of the well data and samples indicated the high kaolinite percentage, clay/fluid interaction and salinity difference between formation water and invaded fluid is responsible for damage. Clay minerals seem to be the main contributor for the reservoir damage. The diagnosis of the formation damage problem revealed that, 1) the reservoir damage mechanisms could be generated by (deflocculating of kaolinite clay by non-equilibrium water-based fluids, Salinity chock may be responsible for the clays dispersion, 2) clays/fluid interaction led to block the pore throats and cause a severe permeability reduction in the studied zones, where un appropriate stimulation fluid was used in the workover operations and, 3) the integrated workflow was effective and can help diagnose formation damage problems in the entire oil and gas wells. It is highly recommended to minimize fluid invasion into the formation by controlling the overbalance, avoid long time of completion fluid in the boreholes, especially in depleted reservoir pressure, plus present of sensitive formation minerals.

Figure 1. Scanning electron micrograph of sample 10875 ft, showing pore filling clays and quartz overgrowths Clays consist almost entirely of kaolinite in the form of vermi-form booklets, magnifications 115x/575x.

Key words: reservoir damage, stimulation fluid, xrd.
DIFFERENT TYPES OF CLAY AND THEIR SUITABLE STABILIZERS

Jothibus Ramasamy, Mohammad K. Arfaj and Md Amanullah

EXPEC Advanced Research Center, Saudi Aramco, Dhahran, Saudi Arabia 31311.

Wellbore stability is the top priority for oil and gas industry while drilling. Precautions and preventive measures are always considered during the preparation of drilling program to identify, eliminate/mitigate drilling methods and practices that could potentially cause borehole instability. Clay formation is one such factor to consider for potential borehole instability as certain clay types pose danger of swelling and dispersion when in contact with water. This scenario will lead to well pack off and borehole collapse. Clay stabilizers are often used in water based drilling mud that is used to drill across clay formation. The clay stabilizers inhibit swelling of clay by ion exchange mechanism as well as forming hydrophobic film on the surface of the formation preventing water to get in contact with clay minerals in the formation. There are different types of clay stabilizers used in the drilling mud depending on the type of clay minerals present in the formation such as smectite, illite, kaolinite and chlorite. These clays have different composition and morphology. Therefore, identifying a suitable stabilizer is very critical to prevent borehole stability issues. Clay stabilizers are broadly classified into few groups namely inorganic salts, cationic inorganic polymers, organic cationic polymers, organic anionic polymers and non-ionic organic polymers. Choosing an appropriate stabilizer is possible by detailed clay-fluid interaction studies. Quantity of clay stabilizer to be used in the fluid depends on the type of clay and its ion exchange capacity. In this paper, different types of clays and their suitable stabilizer including different methods of long term shale inhibition evaluation methods have been explained in detail.
APPLICATIONS OF LAPONITE NANOCLAY IN DRILLING FLUIDS

Jothibasu Ramasamy

EXPEC Advanced Research Center, Saudi Aramco, Saudi Arabia

INTRODUCTION
Laponite is a synthetic smectite clay having similar structure and composition of hectorite, which is a natural clay mineral. The two-dimensional nano-sized laponite exhibits excellent cation exchange capacity with interlayer cations. In the recent years laponite has been evaluated its applications in drilling fluids for oil and gas industry and found to be an useful additive for shale inhibition, to provide rheology, for nano-pore plugging as well as to reduce pipe sticking. Wellbore instability is mainly caused by collapse of shale formation due to insufficient inhibition. Shale stabilizers or shale swelling inhibitors are added to drilling fluids to prevent shale from hydration and swelling. Laponite has been found to have excellent shale stabilization property mainly by electrostatic interaction\(^1\). Another unique characteristic of laponite is its dispersibility in water. An important property of a rheology modifier is its ability to disperse in a particular medium. Laponite has been used as rheology modifier for water based mud systems\(^2\). Laponite based drilling fluid has the potential to minimize the occurrence of pipe sticking while drilling. Covalently functionalized laponite clay also can be produced by condensation reactions. Functionalization includes substituents like hydrophilic as well as hydrophobic groups and can be explored for oil based mud systems for emulsification and rheology modification applications. This review captures recent developments of laponite nanoparticle in drilling fluid applications\(^1\).

RESULTS AND DISCUSSION
Laponite has multi-functional characteristics such as inhibition of shale swelling, plugging Nano pores in the wellbore as well as providing rheological property even at extreme temperature conditions.

Shale stabilization: Shale hydration is one of the main causes of wellbore instability during drilling operations. Nanoscale laponite has positive charges on the periphery and negative charge on the face of the clay layers (Figure 1). Due to this charge distribution, laponite been studied for shale inhibition applications using linear swelling measurement, immersion experiment and shale recovery test. The results revealed that laponite has better inhibition property than widely used regular shale inhibitors like potassium chloride and polyamines. Laponite plugs clay interlayer by electrostatic interaction. Laponite also forms nanofilm on the wellbore wall so that permeability of shale formation is significantly reduced, thereby reducing water invasion into the formation. These unique properties of laponite stabilize shale formation and prevent borehole instability issues.

Fig. 1. Nano scale laponite.

Rheological Property: It is an important property of a drilling fluid to suspend solids in the fluid as well as carry cuttings to the surface. Laponite dispersions display excellent heat resistance with little change in viscosity of the dispersion, an important property to achieve flat-rheology water based mud systems. Laponite is also compatible with other drilling fluid additives and display better salt tolerance than other clays like bentonite and sepiolite dispersions. In addition, filtration control experiments revealed that laponite dispersion formed a thin and compact filter cake than bentonite dispersion reducing the likelihood of pipe sticking.

CONCLUSION
Laponite nanoparticles has excellent characteristics in terms of size and charge. These properties have been used in drilling fluids application as shale stabilizer by electrostatic interaction with clay formation as well as forming nano film. Due to its dispersibility in water, laponite has been evaluated for its rheological property and found to provide stable dispersion even at extreme temperature conditions. Further functionalization of laponite is also possible for other drilling fluid applications such as emulsifier for oil-based mud.

REFERENCES
Silver nanomaterials, especially nanowires are being intensively studied for new electronic devices manufacturing, such as touch screen or solar panels. Silver is a good candidate because it has a high electric conductivity, is quite inexpensive and can easily be synthesized as a nanowire in optically transparent percolation networks. Sulfidation is a cost-effective green passivation strategy because it happens naturally on silver material, preserve the optical and electrical properties of the NW and prevent dissolution, which in turn limits the potential for Ag\(^+\) release and cytotoxicity. Experimentally, the proposed path for sulfidation is via atomic layer deposition (ALD). With this method, atom thick monolayers are sequentially deposited on the surface allowing a full control over the film thickness and purity. Scanning this surface with STM help to identify the intermediate configurations of adsorbed sulfide. However, the adsorption mechanism has not been investigated yet. DFT simulations on Ag surfaces, relevant for nanowire cases ([100], [110] and [111]), combined with H₂S, HS⁻ and H⁺ absorbed and in gas phase are used to reconstruct the different steps that lead to sulfide adsorption on silver nanowires. This is of great interest to be able to tune conductivity properties at the interconnection of the nanowires.
Clay Minerals Detected by the CheMin XRD Instrument in Gale Crater, Mars and Implications for Ancient Aqueous Environments


1 NASA Johnson Space Center, Houston, TX 77058; 2 NASA Ames Research Center; 3Planetary Science Institute; 4 NPP at Goddard Space Flight Center; 5 Jacobs at NASA JSC; 6 NPP at NASA JSC; 7 Chesapeake Energy; 8 Carnegie Institute for Science; 9 Jet Propulsion Laboratory; 10 University of Arizona; 11 Lunar and Planetary Institute; 12 California Institute of Technology; *corresponding author: elizabeth.b.rampe@nasa.gov

The Mars Science Laboratory Curiosity rover landed in Gale crater in August 2012 to study the composition and sedimentology of a stratigraphic sequence deposited ~3.5 Ga ago in lacustrine, fluvial-deltaic, and eolian environments. Orbital visible/short-wave infrared reflectance spectra indicate a change in mineralogy within the sequence, where Fe/Mg-smectite is present in lower strata, sulfate minerals appear stratigraphically above the smectite-bearing units, and hematite has a patchy occurrence. The observation of a variable secondary mineral assemblage within the sequence suggests changes in aqueous conditions between strata.

The Chemistry and Mineralogy (CheMin) instrument on Curiosity is an X-ray diffractometer and X-ray fluorescence spectrometer located in the body of the rover. CheMin analyzes powdered rock samples and loose sediment samples. It operates in transmission geometry, uses a Co X-ray source, and collects diffraction data from 4-52 °2θ with an angular resolution of ~0.3 °2θ. Rietveld refinements of the CheMin diffraction data can be used to quantify well-crystalline minerals to a detection limit of ~1 wt.%. The CheMin team performs full-pattern fitting analyses of diffraction data using FULLPAT to quantify clay minerals and X-ray amorphous materials.

Of the 27 rock and sediment samples analyzed by CheMin to date, phyllosilicates have been found in almost all fluvial-lacustrine rocks sampled at Gale crater and compose up to 30 wt.% of the rocks. Most clay minerals have a 10 Å basal spacing, indicative of a collapsed smectite or illite. The lack of a correlation between clay mineral abundance and K content measured by the Alpha Particle X-ray Spectrometer suggests the 10 Å phyllosilicates are collapsed smectite. Differences in smectite structure and composition between samples may signify changes in aqueous conditions. One sample contains smectite expanded to ~13.5 Å, which may be from partial chloritization during early diagenesis. Two samples have ~9.6 Å basal spacings, which could be a completely collapsed smectite or a different phyllosilicate like ferripyrophyllite. CheMin diffraction data and evolved H2O(v) analyses by the Sample Analysis at Mars instrument indicate structural changes in clay minerals within the stratigraphy. Samples collected from the base of the section have trioctahedral smectite (i.e., saponite), and the smectite evolves to have more dioctahedral character going up section until the smectite is 100% dioctahedral. This change in structure may indicate a change in aqueous alteration conditions and intensity, from a closed system at the base to open system alteration moving up section.
Gibbsite solubility in concentrated sodium hydroxide is important to many industries, including pulp and paper production, alumina refining, and management of alkaline nuclear waste. At lower sodium hydroxide concentrations (< 6 molal), the solubility is well described by common thermodynamic models, but those models become increasingly more complex at high hydroxide concentrations. At extremely high hydroxide concentrations, very small changes in hydroxide concentrations lead to large changes in gibbsite solubility. Similarly, gibbsite solubility is between 3 and 15 times more soluble in concentrated alkaline aqueous electrolyte solutions of NaNO₂ and NaNO₃ than in dilute solutions of the same hydroxide concentrations. This study will take a historical look at our physical understanding for these “anomalous” behavior of gibbsite solubility. The presentation will start with the study by Barney (1976) of gibbsite solubility in alkaline nuclear waste, leading to what the nuclear industry calls “The Barney Diagram”, and end with a modern description of the structure of aqueous sodium hydroxide solutions. The change of hydroxide solution structure with concentration will be correlated to the Hammett Acidity Parameter. Solutions with a rapidly changing Hammett Acidity Parameter as a function of concentration, in turn, are correlated to large shifts in gibbsite solubility.
Fe(II) in minerals is known to abiotically reduce a variety of environmental contaminants such as chlorinated solvents, nitrite, and nitrobenzene. It is often unclear, however, whether the Fe(II) source is structural Fe(II) such as that found in clay minerals and magnetite, sorbed Fe(II) on the mineral surface, or a transient reactive mineral phase. Recently, we have observed that TCE is not reduced by structural Fe(II) in magnetite and clays, but rather that addition of Fe(II) and precipitation of a reactive mineral precipitate were required for reduction to occur. Here, we investigated whether formation of a reactive mineral precipitate is also required for nitrite reduction by a reduced sediment collected in Iowa. Sterilized sediments alone did not reduce nitrite, but reduction of nitrite to nitrous oxide was observed when Fe(II) was added. To explore whether a reactive mineral intermediate is forming, we analyzed samples before, and after, reaction with aqueous $^{57}$Fe(II) and nitrite using Mössbauer spectroscopy. In addition, we monitored sediment redox potential to determine whether nitrite reduction rates correlated with the oxidation-reduction potential (ORP) of reactive mineral precipitates. Our work provides important insights into the mechanism of abiotic nitrite reduction by floodplain sediments.
MINERAL NANO-COLLOID AND SMALL COLLOID FACILITATED RELEASE OF ORGANIC CARBON FROM COLUMBIA RIVER AND TIM’S BRANCH RIPARIAN SEDIMENT

Kenton Rod*1, Kaizad Patel2, Kumar Swatantar2, Elizabeth Cantando3, Weinan Leng3, and Ravi Kukkadapu2

1Washington State Department of Ecology, 3100 Port of Benton Blvd., Richland, WA 99354; 2Pacific Northwest National Laboratory, 902 Battelle Blvd., Richland, WA 99354; 3VT NanoEarth, 1991 Kraft Drive, Blacksburg, VA 24061

We are on the frontier of an improved understanding of fate and transport of natural organic carbon (OC) in aqueous systems in such that the operational definition of dissolved OC being less than 450 nm is not sufficient. In aqueous systems, including groundwater, nano-colloids (1-100 nm diameter) and small colloids (<450 nm diameter) provide a vast store of surfaces to which OC can sorb, precluding its normal bioavailability. Because nanomaterials are ubiquitous and abundant throughout Earth systems, it is reasonable that they would play a significant role in biogeochemical cycles. As such, mineral nano-colloids and small colloids (MNC and MSC), formed through mineral weathering and precipitation processes, are both an unaccounted-for reservoir and unquantified flux of OC and nutrients within watersheds. They may also serve as a bridge between organic and inorganic nutrient cycles. In groundwater systems OC can adsorb to mineral colloid (MC) surfaces (MC-OC) providing protections from biodegradation. A series of water extractions were conducted with synthetic groundwater, specific for each sediment, under 1) oxic and 2) anoxic conditions for each of two riparian sediments from 1) Columbia River, Washington and 2) Tim’s Branch, South Carolina. Total colloids in the extract were centrifuged to specific size fractions (size based on silicate density of 2.65 g cm⁻³) and measured for concentration by precision UV-Vis. Similarly, OC in the extract was quantified by combustion carbon analyzer. Of the OC released from Columbia river sediments under aerobic conditions all were from <6 nm colloid fraction and was considered to effectively be dissolved OC. The anerobic extraction of Columbia River sediments resulted in 26% of released OC sorbed to 100-450 nm fraction and 3% from 6-100 nm fraction. A much higher ratio (50%+) of OC released from Tim’s Branch sediment was associated with mineral colloids. For aerobic extraction 15% of released were sorbed to the 100-450 nm fraction and 18% were sorbed to 6-100 nm fraction. The anaerobic extraction from Tim’s Branch sediment yielded 8% sorbed to the 100-450 nm fraction and 38% were sorbed to 6-100 nm fraction. No difference was found in the respiration rates measured from the extracted waters. This study demonstrates that mineral facilitated release of OC in riparian sediments is both significant and variable between locations.
Iron (Fe) bearing oxide, sulfide, and silicate minerals are important components of natural soils, sediments, and aquifers, i.e. the subsurface realm of the critical zone. Such phases engage in redox reactions with inorganic and organic compounds that impact a wide variety of geological and environmental process, such as sediment diagenesis, chemical weathering, and the mobility and fate of organic and inorganic contaminants. Because Fe-bearing minerals are typically highly insoluble in circumneutral pH, near-surface environments, their redox transformation takes place by way of chemical reactions at the mineral-water interface. Microorganisms can contribute in a dramatic way to both reductive and oxidative transformations of solid-phase Fe-bearing minerals, through mechanisms referred to collectively as “extracellular electron transfer” (EET) that take place external to the cell surface. Reductive EET pathways have been studied extensively in the context of microorganisms that couple heterotrophic metabolism to dissimilatory reduction of Fe(III)-oxide and Fe(III)-phyllosilicate minerals. Less is known about oxidative EET metabolism, particularly in relation to weathering of insoluble Fe(II)-bearing sulfide and silicate phases. This presentation will summarize (1) previous and ongoing experimental information on kinetic and thermodynamic controls on the microbial reduction of Fe(III)-oxides and Fe(III)-phyllosilicates; and (2) new experimental studies (combination of in situ geochemistry, microbiological experimentation, and genomic sequencing) that reveal previously unrecognized pathways whereby microorganisms may accelerate oxidative weathering of insoluble Fe(II)-bearing mineral phases.
Investigating the influence of Ca on soil organic carbon dynamics in a Swiss subalpine grassland.

Mike C. Rowley¹, S. Grand¹, J. Spangenberg¹ & E.P. Verrecchia¹.

¹Institut des Dynamiques de la Surface Terrestre (IDYST), Université de Lausanne, Switzerland.

Geochemical indicators are emerging as important predictors of soil organic carbon (SOC) accumulation and persistence¹, but the role of Ca has largely been overlooked². In this study, we investigated the effects of Ca on SOC by comparing 6 profiles that had developed under similar conditions for soil formation, except that 3 contained CaCO₃ (CaCO₃-bearing), and 3 did not (CaCO₃-free)³. Our hypothesis was that an increased Ca availability, released during the dissolution of CaCO₃, would positively influence the storage of occluded SOC at our CaCO₃-bearing site, through its effects on aggregation.

To investigate the role of occlusion in our profiles, we fractionated samples by density (1.6 g cm⁻¹) and sequential sonication into three light fractions (LFs; free-light fraction and two occluded fractions) and a mineral-associated fraction (HF). Following carbonate removal, the organic carbon content and δ¹³C values of the bulk soil and density fractions were quantified, while X-ray photoelectron spectroscopy was also performed on a subset of the fractions.

Bulk SOC content was approximately twice as high in the CaCO₃-bearing profiles relative to the CaCO₃-free, while δ¹³C values of bulk SOC were lower at CaCO₃-bearing profiles. Occluded SOC was an order of magnitude more abundant in CaCO₃-bearing profiles, supporting the idea that Ca positively influences occluded SOC pools; but the occluded pool was small overall, never accounting for more than 10 % of total SOC.

Instead, it was the HF that was of key interest. The HF SOC content was approximately twice as high in the CaCO₃-bearing profiles relative to the CaCO₃-free. The CaCO₃-free profiles displayed the typical shift to higher δ¹³C values from LFs to HF. Contrastingly, in the CaCO₃-bearing profiles, the δ¹³C values of the HF were more similar to the LFs. This suggests that the LFs had undergone more oxidative transformation at the CaCO₃-bearing profiles; but, this transformation may have increased the propensity of SOC to be stabilised in the mineral-associated fraction (HF) of soils with an increased Ca availability.

Overall, a higher Ca availability was linked to a two-fold increase in the mineral-associated SOC content of a Swiss subalpine grassland.


CLAY-BASED BIONANOCOMPOSITES FOR HEALTH AND ENVIRONMENTAL APPLICATIONS

Prof. Eduardo Ruiz-Hitzky

Materials Science Institute of Madrid, CSIC, c/ Sor Juana Inés de la Cruz 3, E-28049 Madrid, Spain

It is widely known the ability of clay minerals to interact at the nanometric scale with organic matter coming from living beings, resulting in highly functionalized hybrid materials whose properties derive from the synergy between the two types of components, acting in certain cases as bioinspired or biomimetic systems. When the organic component is a biopolymer, the products of these assemblies were called bionanocomposites (1) because of their relationship with the well-known polymer-clay nanocomposites, though in the present case comprising a component of biological origin (2). Smectites are commonly employed to produce bionanocomposites though other types of clays, such as vermiculite, halloysite, and especially fibrous clays (sepiolite and palygorskite), can be also advantageous nanofillers for the production of those biohybrid materials. This lecture aims to introduce recent contributions on that topic developed by our research group at the ICMM-CSIC, highlighting the wide diversity of materials that can be prepared for application in the fields of Sustainability, Biomedical Engineering and Healthcare. Examples range from the removal of water pollutants to virus-clay systems for more efficient vaccines, incorporating polysaccharides, proteins and nucleic acids (3,4). More recently, nanocellulose-clay bionanocomposites including sepiolite and palygorskite leads to hetero-nanofibrous hybrid films named as hybrid nanopaper (5). Clay-based bionanocomposites come along as a trending topic that incorporates the abovementioned sustainable, ecofriendly and low-cost components. It should be expected it grows-up rapidly by producing materials with complementary functionalities, such as electrical conductivity, magnetic response, or specific bioactivity. These characteristics may deserve improving applications, e.g. in the removal of toxic pollutants (heavy and radioactive metals, dyes, pharmaceuticals, dioxins, polyaromatic molecules, etc) and microplastics in marine environment, carriers and adjuvants of drugs and vaccines, respectively, as well as tissue engineering (bioactive dental materials, bone replacements, etc.) or clinical bandages, among others.

**Mg/Al LDH obtained via transformation of minerals for the removal of selected elements from acidic and alkaline wastewaters**

Karolina Rybka*1 and Jakub Matusik1

1AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Department of Mineralogy, Petrography and Geochemistry, al. Mickiewicza 30, Krakow, 30 059, Poland

A growing water pollution can be a result of both natural and industrial processes. The structure of Layered Double Hydroxides (LDH) comprises of positively–charged brucite-like layers built of divalent (MII) and trivalent (MIII) metals. The charge is balanced with the intercalated hydrated anions, what makes them perfect materials for the anions removal. Nevertheless, besides the effectiveness, the low price is also of interest for the industry. Therefore, the first goal of this study was to obtain Mg-Al LDH using magnesite and halloysite as cheap and abundant sources of Mg and Al, to substantially lower the final price of the material. LDH adsorption behavior is well known from many experiments, mostly in single element systems. In contrast, this study focused on using waters with multi-element chemical composition and extreme pH conditions (Acid Mine Drainage (AMD) water with pH = 2.2 and Industrial Water (IW) water with pH = 9.0). The used Mg-Al LDH was synthesized in three different variants, with varying contribution of minerals as sources of MII or MIII. First, a reference sample (Mg/Al) was synthesized using only chemical reagents: MgCl₂·6H₂O and AlCl₃·6H₂O as Mg and Al sources. For the second material (M/Al), magnesite was used instead of Mg-chloride. For the third material (M/Hall), magnesite was used as a source of Mg, and Al-chloride was replaced by halloysite (Hall). All materials were synthesized by a co-precipitation method with prior dissolution of the minerals. All materials were characterized by XRD and FTIR before and after adsorption experiments. The adsorbent dosage was 5 g/L. Initial and equilibrium concentrations were measured by ICP-OES. Regardless of the material variant, the XRD patterns confirmed the presence of LDH. For the M/Al gibbsite admixture was detected. All materials showed the presence of carbonates in the interlayer space which was confirmed by the bands in the 1410-1365 cm⁻¹ region of FTIR spectra. The chemical analysis of investigated waters showed, that main ions found in AMD were SO₄²⁻ (4052.45 mg/L) and Fe (1138.90 mg/L). SO₄²⁻ and V were present in the highest concentrations (801.16 and 168.13 mg/L, respectively) in the IW water. In general, even in a system with a lot of competitive ions, all materials effectively removed main pollutants from both waters. In particular, most of anionic forms, despite high concentration of sulphates, were almost completely removed. However, the initial pH of waters significantly affected the stability of the materials, which was indicated by the release of Mg. Also, the XRD patterns of all materials after AMD adsorption experiments confirmed dissolution of the LDH, as well as the shift of the basal peaks indicating the interlayer expansion. The FTIR spectra of all samples showed the band at 1110 cm⁻¹ attributed to the presence of intercalated sulphates. Also, the band at 1365 cm⁻¹ was replaced by the band at 1430 cm⁻¹, which indicates the change of carbonates species. The XRD patterns of samples treated with IW did not change significantly. Also, the FTIR spectra did not exhibit any significant changes beside the SO₄²⁻ band at 1110 cm⁻¹ in the Mg/Al spectrum.

This project was supported by the National Science Centre Poland, under a research project awarded by Decision No. 2017/27/B/ST10/00898.
DIFFERENT APPROACHES TO TRANSFORMATION OF SELECTED MINERALS INTO LAYERED DOUBLE HYDROXIDES

Karolina Rybka*1 and Jakub Matusik1

1AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Department of Mineralogy, Petrography and Geochemistry, al. Mickiewicza 30, Krakow, 30 059, Poland

Layered Double Hydroxides (LDH) are widely studied as promising materials in many different fields, such as catalysis, drug delivery and wastewater treatment. The LDH formula is the following: \([\text{M}^{II}_{1-x}\text{M}^{III}_x\text{OH}_2]^{x+}[\text{A}^n]_{y/n} \cdot y\text{H}_2\text{O}\), where \(\text{M}^{II}\) is a divalent metal, \(\text{M}^{III}\) is a trivalent metal and A is an anion. The layered LDH structure generates positive charge balanced by the weakly bonded hydrated anions. This is a reason for various applications of LDH as anion exchangers. The LDHs synthesis is straightforward, however, the excessive use of chemical reagents makes the whole process expensive. Currently, many studies are devoted to obtaining LDH, where different materials serve as \(\text{M}^{II}\) and \(\text{M}^{III}\) sources. The use of abundant, easy accessible and cheap materials can significantly lower the final price of an adsorbent. Therefore in this work, Mg/Al LDH was synthesized with different contributions of minerals as precursors of Mg and Al: magnesite from Grochow deposit (Poland) and halloysite from Dunino deposit (Poland). Three variants of Mg/Al LDH were synthesized: reference sample (Mg/Al) obtained from chemical reagents (MgCl2·6H2O and AlCl3·6H2O), sample obtained with magnesite as a Mg source (M/Al) and sample obtained via transformation of magnesite and calcined (750°C, 5h) halloysite (M/Hall). All substrates were dissolved to obtain Mg/Al solution. All materials were synthesized via co-precipitation method with the pH set and constantly controlled at 10. The precipitates were aged for 2 h, washed with redistilled water and dried at 60°C. The starting minerals and the obtained materials were characterized by XRD, FTIR and SEM. All materials were dissolved in concentrated HCl and their chemical composition was determined through AAS measurements. Moreover, the stability of materials in pH range of 2-8 was investigated. For that, the materials were stirred in solutions with pH = 2, 4, 6 and 8 for 24 h, then the concentration of released elements was measured by AAS. The XRD pattern of raw magnesite sample showed the presence of quartz admixture. The content of Mg was equal to 25.7%. The XRD pattern of halloysite sample exhibited reflections characteristic for halloysite, kaolinite, quartz and iron minerals. The chemical analysis revealed, that the content of Al was equal to 16.73% and Fe equal to 19.34%. Diffractograms of all synthesized materials showed peaks characteristic for LDH as compared to hydrotalcite standard. In the case of M/Al the additional formation of gibbsite was confirmed. The FTIR spectra of all materials showed bands in the regions 3700-3400 cm\(^{-1}\) for OH stretching vibrations, 1540-1350 cm\(^{-1}\) for the interlayer carbonates and <1000 cm\(^{-1}\) for the lattice vibrations. The M/Al spectrum also showed a band at 3550 cm\(^{-1}\) characteristic for Al-OH vibrations. The SEM images of obtained materials showed agglomerates of different size up to 100 µm. Moreover, in the M/Al images the grains of gibbsite were observed. The chemical analysis revealed, that the molar ratio \(\text{M}^{II}/\text{M}^{III}\) was 2.8 and 5.6 for Mg/Al and M/Hall, respectively. Because of gibbsite in the M/Al sample, the Mg and Al content was not determined. The stability experiment showed, that the materials are stable in the pH range of 4-8. At pH = 2, the percent of released Mg was found to be: 8.85, 22.03 and 0.06% for the Mg/Al, M/Al and M/Hall, respectively.

This project was supported by the National Science Centre Poland, under a research project awarded by Decision No. 2017/27/B/ST10/00898.
CALCIUM-FACILITATED AGGREGATION AND PRECIPITATION OF U$_{60}$ IN THE PRESENCE OF NA-MONTMORILLONITE

Luke R. Sadergaski$^1$, Meena Said$^1$, and Amy E. Hixon$^*$

$^1$University of Notre Dame, Department of Civil & Environmental Engineering & Earth Sciences, Notre Dame, IN 46556.

In order for nuclear energy to be widely accepted, scientists need to (i) gain a better understanding of how uranium (U) contamination can be tracked and managed in the biosphere and (ii) design safe geologic repositories for the long-term storage of nuclear waste. The transport of U contamination has been addressed in part by sorption experiments of discrete U(IV) (e.g., UO$_2^{2+}$) to various minerals in many geochemical systems. However, there is an absence of research regarding the behavior of U-based nanoclusters in the environment, which is an important aspect to consider given their high solubility and persistence when dissolved in solution.

This study uses batch sorption experiments to examine interactions between the uranyl peroxide nanocluster [UO$_2$(O$_2$)(OH)]$_{60}^{-}$ (U$_{60}$) and Na-montmorillonite (SWy-2), plagioclase (anorthite), or quartz (SiO$_2$) as a function of time (20 min–122 days), U$_{60}$ concentration (0.5–2 mg mL$^{-1}$), and mineral concentration (10–20 mg mL$^{-1}$). SWy-2 was studied in both its untreated form as well as after two different pretreatments, denoted ‘partially-treated’ and ‘fully-treated’. U$_{60}$ removal from solution was tracked using inductively-coupled plasma optical emission spectroscopy and dynamic light scattering measurements were used to calculate changes in the hydrodynamic diameter (D$_H$) of U$_{60}$ in solution; an increase in D$_H$ could be indicative of the formation of aggregates. The solid phases were characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS).

U$_{60}$ was removed from solution in the presence of untreated and partially-treated SWy-2. However, U$_{60}$ was not removed from suspensions containing anorthite, quartz, or fully-treated SWy-2, even after several months. The removal of U$_{60}$ from suspensions containing untreated SWy-2 is promoted in part by the exchange of Li$^+$ counterions, normally weakly associated with U$_{60}$ in solution, for Ca$^{2+}$ ions naturally present in the clay. In solution, Ca$^{2+}$ ions induce the aggregation of nanoclusters, which precipitate on the surface of SWy-2. Ca-rich U$_{60}$ aggregates associated with SWy-2 were identified and characterized by SEM-EDS, Raman spectroscopy, and XPS.

Although cations such as Ca$^{2+}$ enhance the mobility of discrete U(VI) through the formation of neutrally-charged ternary species (e.g., Ca$_2$UO$_2$(CO$_3$)$_3$(aq)), it appears that low concentrations of Ca$^{2+}$ may be responsible for immobilizing U$_{60}$ in the form of precipitates. Therefore, the fate and transport of uranyl peroxide nanoclusters in environmental systems may be considerably dependent upon the concentration of naturally-abundant cations and further research in this area is warranted.
Surface Hydration and Hydroxyl Configurations of Gibbsite and Boehmite Nanoplates

Michel Sassi*1, Zheming Wang1, Eric D. Walter2, Xin Zhang1, Hailin Zhang1, Xiaohong S. Li3, Aashish Tuladhar1, Mark Bowden2, Hongfei Wang4, Sue B. Clark3,5, and Kevin M. Rosso1

1Physical Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352, USA, 2Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99352, USA, 3Energy and Environmental Division, Pacific Northwest National Laboratory, Richland, Washington 99352, USA, 4Department of Chemistry, Fudan University, Shanghai 200438, China, 5Department of Chemistry, Washington State University, Pullman, Washington 99164, USA.

The discontinuation of the bulk structure at the interface between metal oxide particles and water leads to altered bonding characteristics and unique facet-dependent molecular environments. Surface hydration and hydroxylation add further complexity to the interface, details that for metal (oxy)hydroxides are especially difficult to isolate from the background signal of bulk structural hydroxyls. Here, we probe for the first time the surface hydroxyl structures and the effect of hydration on basal surfaces of gibbsite (α-Al(OH)3) and boehmite (γ-AlOOH) nanoplates under ambient conditions, using the interface-sensitive technique vibrational sum frequency generation (VSFG) spectroscopy. VSFG spectra of the hydroxyl stretching modes at the interfaces with adsorbed water layers compared directly to Raman and infrared spectra of the bulk modes show that while gibbsite surface frequencies were sharp and nearly identical to those in the bulk, boehmite surface hydroxyls displayed a very different broad spectrum of states as shown in the Figure. Ab initio molecular dynamics simulations of both basal surfaces with and without hydration waters reveal that gibbsite surface hydroxyls interact only weakly with overlying hydration waters remaining essentially unperturbed, whereas those on boehmite can interact more strongly facilitated by higher configurational degrees of freedom at the interface and there is more extensive H-bonding on boehmite surface under ambient conditions. The findings clearly unveil substantial differences in the hydrated interfacial dynamics of these two otherwise similar materials, with implications for their interfacial chemistry, wettability, and rheology.

VSFG and Raman spectra of boehmite surface and bulk hydroxyl groups.
THE FORMATION OF INCIDENTAL SILVER-BEARING NANOPARTICLES IN ORGANIC MATTER

Michael Schindler¹, Odeta Qafoku², Libor Kovarik², Daniel Perea², Michael Hochella²

¹University of Manitoba, 125 Dysart Road, Winnipeg, MB R3T 2N2 Canada; ²Pacific Northwest National Laboratory, 3335 Innovation Boulevard, Richland, WA, 99354 USA;

Silver nanoparticles (Ag-NPs) have recently been the focus of intense research because of the potential risk they pose to humans and other living organisms. The toxicity of Ag-NPs to a variety of organisms has been demonstrated in a number of recent studies1. In this study we show that incidental Ag-NPs form when Ag-Cl-bearing pore water encounters organic matter. Samples were collected in an organic-rich surficial layer on Ag-Co-As-bearing mine tailings in Cobalt, Northwestern Ontario, Canada. The surficial tailings material has a near neutral pH and elevated concentrations of Ag (125 mg/kg), As (12243 mg/kg) and Co (3869 mg/kg). A Focused Ion Beam section was removed from an organic grain that was partially mineralized by Fe-As-bearing pore solutions. Subsequent Transmission Electron Microscopy examinations indicate the concurrence of As-rich and Fe-hydroxide layers (most likely ferrihydrite) within the organic rich matrix. Silver-bearing nanoparticles also appear to be within ferrihydrite layers or attached to those. Examination with high resolution microscopy indicated that the nanoparticles were composed of native silver and acanthite, Ag₂S. Furthermore, both types of Ag-bearing nanoparticles appear embedded in a chlorine-rich halo, which suggests that Ag was initially transported as Ag-chloride complexes and later was sequestered by organic matter as native Ag and Ag₂S. These observations indicate that engineered Ag NP’s released into the environment can be stabilized in the soil surface via attachment or incorporation with organic matter.

References:
DEGRADATION OF MICAS AND THE FORMATION OF KAOLINITE LAYERS: POTENTIAL INFLUENCES ON POTASSIUM UPLIFT IN TEMPERATE ECOSYSTEMS

Paul A. Schroeder*1, Daniel D. Richter2, and Sophia C. Sanders1

1Department of Geology, University of Georgia, Athens, GA, 30602-2501; 2Nicholas School of the Environment, Duke University, Durham, NC, 27708

The Calhoun Critical Zone observatory (CCZO) in SC provides valuable insight into the interactions between all biotic and abiotic components at the Earth’s surface where rock meets life. Biotite [K(Mg,Fe)3AlSi3O10(OH)2] and phengite [K(Mg,Al,Fe)2(Al,Si)4O10(OH)2] from a deep core (0 to 20 meters) in the CCZO are thought to influence the cycling of potassium, a factor of plant nutrition at depth. As these micas weather and structural ferrous iron oxidizes, potassium is released in order to satisfy a layer charge balance. More intensely weathered biotite and phengites contain lower relative abundances of potassium due to higher levels of oxidation, where the 2:1 structure is maintained. As potassium content of weathered micas near the surface and 2:1 layers become less abundant, the 2:1 layers are restructured to 1:1 layers kaolinite [(Al2Si2)O5(OH)4]. Using an electron microprobe, sand-sized grains were analyzed for their elemental composition using energy dispersive spectroscopy (EDS). Whole grain mounts were also examined in optically. Notably, weathered grains displayed “frayed” ends when viewed perpendicular to the principle c-axis. Analysis of these weathered grain ends in comparison to less weathered centers of grains yielded less relative percentage of potassium on the ends. Near the surface, many more kaolinite grains were observed yet a continuous range of compositions between end member mica and kaolinite were found at all depths. Evidence for fixed potassium in biotite and phengite supports the notion that reservoirs are available to supply rooted zones as uplift and chemical erosion proceeds. Although the loss of potassium occurs, persistence of lower amounts of potassium in the near-surface clays suggest that the degraded micas can still serve as a stock for nutrient cycling. As subsurface conditions become reducing due to low oxygen supply during wet conditions, then the ferric iron in the 2:1 structure can be reduced, necessitating uptake of ions such as potassium and ammonium to compensate for layer charge changes. This implies that oscillating seasonal reducing and oxidizing cycles (fall/winter and spring/summer, respectively) create the potential for degraded biotite and phengite to act as refugia for nutrients in the subsurface CZ.
KIRUNA NATURAL ANALOGUE (KiNa)

Patrik Sellin1, H. Albert Gilg2, Ulf B. Andersson3, Elizaveta Klein4, Daniel Svensson1, Olivier X. Leupin4, Simon Norris5, W. Russell Alexander6
1SKB, Evenemangsgatan 13, SE-169 03 Solna, Sweden; 2Chair of Engineering Geology, TU Munich, Arcisstr. 21, 80333 München, Germany; 3Luossavaara-Kirunavaara AB, Research & Development, FK9, 981 86, Kiruna, Sweden; 4Nagra, Hardstrasse 73, 5430 Wettingen, Switzerland; 5RWM, Thomson Avenue, Oxfordshire, OX11 0GD, United Kingdom; 6Bedrock Geosciences, Veltheimerstrasse 18, 5105 Auenstein, Switzerland.

Disposal of high level radioactive waste is based on multi-barrier systems, where the barriers are supposed to retain their properties for hundreds of thousands of years. To demonstrate long term stability, experimental results can be complemented with the studies of natural systems (Natural Analogues). Bentonite is a common barrier material in many repository concepts. Bentonite deposits are generally millions of years old and the material is therefore a natural analogue of itself. The environment in a bentonite deposit is however rather different from a repository environment and observations cannot always be transferred.

Significant clay alteration zones have been encountered in the Kiruna (Lapland, Sweden) magnetite(-hematite)-apatite deposits, which are hosted in weakly to strongly metamorphosed intermediate to acid volcanic and subvolcanic rocks. These up to 50 m thick soft clay alteration zones occur within ores and within the country rocks along the ore contact of the southern parts of the Kirunavaara ore body. They are found at various levels to depths of at least 1200 m below the surface, in zones further into the hanging wall and footwall lithologies of the deposit. The predominant clay mineral in the alteration zones of all deposits is a dioctahedral Fe-poor montmorillonite (Rieger 2017). K-Ar data of various Na-exchanged size fractions from two clay-altered gneiss samples from the nearby Johannes ore body, Malmberget, which are dominated by R3-ordered illite-smectite, yield age values ranging from 837 ± 14 Ma to 941 ± 15 Ma (Gilg et al. 2017, Rieger 2017).

In many respects, the clay layers in the Kiruna deposits resemble a bentonite barrier in a repository: the clay layers are in the meter scale, the surrounding is fractured rock under the water table and the magnetite could serve as an analogue for an iron corrosion product. A project has been initiated to further study the Kiruna clay with focus on:

- understanding the very long-term behavior of bentonite under conditions of direct relevance to deep geological disposal;
- examination of long-term iron oxide minerals - bentonite interaction;
- the potential erosion properties of bentonite.

So far, preliminary investigations have confirmed a high degree of montmorillonite, a substantial swelling pressure at high dry density, a low hydraulic conductivity and somewhat surprisingly low interaction with the magnetite.

References
MINERALOGY AND WATER CONTENT INTERACT TO CONTROL SOIL ORGANIC MATTER STABILIZATION

Itamar Shabtai\textsuperscript{1}, Srabani Das\textsuperscript{1}, Thiago Inagaki\textsuperscript{2}, and Johannes Lehmann\textsuperscript{1}

\textsuperscript{1}School of Integrative Plant Science, Cornell University, Ithaca, NY 14853; \textsuperscript{2}Technische Universität München, Freising, Bavaria, Germany.

Our current understanding of soil organic carbon (SOC) stabilization highlights the importance of microbial processing and mineral protection of microbially processed C. Soil water dynamics can influence how SOC is stabilized by driving mineral weathering and microbial activity. To understand how long-term soil water content shapes these mechanisms, we studied fallow soils from upstate New York situated on a naturally occurring water content gradient. Across the study site, soils with higher long-term water content contained more persistent SOC, resulting in greater SOC accumulation. To investigate the mechanisms underpinning SOC accumulation and stabilization in long-term wetter soils, we isolated particulate and mineral-associated SOC fractions and measured their C and N contents and isotope ratios, and performed $^{13}$C NMR and C-NEXAFS spectroscopy to investigate the chemical nature of SOC in these fractions. In long-term wetter soils the microbial biomass was higher and C:N ratio of mineral associated SOC was lower, indicating greater microbial processing and transfer to mineral phases of C inputs. Higher long-term water content gave rise to higher soil Ca, likely due to subsoil carbonate dissolution and capillary rise. Soil Ca reduced SOC mineralization in wetter soils, despite having higher SOC content and higher microbial biomass. Ca-mediated SOC stabilization was confirmed in incubations of soil with labelled litter ($^{13}$C-$^{15}$N), which demonstrated that artificially elevating soil Ca reduced SOC mineralization. $^{13}$C NMR and C-NEXAFS spectroscopy revealed that mineral associated SOC in wetter soils was more carboxylic and less aromatic than in drier soils. Carboxylic functional groups may have been preferentially stabilized by interactions with Ca. Current work involving isotopic tracing on soils incubated with labelled litter ($^{13}$C-$^{15}$N) and aims at uncovering the molecular mechanisms underlying Ca-mediated organo-mineral interactions.
Dissolved organic matter plays important role in clay colloid transport

Jianying Shang, Chaorui Yan
China Agricultural University

The stability and transport of clay colloids in groundwater are strongly influenced by colloid interactions with dissolved organic matter (DOM). Protein is an important DOM component that is ubiquitous in natural water, reclaimed water, and soil solutions. To date, the interactions between clay colloids and proteins have not been fully studied. The objective of this study was to examine the effect of bovine serum albumin (BSA), a representative protein, on the stability, aggregation, and transport of kaolinite colloids under neutral pH conditions. Hydrodynamic diameter and ζ-potential measurements, stability tests, and column transport experiments were performed in salt solutions with a range of ionic strengths and different BSA concentrations at pH 7. Additionally, BSA-kaolinite colloid interactions were studied using TEM and batch adsorption experiments. The experimental results showed that BSA prevented colloid aggregation and increased the stability and transport of colloids, especially at high ionic strength, even though the charges of kaolinite colloids were less negative in the presence of BSA. Theoretical calculation of the interaction energies indicated that XDLVO theory, in which the steric force is considered due to BSA adsorption, could correctly quantify the interaction energies in the presence of BSA. This study demonstrated that the role of protein needs to be determined in order to better predict the overall effect of DOM on particle aggregation and transport in the soil environment.
Isotope dilution mass spectrometry is the analytical technique that yields the highest precision and accuracy for rare earth element (REE) concentrations. Samples can be analysed using either thermal ionization mass spectrometry (TIMS) or multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). However, both analytical platforms typically require the REEs to be separated into various ‘cuts’ to be analysed individually, a process that is extremely time consuming and expensive. This is necessary to minimize isobaric interferences from neighbouring REEs and polyatomic interferences from lighter REE oxides, as well as to fit the large mass range of the REEs into analytical runs. In an effort to dramatically increase sample throughput, we recently evaluated the potential to directly analyse unseparated REE samples using the Nu Plasma II MC-ICP-MS, an instrument equipped with ‘zoom lens’ ion optics and sixteen Faraday detectors that can be configured to measure all REE isotopes in three cycles of a single run (Figure 1). The instrument was tuned to minimize oxide production (~0.05% NdO/Nd with a sensitivity of 0.2 V ppb⁻¹), and all samples were internally corrected for mass fractionation using the $^{153}$Eu/$^{151}$Eu ratio, and online isobaric interference corrections for Ce, Nd and Yb were applied to the La, Ce and Lu values, respectively. Spike/sample isotopic ratios for Ce, Nd, Sm, Eu, Gd, Dy, Er, and Yb were measured accurately within 2% of accepted natural values in single analyses on various artificial mixed standards. La and Lu were 2.5% and 5-10% off from expected values due to more demanding interference corrections. This demonstrates the ability to produce REE patterns of comparable quality to traditional methods involving REE separation, with sample preparation and analytical times that are comparable to runs against external standards by single-collector ICP-MS.

Figure 1: Nu Plasma II Faraday Configuration

<table>
<thead>
<tr>
<th>Mean 1</th>
<th>Mean 2</th>
<th>Mean 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>152</td>
<td>169</td>
<td>182</td>
</tr>
<tr>
<td>149</td>
<td>166</td>
<td>179</td>
</tr>
<tr>
<td>147</td>
<td>164</td>
<td>177</td>
</tr>
<tr>
<td>146</td>
<td>163</td>
<td>176</td>
</tr>
<tr>
<td>145</td>
<td>162</td>
<td>175</td>
</tr>
<tr>
<td>144</td>
<td>161</td>
<td>174</td>
</tr>
<tr>
<td>143</td>
<td>160</td>
<td>173</td>
</tr>
<tr>
<td>142</td>
<td>159</td>
<td>172</td>
</tr>
<tr>
<td>141</td>
<td>158</td>
<td>171</td>
</tr>
<tr>
<td>140</td>
<td>157</td>
<td>170</td>
</tr>
<tr>
<td>139</td>
<td>156</td>
<td>169</td>
</tr>
<tr>
<td>138</td>
<td>155</td>
<td>168</td>
</tr>
<tr>
<td>137</td>
<td>154</td>
<td>167</td>
</tr>
<tr>
<td>136</td>
<td>153</td>
<td>166</td>
</tr>
<tr>
<td>134</td>
<td>151</td>
<td>164</td>
</tr>
</tbody>
</table>
Free energy of aggregation of charged colloids (smectite clay) in liquid water from molecular dynamics simulations

Xinyi Shen¹, *, Ian C. Bourg¹,²

¹Department of Civil and Environmental Engineering, Princeton University, Princeton, NJ 08544, USA; ²Princeton Environmental Institute, Princeton University, Princeton, NJ 08544, USA

Clay minerals are one of the most important constituents of soils, sediments, and sedimentary rocks. The aggregation of clay nanoparticles, in particular, strongly influences porosity and permeability and is highly sensitive to both short- (hydrogen bonding, ion solvation) and long-range (charge screening) geochemical interactions. Simulation predictions of clay aggregation and swelling, to date, have relied almost exclusively on coarse-grained simulation techniques that rely on effective inter-particle potential models. Most such models are based on the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of long-range colloidal interactions and they neglect the short-range interactions that stabilize the crystalline hydrates (1-, 2-, and 3-layer hydrates). All-atom molecular dynamics (MD) simulations have the potential to help inform existing models but have focused almost exclusively on the crystalline hydrates.

To bridge this gap, our research uses all-atom MD simulations to examine the energetics of a pair of smectite clay nanoparticles suspended in bulk liquid water at interparticle distances up to 3 nm as a function of salinity (0 to 1 M) and counterion type (Na, K, Ca). Results are compared with the predictions of DLVO theory and analyzed to identify non-DLVO contributions to the aggregation free energy, including specific interactions between charged species in the electrical double layer (EDL) and short-range hydration effects.
LABILE FE(III) FROM SORBED FE(II) OXIDATION IS THE KEY INTERMEDIATE IN FE(II)-CATALYZED FERRIHYDRITE TRANSFORMATION

Anxu Sheng¹, Juan Liu¹, Xiaoxu Li¹, Odeta Qafoku², Richard Collins³, Adele Jones³, Carolyn Pearce², Chongmin Wang², Jinren Ni¹, Anhuai Lu¹, Kevin M. Rosso*²

¹Peking University, Beijing, China; ²Pacific Northwest National Laboratory, Richland, Washington, United States; ³UNSW Sydney, Sydney, New South Wales, Australia.

Ferrihydrite (Fh) is the most bioavailable form of Fe(III) in the environment. In suboxic conditions, aqueous Fe(II) rapidly catalyzes Fh transformation to more stable phases such as lepidocrocite (Lp) and goethite (Gt), but mass transfer pathways have remained unclear. Here, using a selective extractant, we report isolation and quantification of a critical intermediate Fe(III) species involved, one that is more labile than the Fe(III) in Fh, that forms by oxidation of aqueous Fe(II) on the Fh surface. Comparison of time-dependent concentrations of solid-associated Fe(II) and labile Fe(III) against the kinetics of phase transformation showed that the accumulation of labile Fe(III) is constitutively related to Lp/Gt formation in a manner consistent with classical nucleation theory. ⁵⁷Fe isotope tracer experiments confirmed the origin of labile Fe(III) from the oxidation of sorbed Fe(II). A transformation mechanism entailing Lp/Gt product crystallization through olation and oxolation reactions that construct dense ordered networks from labile Fe(III) is implied, the rate of which is greatly accelerated by Fe(II).
Electron transfer capacity of lignin for dissimilatory iron reduction in clay minerals

Yizhi Sheng1, Hailiang Dong1,2, Qiang Zeng2, Jinglong Hu2, Ethan Coffin1, Hongyan Zuo1, Shuisong Ni3, Andre J. Sommer3, Ravi K. Kukkadapu4

1 Department of Geology and Environmental Earth Science, Miami University, OH 45056, USA.
2 State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing 100083, China
3 Department of Chemistry and Biochemistry, Miami University, Oxford, OH 45056, USA
4 Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352, USA

Soil organic matter (SOM) is a large carbon reservoir, which contains more carbon than global vegetation and the atmosphere combined. A small perturbation to this reservoir will have a large impact on the global carbon cycle. Lignin, a class of organic polymers formed within plants and some algae, is one of the most predominant SOM reservoirs, and its polymeric structure makes it resilient to biodegradation. Studies have shown that certain humic substances can serve as both electron shuttle and electron donor for dissimilatory iron reduction, but there is still a knowledge gap for the role of lignin in Fe redox processes in soils and sediments. In order to study whether soil minerals play a significant role in affecting electron transfer capacity of lignin, we selected a clay mineral, Fe-rich smectite (nontronite NAu-2) (0.05-0.2 µm particle size; 5g/L in bicarbonate buffer) and two types of kraft lignin with a distinct solubility (0.25-5.0 g/L), incubating with Shewanella putrefaciens CN32 (~1×10^8 cells/L) under strictly anaerobic condition for ~500 hours. Lactate was dosed in certain experiments to provide additional electron donor/carbon source. Fe(II) concentration in NAu-2 were monitored over time. Aqueous organic chemistry and electron donating capacity were characterized at the end of bioreduction experiments.

The results showed that similar to humic substances, lignin served as both electron shuttle and donor for dissimilatory Fe(III) reduction in clay minerals. Rapid reduction of structural Fe(III) to Fe(II) occurred at the beginning of all experiments with lignin, possibly owing to release of “stored electrons” from the lignin, where some functional groups may be in a reduced state. Subsequently, structural Fe(III) in biotic groups was consistently reduced, where Group I (NAu-2+lignin+lactate+CN32) exhibited the highest rate and extent followed by Group II (NAu-2+lignin+CN32) and Group III (NAu-2+lactate+CN32), highlighting the dual role of lignin as both electron shuttle and electron donor. The electron transfer system activity and electrochemical analysis further supported the electron donating role of lignin. Dissolved organic carbon largely remained unchanged, suggesting that most of the lignin (mainly high molecular weight) was not mineralized to CO₂ and did not adsorb to NAu-2 surface. However, excitation emission matrix (EEM) fluorescence analysis showed that some protein-like and fulvic acid-like compounds decreased after lignin interaction with nontronite and CN32, suggesting that these compounds may have oxidized. Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and Two-dimensional Nuclear Magnetic Resonance (2D-NMR) spectroscopy together revealed the stability of the main lignin structure but variation of certain organic functional groups and components after lignin reaction with NAu-2 and CN32 cells. This finding helps us to better understand the electron transfer capacity of SOM and has significant implications for Fe-C cycle in soils and sediments.
Transverse Electron Exchange Pathways in Nontronite from First Principles

Pauline Simonnin*1, Hailiang Dong2, Anke Neumann3, Kevin M. Rosso1

1Pacific Northwest National Laboratory, Richland, WA, USA; 2Miami University, Oxford, OH, USA; 3Newcastle University, Newcastle, UK.

Iron-bearing clay minerals are important redox-active components of the subsurface and engineered barriers. Their interfacial reactivity plays an essential role in environmental processes such as biogeochemical cycling of various elements and contaminants. A detailed mechanism of Fe(II) surface speciation and interfacial electron transfer (ET) to Fe(III) in the octahedral sheet is still under debate despite its well-established consequence as one of the most effective reductants in anoxic environments. Recent developments have shown that edge-bound Fe(II) adsorption complexes at different surface sites may coexist on different edge facets. It has also been shown that complexes at ferrinol FeO(H) edge sites are the most energetically favorable and ET at these sites is facile and coupled to proton exchange. However, ET from Fe(II) sorbed to the external basal surface to octahedral Fe(III) is predicted to be predominantly thermodynamically uphill. A major enduring uncertainty in experiments is the extent to which Fe(II) can displace interlayer cations through cation exchange and there become a more effective reductant for Fe(III) in the octahedral sheet. Herein, we apply density functional theory (DFT) calculations to provide atomistic insights into the valence-interchange ET energetics and kinetics between Fe(II) in the interlayer site and an Fe(III) in the octahedral sheet, which reveals a lower ET barrier due to desolvation of interlayer Fe(II).

Hypothetical structure model of ideal nontronite with Fe(II) ions occupying the interlayer space.
HANFORD SOIL AND GROUNDWATER: PRODUCTION MISSION OVERVIEW

Brett C. Simpson*, Mark B. Triplett, and Mark D. Freshley

Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99352;

The success of the Manhattan Project of splitting the atom at industrial scale is arguably the most consequential effort undertaken by humans. In addition to creating a new geopolitical order after World War 2, this success resulted in the use of nuclear weapons and nuclear power; the discovery of several new element-isotopes; and opening entirely new domains of physics, chemistry, and engineering. There were three primary areas that supported the production mission. The 300 Area included uranium fuel fabrication facilities and research laboratories that resulted in discharges of process waste containing uranium. The 100 Areas included nine plutonium production reactors and discharges from these reactors led to soil and groundwater contamination from hexavalent chromium and strontium-90. The 200 Area included five chemical separations plants and other facilities that supported the plutonium production. These facilities discharged process liquids directly to the soil which has contaminated large areas of the soil and underlying groundwater. The 200 Area also includes underground storage tanks containing radioactive chemicals resulting from the separation of plutonium. Some of those tanks have leaked causing additional areas of soil and groundwater contamination. A framework that presents which facilities and processes contributed to which type of contamination is explained and how previous notions regarding the behavior of contaminated materials in the environment have changed as surveillance, sampling, analysis, and testing has been conducted over the lifecycle of the Hanford Site. Additionally, parallels between the novelty and uncertainty associated with solving technical, organizational, and operational challenges that the production mission faced, and challenges currently faced by the environmental remediation of complex sites mission will be compared.
A Hanford Perspective on Environmental Remediation: Workshop Overview

Frances N. Smith¹ and Debra S. Barnett¹

¹Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99352

The Hanford Site in south-central Washington State is home to legacy nuclear waste and infrastructure generated from the Manhattan Project of World War II and the Cold War. Starting in the late 1980’s, focus turned from plutonium production to environmental remediation. The complexity and magnitude of the clean-up mission requires partnerships between multiple agencies and stakeholders, technology development and application, fundamental scientific research, and future vision for closure and use of the remediated land. This eight-part workshop captures the industrial roots of the Hanford Site that led to the legacy contamination challenges being addressed today, outlines the policy and parties involved with the clean-up mission, takes a deep-dive into each of the remediation focus areas (River Corridor, Central Plateau, and Tank Farms) while describing technical challenges and examples of solutions for each, and concludes with a discussion of the concept of end states for environmental remediation efforts. The Hanford Site is used as an example of a high-level nuclear waste remediation site with the idea that approaches, technologies, and fundamental research demonstrated here are applicable to other sites around the world.

While this workshop is a tangible outcome of mentoring and presentation development by inter-generational and interdisciplinary teams, it is also part of a greater effort to capture and transfer key institutional knowledge to the next generation of leaders in these technical research spaces at Pacific Northwest National Laboratory (PNNL). When technical missions span decades, it is essential to bring new scientists and engineers up to speed quickly with regards to the context and history of the problem being addressed so that they can contribute their bright and cutting-edge techniques to persistent challenges as efficiently as possible. Furthermore, the retirement of leaders in the field is accompanied by decades lost of knowledge and strategic relationships if efforts are not undertaken to ensure a smooth transfer of knowledge and expertise within and between organizations. By inviting the next generation of leaders to present on these large-scale topics with the support of their mentoring teams, we envision a broader, stronger, and deeper team of experts to steward the research, technology, and solutions needed to address the environmental remediation of the Hanford Site into the future.
Mobility of actinides (+3, +4, and +6) in the presence of dolomite – Effect of EDTA and ionic strength

A. Kirstin Sockwell¹, Frances Zengotita¹, Alexis Vento², Donald T. Reed³, Juliet Swanson³, John Dickson², Yelena Katsenovich², Hilary P. Emerson⁴

¹University of Notre Dame, Notre Dame, IN 46637; ²Applied Research Center, Florida International University, Miami, FL 33174; ³Los Alamos National Laboratory, Carlsbad, NM 88220; ⁴Pacific Northwest National Laboratory, Richland, WA 99354.

Risk assessment models for long-term storage of nuclear waste requires an understanding of the waste as well as the surrounding environment and its potential for interaction with the waste. The Waste Isolation Pilot Plant (WIPP) in Carlsbad, New Mexico was created for subterranean storage of legacy transuranic (TRU) nuclear waste. The location of the site, within the Salado Formation, primarily consists of halite (NaCl) and, consequently, features a high ionic strength environment. A potential release event identified by the WIPP performance assessment is based on the movement of released waste with groundwater through the highly transmissive Culebra Member, which is located above the WIPP. Along with the presence of organic ligands utilized in waste reprocessing (e.g. EDTA), dolomite or intrinsic actinide colloids may provide a mode of transportation for actinides.

This work set out to develop a better understanding of the behavior of actinides in the high salt environment of the WIPP and in the presence of EDTA and other contaminants. We observed an increase in removal of Nd(III) by dolomite in increasing ionic strength systems, potentially due to an increase in dolomite dissolution and secondary coprecipitation processes. Preliminary mineral dissolution studies further support the increased dolomite dissolution in higher ionic strength systems in the presence of co-contaminants like EDTA. Batch sorption studies investigating sorption to dolomite in varying ionic strength systems showed that the presence of EDTA significantly decreased removal of aqueous Nd(III) and Th(IV), while U(VI) remained in solution regardless of the addition of EDTA. Three size separation steps were used to investigate the association of the contaminants with different sized particles potentially as intrinsic actinide colloids or in association with dolomite colloids. An increased association of Nd(III) and Th(IV) with particles <80 nm was observed in the absence of EDTA. The addition of dolomite further increased the association of Nd(III) and Th(IV) with this size fraction. Finally, increasing ionic strength appears to have increased the mobility of the contaminants in the presence and absence of EDTA and dolomite.
NON-CLASSICAL CRYSTAL GROWTH PATHWAY: ORIENTED ATTACHMENTS DIRECT CRYSTAL MORPHOLOGIES AND STRUCTURES

Miao Song¹, Jaewon Lee¹, Jaehun Chun¹, Dongdong Xiao¹, Gang Zhou², Ning Lu³, Elias Nakouzi¹, Dongsheng Li*¹

¹Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, USA; ²Division of Titanium Alloys, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China; ³Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA

In contrast to the classical monomer-by-monomer addition models, crystallization by addition of particles, ranging from multi-ion complexes to fully formed nanocrystals, is now recognized as a common phenomenon. Although experimental observations clearly demonstrated crystallization by particle attachment, especially oriented attachments, many fundamental aspects remain unknown, such as the interplay of solution structure, interfacial forces, and particle motion. Here we use in situ transmission electron microscopy and atomic force microscopy to directly observe and measure the particle motion and interfacial forces, respectively. Integrating theoretical calculations and simulations, we revealed the orientation dependent attachments of particles, interfacial structures, and the factors that affect them, such as temperature, pH, ionic strength, particle shapes, and solvents, etc. In addition, we also demonstrated that strain relaxation at the grain boundaries, induced via oriented attachments, forming twin structures. The specific systems that we investigate are metal (Ag and Au), oxides (TiO₂), and minerals (mica), etc. The work provides a deep understanding of mechanisms of oriented attachments and factors control the process and thus provide a guide to design and fabricate the morphologies and structures, which are closely related with material properties and functions.
Iron (oxyhydr)oxides are highly reactive, environmentally ubiquitous organic matter (OM) sorbents that act as mediators of terrestrial and aqueous OM cycling. However, current understanding of iron (oxyhydr)oxide affinity for OM is limited primarily to abiogenic oxides and temperate systems. Bacteriogenic iron (oxyhydr)oxides (BIOs), common to quiescent waterways and soil redox transitions, possess a high affinity for oxyanions (i.e., arsenate and chromate) and suggests that BIOs may be similarly reactive for OM. Additionally, research investigating permafrost OM has recently intensified due to the unknown effects of increasing global temperatures on one of the largest terrestrial C pools (~1700 Pg C), but little is known concerning the geochemistry of permafrost organomineral associations. Exploring organomineral-driven interactions are critical to environmental OM stability; therefore, we investigated these understudied systems using a combination of batch experiments, scanning transmission X-ray microscopy, X-ray absorption spectroscopy, Fourier transform infrared spectroscopy, and Fourier transform ion cyclotron resonance mass spectrometry. We found BIOs are capable of sorbing leaf litter-extracted DOM and Suwannee River Humic/Fulvic Acid (SRHA/SRFA) and have sorptive preference for distinct organic carbon compound classes at the biomineral interface. For the permafrost system, our results indicate Fe(III), Fe(II), and mixed valence phases associated with OM throughout a Pleistocene permafrost chronosequence (19,000, 27,000, and 36,000 years old). Our findings showcase the pervasive presence of iron-mediated C interactions that occur through diverse OM and soil composition-dependent processes. Predicted OM stability is likely governed by these processes, making research investigating OM stabilization with increasing temperature of paramount importance.
Initial and advanced stages of mineral transformation in alpine and subalpine soils of SE Alaska

Diogo Spinola\textsuperscript{1, 2}, Tom Trainor\textsuperscript{1}, Raquel Portes\textsuperscript{2}, Rebecca Lybrand\textsuperscript{3}, Jennifer Fedenko\textsuperscript{3}, Ashlee Dere\textsuperscript{4}, David D’Amore\textsuperscript{2}

\textsuperscript{1}University of Alaska Fairbanks, Department of Chemistry and Biochemistry, Fairbanks, AK;
\textsuperscript{2}USDA Forest Service, Pacific Northwest Research Station, Juneau, AK;
\textsuperscript{3}Department of Crop and Soil Science, Oregon State University, Corvallis, OR;
\textsuperscript{4}University of Nebraska, Department of Geology, Omaha, NE.

The perhumid climate of the coastal temperate rainforest in SE Alaska favors high rates of mineral weathering and soil formation. The rapid melting of mountain glaciers of the region exposes vast areas of bedrock to chemical weathering and soil formation. However, little is known about the soil mineral transformation in the region. In this study, we evaluated mineral transformation in alpine and subalpine soil profiles sampled near Juneau, AK (Fig. 1). Both soils formed from similar parent material (tonalite) and on ridgetop topographic positions. The alpine pedon formed on sediments that accumulated in cracks on rocks. The soil profile has a 30 cm depth and has slightly weathered A and Bw horizons. The subalpine pedon has > 50 cm depth, contains many rock fragments with a horizon sequence of O, E, Bh, Bhs, and Bs/C horizons. Our results identified a common mineral assembly of primary minerals: biotite, chlorite, quartz, and minor plagioclase in both soils as detected by the XRD analysis of the oriented clay fraction (<2 µm). The secondary assemblage was more heterogeneous between the alpine and subalpine soils, with a clear signal of chemical weathering, mainly on biotite and chlorite. In the alpine soil, the biotite weathered into hydrobiotite with a broader peak in the Bw horizon indicating slightly more advanced weathering. The chlorite peaks remained virtually unaltered. Conversely, the alteration products in the subalpine soil showed a greater degree of weathering. Hydrobiotite was detected in the Bs/C and Bhs horizons, yet showed evidence of transformation to vermiculite in the Bh and E horizons. Chlorite was present in the Bs/C horizon but was transformed to a hydroxyl-interlayered mineral (HIM) in the other horizons. Overall, our preliminary results demonstrated an incipient weathering in the alpine soil, with biotite weathering to hydrobiotite whereas in the subalpine soil the biotite is transforming into hydrobiotite, then to vermiculite, and chlorite to HIM. We suggest the following mineral weathering sequence is taking place: biotite/chlorite -> hydrobiotite-> vermiculite/HIM. Future additional treatments will help to confirm the weathering products of biotite and chlorite. As glaciers retreat and expose primary minerals to weathering, the formation of reactive secondary mineral surfaces will impact overall ecosystem carbon and nutrient dynamics.

Fig1. Alpine and subalpine profile.
**TcO₂ oxidative dissolution by manganite and bixbyite under anaerobic conditions**

Jordan Stanberry, Ilana Szlamkowicz, David Magno, Vasileios Anagnostopoulos

Environmental Radiochemistry Group, Department of Chemistry, University of Central Florida, Orlando FL, 32816

Manganese minerals are prolific thanks to mineral cycling (propagated by microorganisms), which regenerates Mn(III) and Mn(IV) mineral species under aerobic and suboxic environments. They are among the strongest natural oxidizers due to their high redox potential, which allows them to oxidize almost any metal or metalloid reduced species. Manganese oxides have been reported to oxidize Cr(III) to Cr(VI), As(III) to As(V), and U(IV) to U(VI), processes that can either enhance natural attenuation or facilitate contaminant transport.

Tc-99 is a radionuclide is a by-product from uranium fission during nuclear power and nuclear weapons production. The massive expansion of nuclear programs in the 20th century saw a proportional creation of waste products including Tc-99. Nevertheless, improper waste management resulted in the accidental or intentional release of Tc-99 into the environment. The mobility of Tc-99 in the environment is dependent on its oxidation state: Tc(VII) in the form of TcO₄⁻ is highly soluble and mobile in the environment, whereas, Tc(IV) forms are generally insoluble and immobile in the environment. Remediation efforts have utilized this dichotomy by focusing on the reduction of TcO₄⁻ to TcO₂.

In this study, we investigate for the first time the effect of common Mn(III) minerals, such as α-Mn(III)₂O₃ (bixbyite) and γ-Mn(III)OOH (manganite) on TcO₂ stability under anaerobic conditions. We studied the TcO₂ oxidative dissolution at different pH values, and different solid:liquid ratio suspensions and we investigated if the presence of divalent cations, such as Ca²⁺ and Mn²⁺, affected the oxidizing capacity of the Mn-minerals due to sorption on their surface. X-ray powder diffraction (XRD) and Fourier-transform Infrared Spectroscopy (FTIR) were performed on the pre- and post-dissolution γ-MnOOH and α-Mn₂O₃ to determine any changes in the mineral structure due to their redox reaction. We found that despite having the same oxidation state of manganese, these two minerals exhibit very different behavior. Oxidation of TcO₂ by α-Mn₂O₃ is pH dependent (oxidation is significantly higher at pH 6.1 compared to 8.5), increased when the amount of α-Mn₂O₃ increased in the suspension was not affected by Ca²⁺ sorption. On the other hand, γ-MnOOH oxidized TcO₂ at pH 6.1 but not at pH 8.5. Furthermore, the amount of manganite in the suspension did not affect oxidation, which practically remained the same even after increasing the mineral amount 30 times. XRD studies revealed that the post dissolution γ-MnOOH contained new peaks generally found in hausmannite (Mn₃O₄), a Mn(II,III) oxide. The results indicate that both minerals are can be a liability for the long-term stability of TcO₂ at sub-neutral pH values, whereas release of Tc-99 at pH values ~8 are much lower.
Manganese oxides are ubiquitous minerals that have strong oxidizing properties. Their potential to oxidize metals regularly outweighs their relative concentration due to regeneration of Mn(III) and Mn(IV) mineral forms by microorganisms and mineral cycling even under suboxic conditions. Due to their high standard redox potential, manganese oxides are known to oxidize almost all reduced metal and metalloid species in the environment. For example, they have been found to oxidize Cr(III) to Cr(VI), As(III) to As(V) and U(IV) to U(VI) under a wide array of environmental conditions.

Tc-99 is a radionuclide with no natural abundance that was introduced to the environment by human activity. It is produced during the fission of uranium for nuclear power and nuclear weapons productions. During WWII and the Cold War, significant amounts of Tc-99 was produced, and improper waste handling led to accidental or intentional release into the environment. The mobility of Tc-99 is dependent on its oxidation state: Tc(IV) forms being rather immobile and Tc(VII) (e.g. TcO4-) forms being highly mobile. Taking advantage of the redox chemistry of Tc-99, remediation efforts have focused on the reduction of Tc(VII)O4- to Tc(IV)O2. However, the effect of manganese oxides on potential TcO2 oxidation to pertechnetate has not been studied.

In this study, we investigated for the first time the potential of synthetic birnessite (Mn2O4) to oxidize TcO2 under anaerobic conditions at different pH values, with different mineral solid:liquid ratio suspensions, as well as the presence of divalent cations common in groundwater. X-ray powder diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) were performed on the pre- and post-dissolution birnessite to determine any changes in the mineral that resulted from the redox reaction between the two solid phases. We found that TcO2 is substantially oxidized by birnessite at both pH 6.1 and pH 8.5, releasing up to 75% of the initial Tc-99 into the aqueous phase over approximately 10 days. The degree and rate of TcO2 oxidation did not appear to vary by increasing the amount of birnessite in the suspension. While sorption of Ca2+ and Mn2+ did not affect the initial rate of Tc-99 release, it did decrease the maximum release of Tc-99 in the aqueous phase (plateau phase), indicating that calcium and manganese are sorbed on birnessite redox active centers that are play role in the redox reaction between the two solid phases. XRD and FTIR studies revealed that the redox process led to a disruption of the ordered layer stacking in birnessite, but not a significant amount of new mineral phases was detected. The results indicate that birnessite is an environmental liability regarding the remediation of Tc-99 under anoxic conditions. While divalent cations mitigate the oxidation of Tc-99 by birnessite to some degree, substantial oxidation still occurs.
Mineral precipitation is one of the natural processes that significantly affects such actively developing technologies as CO₂ sequestration, oil and gas extraction, hydraulic fracturing, and toxic heavy metals remediation. The most puzzling geochemical questions are related to the ability to predict the evolution of rock matrix properties such as porosity and permeability during exposure to reactive flow that results in mineral precipitation on the surface of pores. It has been a great challenge for scientific community to capture and distinguish the most important factors that govern mineral formation in porous materials and couple physical and chemical processes happening on length and time scales that can differ from each other by several orders of magnitude. Here, we will present results on combining X-ray tomography experiments with fluid dynamics simulations that allows us to uncover coupling between reactant transport and local mineral growth in porous matrix. In this study we used the supersaturated solutions containing barium and sulfate ions that form a sparingly soluble salt – barite. We have been able to show that quantitative analysis of X-ray tomography images becomes possible, such as, the total amount of precipitated mineral, cluster analysis, etc. The results confirm a strong correlation between transport of the reactant and amount of precipitated mineral. Additionally, strontium ions were used to model impurity presence in solution. We observed that the addition of impurity (strontium) decreased the growth rate and increased the nucleation rate during precipitation process, indicating that the impurity has opposite effects on the crystal nucleation and crystal growth processes.
INTERFACIAL SCATTERING FROM SMALL SURFACES: ADAPTING MINERAL-FLUID STRUCTURE METHODS FOR MICROCRYSTALLINE MATERIALS

Joanne E. Stubbs

The University of Chicago, Center for Advanced Radiation Sources, Chicago IL 60439

CTR has historically been limited to materials that occur as relatively large, perfect crystals, limiting the list of minerals measured to date to < 20. Peter Eng and I are developing hardware and software tools to make it possible to measure atomic-scale surface structures from smaller crystals. At the moment we're down to around 100 μm, and we hope to push down into the tens of microns size range in the next several years. With synchrotron upgrades promising more coherent x-ray flux, there may be opportunities in the future to use coherent scattering techniques to get at interfacial structures from even smaller crystals, but as of now this idea is somewhat speculative.
AUTOMATED ON-LINE ACTIVE CLAY ANALYZER IN MINERAL SLURRIES

Ruijun Sun* and Lesley McGilp

Saskatchewan Research Council, 125-15 Innovation Blvd., Saskatoon, Canada, SK S7N 2X8

Active clays are swelling clays that do not agglomerate, settle or consolidate easily when mixed with water, it can cause significant challenges for mining operators by tying large volumes of water and require extra resources for treatment. Their presence in slurries complicates solids-water separation, rheological, pipe flow and solids settling behaviors, causing difficulties in many mineral processes, such as extraction, flotation, flocculation, thickening, hydrotransportation and consolidation. An automated and on-line active clay analyzer system has been developed to identify and quantify active clay in mineral slurries by measuring the spectra absorbance of a filtrate using methylene blue as an indicator. Controlled volume of slurry sample can be automatically withdrawn from a process and conditioned in a mixing chamber. Controlled volume of methylene blue (MB) solution is injected in increments into the sample mixture. A filtrate is automatically extracted and analyzed by a spectrophotometer. The spectra absorbance is automatically correlated the cumulative volume of MB and determine the Methylene Blue Index (MBI), as well as clay activity and quantity of active clays in the mineral sample. The automated and on-line active clay analyzer can be used in mining processes including potash, uranium, kimberlite, oil sands and any minerals containing clays or active clays to achieve better process control, save water and cost for tailings management, and reduce tailings volume and footprint for the mining industry.
ROLE OF INTERFACIAL STRUCTURE AND DYNAMICS IN CRYSTALLIZATION PATHWAY SELECTION

Maria L. Sushko*, Guomin Zhu, Lili Liu, Elias Nakouzi, Kevin M. Rosso, James J. De Yoreo

Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352

During non-classical mineral growth via assembly of primary nuclei, nucleation and assembly are assumed to be distinct processes: nanoparticles nucleate randomly and aggregate to form extended structures through Brownian motion in the presence of long-range attractive interactions. Here we investigate the relationship between these two processes and review recent developments in the understanding of the microscopic details of interfacial local environments that redirect growth towards non-classical processes. In several mineral systems our results reveal an inexorable link between nucleation and assembly with nuclei forming almost exclusively within a ~ 1 nm interfacial region of existing particles. The new particles immediately close the gap either through a diffusive jump or via growth of a neck between the seed and new particle, generating aggregates exhibiting features commonly attributed to oriented attachment of independently nucleated particles. We demonstrate that crystallization pathway selection can be manipulated by modifying solution pH and precursor concentration through shifting the balance of chemical potentials of solution species and discuss the nature of interfacial forces driving particle attachment via neck formation or reorientation and diffusive jump in a lattice matching configuration.
SMECTITE FORMATION UNDER ACIDIC CONDITIONS ON EARLY MARS: AN EXPERIMENTAL FLOW-THROUGH ASSESSMENT

Brad Sutter¹,², Silas J. Ralston¹,², Tanya Peretyazhko¹,², and Douglas W. Ming²

¹Jacobs, Houston, TX 77058; ²NASA, Johnson Space Center, Houston, TX 77058.

Smectite on Mars has been detected by orbital and landed instrumentation; however, the detection of associated carbonate deposits is limited. Early Mars may have experienced mildly acidic conditions from volcanically derived sulfuric acid aerosols that allowed smectite formation but prevented widespread carbonate formation. Formation of smectites together with sulfates has been demonstrated in basaltic glass alteration experiments at pH 3 to 4 (H₂SO₄) at 200°C in a closed hydrologic system (batch reactor, 14 days) (Peretyazhko et al., 2018 GCA).

The objective of this work was to evaluate smectite formation from basaltic glass under alkaline to acidic conditions in an open hydrologic system (flow-through reactor, 7 d, 190°C, 17 bar). Previous experiments conducted at 0.25 ml min⁻¹ flow-rate demonstrated deionized water (pH 9.5) solutions yielded serpentine and hematite while pH 3 (H₂SO₄) solutions with 0, 10 and 50 mM MgCl₂ formed boehmite and hematite. Low Si concentrations (< 1mM) allowed serpentine formation (pH 9.5) but inhibited smectite formation between pH 3 and pH 9.5 (Sutter et al., 2018 CMS annual meeting). Lower flow rates (0.01 ml min⁻¹) were subsequently utilized that permitted smectite and kaolinite formation at pH 3 (Fig. 1a) while only serpentine formed between pH 6.5 and 6.8 (Fig. 1b). Higher Si concentrations (~9 mM Si) were achieved in the pH 3 experiments that permitted smectite and kaolinite formation. While lower Si concentrations (< 2.5 mM) allowed for only serpentine formation in the higher pH experiments. The higher Si concentrations in the pH 3 experiments were caused by the much lower flow rate (0.01 ml min⁻¹) that limited removal of Si from the reactor. The previous flow-through experiments utilized a higher 0.25 ml min⁻¹ flow rate that resulted in Si concentrations too low to permit smectite formation. These results demonstrate low leaching rates may be required to permit Si concentrations high enough to allow for smectite formation under acidic conditions on Mars.

However, the presence of kaolinite with smectite in the 7 day as well as 3 day experiments (data not shown) suggest that these phases formed simultaneously as opposed to smectite weathering into kaolinite. Whether kaolinite and smectite are interstratified is unknown and efforts will be taken to assess the nature of these kaolinite-smectite samples. Interstratified kaolinite-smectite have been proposed for Mars but are not necessarily widespread. The formation of smectite under low leaching conditions at low pHs opens the possibility that early Mars geochemical conditions could have been mildly acidic instead of neutral/alkaline with low water to rock ratios and/or low leaching rates.
Use of Spectral Induced Polarization to Characterize Clay Redox Reactivity

Jim E. Szecsody\(^1\)*, Hilary P. Emerson\(^1\), Adam R. Mangel\(^1\), and Jon N Thomle\(^1\)

\(^1\)Pacific Northwest National Laboratory, PO Box 999, Richland, WA 99352

Abiotic and biotic engineered reducing environments are frequently used for contaminant remediation in the subsurface environment, but prediction of long-term reactivity requires characterization of the time-dependent spatial distribution of reactive iron surface phases and microbial biomass in cores, which is challenging at field scale. As recent laboratory studies have shown, multifrequency complex electrical impedance measurements, i.e. spectral induced polarization (SIP), can be useful at identifying some surface redox changes. Results show that there are different frequency-dependent polarization responses for adsorbed ferrous iron, iron sulfides, and zero valent iron. Although clays are typically < 10% of aquifer sediments (although high in fine-grained layers), clays can significantly contribute to the overall redox reactivity of subsurface sediments due to adsorbed ferrous iron, biomass on clays, and structural ferrous iron in some 2:1 clays. In this study, redox changes in clay and sediments with different clay content that are untreated and chemically reduced are characterized by: a) measurement of iron surface phases, and b) reduction rate of chromate, nitrate, and RDX. The SIP response of these sediments with different redox states are also measured to compare with geochemical redox changes. A relative increase in the SIP phase as redox reactions occur indicates the surface has a higher capacitance, or ability to store more electrons. Chemical reduction of a Na-saturated montmorillonite (SWy-1) had a small increase in structural iron in the clay and a small increase in phase response at low frequency (0.001 to 0.1 Hz). Chemical reduction of two high clay content sediments (33 and 44% clay) that resulted in a large increase in adsorbed ferrous iron showed a large increase in phase at low frequency. The phase response may be caused by adsorption of ferrous iron primarily to clays. In contrast, chemical reduction of two low clay content sediments (3.0 and 4.2% clay) resulted in a moderate increase in adsorbed ferrous iron and showed a moderate increase in phase at mid frequency (0.1 to 10 Hz). In a separate experiment, additions of ferrous iron to one low clay content sediment showed a similar increase in phase at mid frequency. In this case, ferrous iron may be adsorbing to clays and Fe oxides. Overall, correlations between iron surface phases and the frequency-specific SIP response may be useful for non-intrusively monitoring redox reactions at field scale.
Manganese minerals are common minerals found in nature. They exhibit strong oxidizing potential and they have the ability to oxidize reduced forms of metals and metalloids, thanks to their high standard redox potential. The oxidation of As(III) to As(V), U(IV) to U(VI), and Cr(III) to Cr(VI) under a wide range of environmental conditions have been reported. This process can have both beneficial (e.g. oxidation of arsenic) and detrimental effects (e.g. uranium and chromium) for the environment. Their oxidation potential is disproportionate to their concentration: small amounts of manganese oxides are able to affect significantly redox properties of dissolved contaminants. Specifically, Mn(III) oxy-hydroxides, such as manganite, are being constantly regenerated in nature thanks to microbial activity mineral cycling.

Iodine is encountered in natural waters as iodide (I⁻), which is highly mobile and shows little to no sorption on natural substrates, whereas iodate (IO₃⁻) can be retained by mineral phases. In this study, we investigate the potential of a common Mn(III) mineral, γ-MnOOH (manganite) to oxidize iodide to iodate and the environmental conditions that affect this redox reaction. For comparison purposes, we conduct the same experiments with α-Mn₂O₃ (bixbyite), which despite being less common in nature, it provides useful information due to the different structure between both Mn(III) minerals (manganite is tunneled and bixbyite is layered).
ATOMISTIC SIMULATIONS OF BRUCITE COMPRESSIBILITY OVER WIDE RANGES OF PRESSURE AND TEMPERATURE

Evgeny V. Tararushkin*1,2 and Andrey G. Kalinichev1,3

1National Research University Higher School of Economics, Moscow, Russian Federation.
2Russian University of Transport, Moscow, Russian Federation
3Laboratoire SUBATECH (UMR 6457 - IMT-Atlantique, Université de Nantes, CNRS), France

Brucite, Mg(OH)2, has a hexagonal layered crystal structure that is held together by hydrogen bonding between the hydroxyl groups of the opposing layers. The behavior of brucite in a wide range of temperatures and pressures is of great interest for fundamental geochemistry and geophysics in order to understand mineral equilibria and water balance in the subduction zones of the upper mantle, because Mg(OH)6 units constitute an important part of layered dense magnesium hydrous silicates, DMHS, (e.g., Wang et al., 2004).

The ClayFF force field (Cygan et al., 2004) has been originally developed for atomistic computer simulations of clays and other layered minerals and their hydrated interfaces. The crystallographic parameters of brucite at 25°C and 1 bar were used, among several others, to develop the original ClayFF parametrization. Here we are using the new recent modification of the force field, ClayFF-MOH, (Pouvreau et al., 2017), which can more accurately account for the bending of Mg–O–H angles in the brucite structure, to test the applicability of this model over very wide ranges of temperature and pressure well beyond the range of its original implementation (up to 400°C and 150 kbar).

The pressure and temperature dependencies of brucite crystallographic parameters, the compressibility of the crystal lattice, the coefficients of thermal expansion, and the vibrational spectra are calculated in a series of classical molecular dynamics simulations using the ClayFF-MOH model and compared with a diverse set of available experimental data, including X-ray diffractometry, neutron scattering, IR and Raman spectroscopy. The results demonstrate that ClayFF-MOH, as simple and approximate as is, can be quite accurate in predicting mineral properties at subduction zone conditions, which greatly expands the area of its applicability.

The research was conducted within the framework of the HSE University Basic Research Program. The calculations were performed on the supercomputer of NRU HSE.

References


INTERACTION OF AQUEOUS SALT SOLUTIONS WITH THE SURFACE OF ETTRINGITE: ATOMISTIC SIMULATION USING THE MODIFIED ClayFF FORCE FIELD

Evgeny V. Tararushkin*1,2, Vasily V. Pisarev1, and Andrey G. Kalinichev1,3

1National Research University Higher School of Economics, Moscow, Russian Federation.
2Russian University of Transport, Moscow, Russian Federation
3Laboratoire SUBATECH (UMR 6457 - IMT-Atlantique, Université de Nantes, CNRS), France

Ettringite, (Ca₆[Al(OH)₆]₂[SO₄]₃·nH₂O, n = 24-27), which has a columnar crystal structure formed by stacked aluminum hydroxide and calcium hydroxide polyhedra. The hydroxide columns are held together by a network of hydrogen bonds formed by H₂O molecules and sulphate ions that occupy the intercolumnar space of the crystal. Ettringite is one of the common phases of cement and plays an important role in cement chemistry as the primary cause of sulfate corrosion in Portland cement. The formation of ettringite is accompanied by volume expansion and can lead to cracking and mechanical damage to concrete. Due to these important consequences of ettringite formation and evolution for the concrete durability, there is a need for a detailed understanding of these processes on the fundamental molecular scale.

Molecular dynamics computer simulations have already been applied earlier to model the crystal structure of ettringite and its interfaces with aqueous salt solutions. Here we are using the new recent modification of the ClayFF force field (Pouvreau et al., 2017) which allows for much more accurate modeling of the edges of mineral particles and their hydrated interfaces by explicitly accounting for the bending of M−O−H angles of the metal hydroxides (Al−O−H and Ca−O−H, in our case). The structure and dynamics of bulk ettringite crystal and its interfaces with NaCl and Na₂SO₄ aqueous solutions are quantitatively evaluated here for the new modified version of the force field, ClayFF-MOH, and compared with the results obtained with the old version, ClayFF-orig. Atomic density profiles for solution species at the interface, atomic distributions at the surface of the crystal, atom-atom radial distribution functions for the intercolumnar and interfacial aqueous species, and the interfacial diffusional mobility of the species were calculated and compared. The results clearly demonstrate the importance of the explicit inclusion of M−O−H angular bending terms for accurate modeling of the mineral systems containing structural and interfacial hydroxide groups. The simulation results showed that for the application of the new more accurate ClayFF-MOH force field leads to the formation of a stronger hydrogen bonding network structure in the intercolumnar space of the ettringite crystal and at its surface, resulting in a stronger immobilization of the water molecules involved, as well as the ions. The ionic adsorption at the ettringite surface is also generally stronger than in the previous model.

The research was conducted within the framework of the HSE University Basic Research Program. The calculations were performed on the supercomputer of NRU HSE.

References
RIVER CORRIDOR GROUNDWATER: PNNL’S CONTRIBUTIONS TO ADDRESS REMEDIATION CHALLENGES

Jonathan Thomle\(^\text{*1}\), Ryan Ekre\(^\text{1}\), Rob Mackley\(^\text{1}\), and Mike Truex\(^\text{1}\)

\(^\text{1}\)Pacific Northwest National Laboratory, Richland, WA 99354
\(^\text{*}\)Presenters

Former activities at the Hanford Site have contaminated groundwater in various locations along the Columbia River Corridor. Characterization and remediation efforts have been addressing contaminant source areas and contaminated groundwater. Remediation has a high priority due to the proximity of contaminants to the Columbia River. The nature of these sources, the contaminants, and the subsurface hydrogeologic properties affect the type of remedies that are most appropriate. To address some of the characterization and remediation challenges, Hanford site contractors have teamed with PNNL to better understand the factors controlling sources and plumes, to adapt remediation technologies to the subsurface hydrogeologic setting of the River Corridor and minimize impact of contaminants on the Columbia River. This presentation will discuss examples of technical capabilities developed at PNNL that are being applied in coordination with the Site Contractor to improve the design, optimization, and performance monitoring of groundwater remediation activities, which will ultimately lead to more efficient cleanup and closure along the River Corridor.
Humid soils show a strong correlation between the abundance of short-range-ordered (SRO) iron and aluminum and organic carbon abundance. This likely stems in part from the association of organic matter and these metals in co-precipitates that readily form in these soils during the oxidation of ferrous iron. Using a variety of experimental setups, our lab has been examining the incipient formation of Fe-C co-precipitates via this oxidation mechanism and assessing the stability and the bioavailability of the organic C under oxic and anoxic conditions. Our experiments include both synthesized ferrihydrite(Fh)-based co-precipitates, as well as isotopically-labeled (57Fe and 13C) co-precipitates formed in soil slurries. Our general approach is to oxidize ferrous Fe (labeled if necessary) in the presence of DOC (labeled if necessary) and then examine the persistence of the co-precipitates after subjecting them to microbial incubations. From an overall net C balance, we find that the oxidative formation of Fe-C co-precipitates only conferred net protection to newly added organic matter and only under strict oxic conditions, whereas in treatments without added DOC or that were exposed to transient anoxia, the addition of iron stimulated net organic matter decomposition. In addition, to explore the influence of mineral transformation, we reacted some Fh—based co-precipitates with Fe(II). We find that the anoxic reaction with Fe(II) generated Fe-C co-precipitates that were capable of retaining more C during an aerobic incubation than the non-Fe(II) reacted controls. Collectively, these findings suggest iron redox dynamics will likely tend to enhance overall net organic matter decomposition in soils, but may also help generate a smaller portion of MAOM that is more persistent. These studies have specifically focused on localized iron dynamics and biogeochemical coupling with organic matter by using well-mixed systems. Spatial heterogeneity and soil structural features have yet to be evaluated and likely the generation of composite MAOM structures composed of SRO-Fe, crystalline-Fe, Al, and clays is a critical step in understanding OM persistence in soils.
PARTIALLY CHLORITIZED SMECTITES: ANALOGUES FOR SMECTITE IN GALE CRATER, MARS

V. M. Tu1, E. B. Rampe2, R. V. Morris2, S. E. Perry3, J. Clark4

1Jacobs JETS Contract, NASA JSC Houston, TX 77058 (valerie.m.tu@nasa.gov), 2NASA JSC, Houston, TX 77058, 3Scripps Institution of Oceanography, La Jolla, CA 92037.

Characterizing the structure and composition of phyllosilicates is important for interpreting the aqueous history of Mars and identifying potential habitable environments. Smectite has been detected at Gale Crater, Mars, via orbital observations and in-situ measurements [1,2] in abundances up to ~30 wt. % of bulk rock [3]. The John Klein (JK) and Cumberland (CB) mudstone samples were analyzed by the Chemistry and Mineralogy (CheMin) X-ray diffractometer and Sample Analysis at Mars (SAM) evolved gas analysis (EGA) instruments onboard the Mars Science Laboratory (MSL) Curiosity rover in order to distinguish clay mineralogy. JK had a collapsed 2:1 smectite with a d-spacing of 10Å, whereas CB smectite did not fully collapse and had a d-spacing of ~13.2Å [2]. It has been suggested that partial chloritization or ‘pillaring’ could be responsible for the expanded CB smectite because pillaring inhibits the collapse of smectites down to 10Å, even under the desiccating conditions on the martian surface [3,4].

Nontronite (NAu-2), montmorillonite (SWy-1), and Fe-saponite (from Griffith Park, CA) samples were selected for Mars analogue pillaring experiments. Smectite samples were Mg- and Al-pillared at various OH:Mg and OH:Al molar ratios, and Mg- and Al-saturations were performed on all three smectites. Mg and Al were selected based on evidence for Mg-bearing fluids in Gale Crater [4] and common partial chloritization reactions in terrestrial soils [e.g., 5]. Pillared clays were analyzed on a PANalytical X’Pert Pro MPD instrument under ambient conditions and under dry N2(g) on a non-ambient Anton Paar stage. Visible-near-infrared spectra were collected on desiccated (200°C in dry N2(g)) Mg(OH)2-pillared samples, and are currently being collected on Al(OH)3-pillared samples. EGA was performed on Mg-pillared samples, previously reported by [4], and EGA is currently being performed on Al-pillared smectites.

Al(OH)3 pillaring causes the partial collapse of smectite structures. When compared to Mg(OH)2 pillaring, Al(OH)3 pillaring generally yields a larger d-spacing, and the basal peak of Mg(OH)2-pillared ferro-saponite or minimally pillared montmorillonite (as previously reported by [4]) is most similar to the expanded smectite present at CB (13.3Å). EGA data of ferro-saponite were previously reported to be inconsistent with CB or JK [4], however additional EGA data are currently being collected and compared to CB and JK. Our laboratory results suggest that early diagenetic reactions causing the partial chloritization of smectite could explain the expanded smectite in the Cumberland sample in Gale crater.

Probing Cation Speciation at Mica-Aqueous Interface Using Vibrational Sum Frequency Generation Spectroscopy

Aashish Tuladhar¹, Marcel D Baer¹, Benjamin A. Legg¹, Narendra M. Adhikari¹, Zheming Wang¹, Christopher Mundy¹, Hong-fei Wang², and James J. De Yoreo¹

¹ Physical & Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99352; ² Department of Chemistry, Fudan University, Shanghai 200433, China

Explicit understanding of the electric double layer (EDL) is of general interest to broad communities of researchers where solid-electrolyte interfaces are relevant (e.g., electrochemistry, environmental chemistry, batteries, heterogeneous catalysis, etc.). Particularly, ion speciation within the Stern layer and its effect on the interfacial environment is of critical importance but yet remains poorly understood largely because the chemical and physical properties within the first nanometer from the surface is extremely sensitive to surface charge and topography, surface-solvent-ion correlations, and interfacial hydrogen bonding environments. Here we exploit the site-specific chemical signature of water at the muscovite-electrolyte interface using a novel azimuthally-resolved vibrational sum frequency generation spectroscopy to address the issue of cation speciation at this model surface. We find that H/D exchange at the muscovite-D₂O interface gives rise to a vibrational peak (~2680 cm⁻¹) originating exclusively from deuterated hydroxyls located below the center of the ditrigonal cavities of the siloxane surface. Monovalent cation salts (NaCl, KCl, CsCl) are observed to attenuate the 2680 cm⁻¹ peak by 70-80%, while divalent and trivalent cation chlorides (ZnCl₂, SrCl₂, AlCl₃) only attenuate it by ~20%. This suggest that the monovalent cations preferentially adsorb in or around the center of the ditrigonal cavity while the larger valence cations prefer to adsorb away from this cavity. Furthermore, we are able to approximate cation affinity towards mica as we find direct correlation between the changes in the water signature and intrinsic cation adsorption free energy.
From Atoms to Aggregates: Large-Scale Molecular Dynamics Simulation of the Dehydration of a Suspension of Smectite Clay Nanoparticles

Thomas R. Underwood*1, and Ian C. Bourg*1

1 Civil and Environmental Engineering, Princeton University, NJ, 08544
Correspondence: thomas.underwood@princeton.edu, and bourg@princeton.edu

Fine-grained sediments and sedimentary rocks play important roles in a variety of modern energy technologies from petroleum geology to geological carbon sequestration and radioactive waste management. However, despite their utility and ubiquity, many of their properties remain poorly understood. In particular, the ability to predict the permeability and mechanics of these media remains a persistent fundamental challenge in the geosciences.

In the present work, we show how large-scale classical molecular dynamics (MD) simulations can help interpret the properties of fine-grained sedimentary material. All-atom simulations containing 30 discrete clay particles are utilized to understand the evolution of a clay nanoparticle suspension during its progressive dehydration. Microstructural (pore size distribution, tortuosity, anisotropy), thermodynamic (enthalpy and free energy of hydration, anion exclusion), mechanical (total suction), and transport properties (diffusion coefficient tensors of water and sodium) are calculated and compared to the experiment.

The presented results provide new insight into the coupled chemistry, mechanics, and transport properties of disordered nanoparticle assemblages and shed light upon the important role of water films in controlling these properties.
Investigation of the nature of mineral-organic associations in an alkaline soil from WA by synchrotron x-ray methods

Tamas Varga¹, Alice Dohnalkova¹, Libor Kovarik¹, Matthew A. Marcus², Swarup China¹, Anil Krishna Battu¹ Olga Antipova², Ravi Kukkadapu¹

¹Environmental Molecular Sciences Laboratory, Earth and Biological Sciences Directorate, Pacific Northwest National Laboratory Richland, WA 99352

²Advanced Photon Source, Argonne National Laboratory, Lemont, IL 60439

Micro- and nanoscale characterization of the chemical state of both metal ions (Ca, Fe, etc.) from soil minerals and C from soil organic matter (SOM) are crucial for understanding SOM stabilization mechanisms as well as soil nutrient dynamics. In order to probe soil mineral – soil organic matter (SOM) interactions in an alkaline soil from Prosser, WA, characterization of the soil at the Environmental Molecular Sciences Laboratory (EMSL) has been complemented by microscale investigation of soil morphology and mineralogy by synchrotron x-ray fluorescence microtomography of soil aggregates, and nanoscale study of mineral-SOM assemblages with scanning transmission x-ray microscopy (STXM) combined with x-ray absorption near edge structure (XANES). Ca mineral–organic associations were found to be critical in SOM stabilization/degradation in this alkaline soil. Details of mineralogy, speciation, and the nature of Ca-organic matter bridging are presented.
The phyllosilicate minerals of meteorites: Extraterrestrial clays in terrestrial laboratories

Michael A. Velbel¹,²

¹Michigan State University, Department of Earth and Environmental Sciences, East Lansing, MI 48824-1115, USA; ²National Museum of Natural History, Department of Mineral Sciences, Division of Meteorites, Smithsonian Institution, Washington, DC 20560-0119, USA.

Meteorites are naturally delivered solar-system samples from asteroids, possibly comets, and larger differentiated rocky planets and moons. They preserve in their chemical compositions, minerals, and textures direct evidence of the processes by which our solar system’s planets and small bodies originated, were modified, and evolved to their present state. Stones or stony meteorites consist mainly of silicate minerals and are subdivided into chondrites and achondrites.

Among achondrites, only nakhlites (clinopyroxenite meteorites from Mars; ~20 presently known) contain phyllosilicate-like materials (~1 vol %). “Iddingsite” in nakhlites resembles its terrestrial counterpart (a smectite-hydroxide assemblage) in composition and in being associated exclusively with olivine. Structural data are sparse from the dominantly amorphous material in nakhlites, and most occurrences of such materials would be more accurately described, on compositional and textural evidence, as clay mineraloids. Transmission electron microscope selected-area electron diffraction data from “iddingsite” in some nakhlites reveal \( d(001) \) spacings consistent with collapsed smectite-group clay minerals and, in a few, serpentine-group minerals.

The two groups of carbonaceous chondrites with the greatest abundances of hydrous minerals (phylllosilicates) are the rare CI (Ivuna) and the more abundant CM (Mighei) groups. CI chondrites contain 68–84 vol % intergrown or mixed-layer serpentine/smectite (saponite). Phyllosilicates in CM chondrites (55–88 vol %) are mainly serpentine-group minerals – \((\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4\). Composition and oxidation state vary with the extent of aqueous alteration. Some phyllosilicates in CR (Renazzo) and CM chondrites formed from amorphous precursors. Inverse modal abundances of olivine and phyllosilicate suggest that at least some of the phyllosilicate formed by aqueous alteration of olivine. Phyllosilicates in CM chondrites also occur locally as partial and complete pseudomorphs after anhydrous silicates (olivine, pyroxene). Their microscopic textures demonstrate unequivocally that the hydrous (phylllosilicate) phase formed by a hydration reaction of water with primary anhydrous silicates. The composition of serpentine after olivine is independent of the composition of the olivine being replaced.

In nakhlites, and in CI and CM chondrites, the textural and compositional relationships between the phyllosilicates and the primary silicates from which they formed have implications for inferring the evolution of solution chemistry during the aqueous alteration. Iddingsite formed by aqueous alteration long after the igneous crystallization of the host nakhlites, likely during multiple episodes rather than occurring as a single discrete datable aqueous alteration event. The predominantly amorphous material of nakhlite iddingsite veins is presently understood to have formed by impact-induced hydrothermal flow upward through the vertical arrangement of nakhlites in their source igneous body on Mars. Thermal metamorphism (including dehydroxylation) after aqueous alteration affected phyllosilicates in some CI and CM chondrites.
Influence of layer charge on the hydration properties of synthetic Na-saturated smectites

Doriana Vinci1,2, Bruno Lanson2,*, Martine Lanson2, Valérie Magnin2, Nathaniel Findling2, Baptiste Dazas3, and Eric Ferrage3

1DiSTeGeo, Univ. Bari, I-70121 Bari, Italy; 2ISTerre, Univ. Grenoble Alpes – CNRS, F-38000 Grenoble, France; 3IC2MP-HydrASA, Univ. Poitiers – CNRS, F-86022 Poitiers, France

Smectite hydration controls dynamical properties of interlayer cations and thus the fate of H2O and pollutants in surficial systems where smectite-based materials (bentonites) often represent a major component of engineered/geological barrier. Smectite crystal chemistry rules their hydration. In particular, Ferrage et al. (2010) and Dazas et al. (2015) described the influence of parameters such as the amount of layer charge deficit on the hydration of tetrahedrally charged trioctahedral smectites (saponites). To complement these studies, the present work (Vinci et al., 2020) investigates the influence of the location of layer charge deficit on smectite hydration. A set of octahedrally charged trioctahedral smectites (hectorites), with a common structural formula inter[Nax, n H2O]oct[Mg6.0-xLix]tet[Si8.0]O20(OH)4 and a layer charge (x) varying from 0.8 to 1.6, was synthesized. Interlayer H2O contents were measured as a function of relative humidity (RH) from H2O vapor (de)sorption isotherms. Relative proportions of the different smectite hydrates and the distribution of interlayer species were determined from X-ray diffraction profile modeling as a function of RH. Finally, Monte Carlo simulations were performed in the grand canonical ensemble to gain further insights into the distribution of H2O molecules and charge-compensating cations within interlayers. Comparison of the results obtained for octahedrally and tetrahedrally charged smectites with contrasting layer charge allowed drawing conclusions: 1) the total amount of interlayer H2O is essentially independent of layer charge amount and location; 2) the evolution of layer-to-layer distance with the amount of layer charge differs for saponite and hectorite as the result of contrasting electrostatic interactions between the 2:1 layer and interlayer cations; 3) contrary to saponite, the RH stability domains for the different hydrates in hectorite are not modified by the amount of layer charge.

INFLUENCES OF ACID TREATMENT ON PROPPANT BEHAVIOR IN FRACTURED SHALES RESERVOIRS: INSIGHTS FROM IN-SITU SYNCHROTRON X-RAY MICRO-IMAGING

Marco Voltolini*1, Timothy Kneafsey1, Seiji Nakagawa1, Sharon Broglin1 and Adam Jew2

1Lawrence Berkeley National Laboratory. 1 Cyclotron Rd, Berkeley, CA 94720; 2SLAC National Accelerator Laboratory. 2575 Sand Hill Rd, Menlo Park, CA 94025

The acid spearhead stage in hydraulic fracturing is a treatment where acid is flown through the newly fractured shale to dissolve debris that might induce clogging along the fracture flowpaths, impacting recovery. This flow of acid fluid can also have an impact on the shale itself, e.g. triggering the fast dissolution of carbonates. This potential development of a mechanically weakened layer might have an impact in the proppant behavior, and consequently on the evolution of the fracture and on production.

The Hydraulic Fracturing Field Test Site (HFTS) project features an active site in the Permian Basin with the Wolfcamp Formation as the source rock. Samples of Wolfcamp Shale drilled from the actual site have been used in our study. We induced closure (by differential stress increase) of a fracture filled with a quartz proppant monolayer on two samples: with and without acid spearhead treatment. 3D images were collected during this process. Another acid-weathered sample was analyzed using a novel “combined 4D imaging + indentation test” approach to test the micro-mechanical response of the sample, including the weathered layer. These experiments have been carried out following the acid injection procedure (fluid chemistry, interaction time) and the production water used in the actual field, to provide a more realistic scenario. The information collected allowed evaluating how the generation of the weathered layer affects fracture conductivity in function of stress, and which processes are linked to the conductivity changes. The imaging + indentation test provides fundamental information about the mechanical behavior expected at the proppant-shale contacts, e.g. highlighting a more ductile or brittle behavior. In addiction to getting the full compliance curve, this approach allows to map the local deformation of the sample during the loading, thus highlighting the generation of fractures, shear bands, and deformation structures in general.
PROPAGATION OF A MISCONCEPTION IN MAINSTREAM
SCIENTIFIC LITERATURE: A FAILURE OF PEER REVIEW

J. M. Wampler

Georgia State University, Department of Geosciences, Atlanta, GA 30302

Batch adsorption experiments typically are done with a constant mass of adsorbent and a constant volume of liquid, while wide variation in the initial concentration of the adsorbate allows for the widely varying values of the quantities needed to determine a useful adsorption isotherm. These quantities are the sorbate aqueous concentration, $c_e$, and the specific amount adsorbed, $q_e$ (amount sorbed per unit mass of adsorbent), at equilibrium. Ideally, an isotherm is independent of the mass concentration of the adsorbent—if more adsorbent were used, more adsorbate would be taken up, but $c_e$ and $q_e$ would both be smaller and their values would still be on the isotherm.

In published research on practical applications of adsorption, such as study of dye adsorption for textile-wastewater treatment, it has become common to include results of batch experiments done with different “adsorbent doses,” because such results can be useful in choosing the optimum amount of adsorbent to use in a practical application. When the amount of adsorbent varies but liquid volume and initial adsorbate concentration are constant in a set of batch sorption experiments, no explanation is needed for decrease in $q_e$ as the amount of adsorbent increases. Nevertheless, a concept of overlapping adsorption sites owing to aggregation of adsorbent particles has been offered as an explanation of decrease in $q_e$ with increasing “adsorbent dose” in dozens of articles published in the past fifteen years. Citations in some of these articles lead back to original publication of the concept in 2003. Most of the articles in which the concept has been offered, apparently without critical thought about the need for the concept, are in journals published by leading scientific publishers, and some of these journals have high impact factors.

The seriousness of the repetition of the gratuitous explanation is not in the physical nature of the concept used for explanation. It is reasonable that aggregation of particles could cause some adsorption sites to be unavailable. The seriousness is in the failure of authors and peer reviewers to think critically about the need for such an explanation. The misconception that has been propagating is not that adsorption sites may overlap; it is that some mechanistic explanation is needed to explain a decrease in $q_e$ with increasing “adsorbent dose.” Mainstream publishers should find a way to ensure that peer reviewers have the time and the incentive needed for critical consideration of the concepts presented in a manuscript.
Clay minerals are integral to many natural and engineered phenomena at the interface of geology and life. Accurate microstructural models of clay minerals are needed to understand the properties of clay-rich media, but have remained elusive due to the nanoscale dimensions of clay layers. Here, we show that layers of the swelling clay mineral montmorillonite exhibit pervasive curvature that arises from the tight coupling of charge and hydration at the layer interface. Three dimensional structures of montmorillonite suspensions from Ångstrom to micron scales in aqua obtained using cryo electron tomography reveal pervasive curvature of layers and their associated ion cloud over a range of electrolyte concentrations and ion types. Curvature modulates the mineral surface potential, which mediates ion distribution profiles at layer interfaces and the interactions between layers. Under many conditions, distinct dense and dilute liquid crystalline states with dramatically different average curvature radii separate via spinodal decomposition. We propose a free energy landscape for hydrated layered minerals that is applicable to a broad range of mineral types, solution compositions including divalent cations, and layer geometries that predicts layered mineral microstructures over a wide range of conditions.
Recycling of waste mineral wool and quarry wastes into high kaolinitic clay for brick manufacturing

G. Wie-Addo, S. Palmer, A. H. Jones, A.M.T. Bell, J. Renshaw, P. A. Bingham

Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield S1 1WB, UK

Wienerberger Ltd, Wienerberger House, Brooks drive, Cheadle Royal Business Park, Cheshire SK8 3SA, UK

ABSTRACT

A reformulated body composition for brick masonry ceramics was prepared mixing clay with industrial wastes (waste mineral wool, slurry dust and filter cake) as raw materials. Mixtures of 4 wt. % of each waste with 96% clay were fired at 950°C and 1040°C. The relevance of this reformulation of clay brick masonry is to maintain brick quality and reduce fuel use in heavy clay brick manufacture using recycled waste streams.

Technological properties of fired ceramics were examined using boiling water absorption, shrinkage, Mercury Intrusion Porosimetry (MIP), thermal analysis (TG/MS), dilatometry and microstructural studies with Scanning electron microscopy (SEM). Chemical (XRF) and mineralogical (XRD) changes in the fired ceramics were also investigated. Properties of fired clay without additives replacement were compared with the reformulated fired body composition.

Results reveal that additives promote development of diopside ferroan \(\text{Ca}_{0.92}\text{Fe}_{0.08}\text{Al}_{0.33}\text{Mg}_{0.53}\text{Si}_2\text{O}_6\), feldspar (albite high-\(\text{Al}_3\text{Na}_1\text{O}_8\text{Si}_3\)), pseudowollastonite (\(\text{Ca}_2\text{O}_3\text{Si}_5\)), potassium aluminium silicate (\(\text{KAl}_3\text{Si}_3\text{O}_{11}\)) as the newly formed phases with hematite (\(\text{Fe}_2\text{O}_3\)), quartz (\(\text{SiO}_2\)) and mullite (\(3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2\)). There was no direct evidence to date from the mineralogical studies of glassy phase formation from Rietveld refinement. The derived wastes ceramics are less porous compared with the ceramics produced using only clays. The additives react with pyrites in clay during sintering producing efflorescence or white stains on the brick surface after firing. This effect is slightly greater than for ceramics produced from clay alone. High temperature water absorption for the ceramics produced using waste derived additives are lower than for the base material. At both firing temperatures the pore diameter ranges from 0.01-1µm correlating with the high temperature water absorption results. Results support raw material substitution for more sustainable heavy clay ceramic manufacture.

Keywords: Kaolinite, Efflorescence, thermal analysis, fired clay based product and porosity.
Fig. 1. Summary of reformulated ceramic body for clay brick masonry
MOLECULAR DYNAMICS SIMULATIONS OF THE ASSOCIATIONS BETWEEN SMECTITE CLAY NANOPARTICLES, SOIL ORGANIC MATTER COATINGS, AND ORGANIC CONTAMINANTS

Jennifer A.R. Willemsen* and Ian C. Bourg

Princeton University, Department of Civil and Environmental Engineering, Princeton, NJ 08540.

Per- and polyfluoroalkyl substances (PFASs) and phthalate esters are persistent and pervasive organic contaminants that pose risks to human health due to their toxicity and endocrine disrupting potential. High levels of these contaminants have been detected in water and soils and a fundamental understanding of their partitioning behavior is essential for developing remediation strategies and for predicting their fate and transport in the environment. Pure smectite minerals have been shown to effectively adsorb these contaminants, but these studies do not take into account the role of soil organic matter (SOM), which is known to readily coat mineral surfaces in the natural environment. In this research, we examine how SOM coatings influence the adsorption of the aforementioned contaminants by smectite clay minerals.

To understand the interplay between clay minerals, SOM, and organic contaminants, we use molecular dynamics (MD) simulations to model a stack of flexible SOM-coated smectite clay sheets with cleaved edges in contact with a bulk aqueous reservoir containing either PFASs or phthalate esters. Our methodology uses the metadynamics technique to facilitate the exploration of the entire simulation cell by the contaminant molecules and reconstruct the associated free energy landscape. The simulation output provides atomistic-level insights that helps discern mineral-SOM-contaminant interaction mechanisms and conformations (i.e. cation bridging, hydrophobic partitioning). In particular, we calculate the free energy, enthalpy, and entropy of adsorption, the affinity of the PFASs and phthalate esters for different clay adsorption sites (interlayer, edge, external basal surface), and examine how the presence of SOM affects the accessibility of mineral adsorption domains. The results are compared to previous studies of contaminant adsorption by pure smectite clay minerals.
Nanomechanical Properties of Organic-Rich Shale and Kerogen by Nanoindentation and Molecular Dynamics Simulations

Tianhao Wu*

Reservoir Engineering Research Institute, Palo Alto, CA 94301, USA

Hydrocarbons from organic-rich shale formations are major sources of oil and gas supply in the United States. Hydraulic fracturing is the common stimulation method to create fractures in shale formations. The nanoindentation tests and molecular simulations have been given much attention to advance our understanding of the microscopic mechanisms in fracturing. In this study, we perform quasi-static indentation and modulus mapping based on a nanoindenter to acquire the mechanical properties at the mineral scale. The results provide direct microscopic evidence for modulus reduction due to water imbibition, explaining the ineffectiveness of hydraulic fracturing in the terrestrial shale. On the other hand, we provide a systematic study on the failure mechanisms of kerogen from organic-rich shale by molecular dynamics simulations. The results indicate that the Mohr–Coulomb failure criterion and tensile strength criterion can describe the failure envelop of the kerogen matrices very well. The kerogen matrices have lower Young’s modulus, compressive strength, tensile strength, and fracture toughness than typical minerals. It reveals that kerogen is a potential weak component in shale, and the fractures may initiate and propagate around kerogen aggregates. The effects of different fracturing fluids, including H₂O, CO₂, and N₂, are also examined. This work provides a practical method to link the nanoscale and macroscale mechanical properties in organic-rich shales and kerogen and sets the stage for investigating the complex mechanisms of hydraulic fracturing in the organic-rich shale formation.
Influence of associated transition metal elements (Ni, Co) on the phyllomanganate-to-tectomanganate transformation: Contrasting origin of similar negative effects

Zhongkuan Wu1,2, Bruno Lanson2,*, Xionghan Feng1, Hui Yin1, Wenfeng Tan1, Xiaoming Wang1, Zhongjun Chen3, and Fan Liu1

1Key Laboratory of Arable Land Conservation, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China; 2ISTerre, Univ. Grenoble Alpes – CNRS, F-38000 Grenoble, France; 3Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China

Phyllo- and tectomanganates are ubiquitous in soils, sediments, and oceanic ferromanganese nodules and are readily associated with many bioessential transition metals, such as Ni and Co. Phyllomanganates, such as birnessite, can convert to tunnel structures (tectomanganates), such as todorokite, during soil and sediment diagenesis, yet the influence of associated metals on the transformation process remains poorly documented, as their mobility and fate during the process. The present work investigates the effect of both Co and Ni presence on the transformation of birnessite into tectomanganates. Two sets of Me-containing birnessite precursors (Me = Co, Ni) were synthesized and subsequently subjected to a mild reflux procedure designed to mimic the phyllomanganate-to-tectomanganate diagenetic transformation. Layered precursors and reflux products were characterized using a combination of mineralogical and geochemical techniques. The results show that Co(III) is structurally incorporated in both layered precursors and reflux products, through the isomorphic substitution of Mn(III). The structural incorporation of Co(III) into the layered precursors leads to an overall reduction of Jahn-Teller distorted Mn(III) octahedra in these minerals, a key factor for their transformation to tunnel structures. As a consequence, the presence of such structural Co(III) disrupts the transformation of birnessite into todorokite, leading to the coexistence of asbolane, a phyllomanganate with an incomplete – island-like – octahedral layer of metal (hydr)oxides, and non-ideal todorokite in the transformation products. Contrastingly, Ni(II) occurs mainly as hydrated Ni(II) and Ni(II) (hydr)oxides in Ni-rich layered precursors, whereas Ni(II) sorbed at particle edges prevail at low Ni content. Layered precursors systematically contain a significant proportion of Jahn-Teller distorted Mn(III) octahedra (~1/3) but no Ni(II) in the MnO2 layers. Consistently, Ni-poor samples fully convert to todorokite. Contrastingly, and despite similar high Mn(III) contents in Ni-rich precursors, hydrolysis of interlayer Ni2+ and polymerization of (Ni, Mg)(OH)2 in phyllomanganate interlayers is kinetically favored during reflux process, and asbolane is formed rather than todorokite. A nitric acid treatment, aiming at the dissolution of the island-like interlayer Me(OH)2 layer, allows an easy and unambiguous differentiation between asbolane and todorokite, the latter being unaffected by the treatment. Both compounds exhibit indeed similar interplanar periodicities and can be confused when using X-ray diffraction.


UNBALANCED ADSORPTION OF CATIONS AT THE SURFACE OF CLAY MINERALS

Hao Xiong*1, Deepak Devegowda1, and Liangliang Huang2

1 Mewbourne School of Petroleum and Geological Engineering, The University of Oklahoma, United States; 2 Chemical, Biological & Materials Engineering, The University of Oklahoma, United States.

Clay minerals are one of the most fundamental and abundant substances on earth and can be used as adsorbents, carbon dioxide storage, and sequestration as well as water purification. Generally, clay minerals have negative surface charges and sorbed cations from solution due to the occurrence of ion exchange. While we do have strong evidence and science to address clay swelling, little to no progress has been made on cation distribution and its impact on fluid behavior. In this work, we use a molecular dynamics (MD) approach to characterize cation distributions when hydrocarbon and water are present in clay-hosted nanopores and to finally quantify its impact on the distribution of water-hydrocarbon mixture.

The results indicate that although the cations are mobile during MD simulations, they are almost located firmly on the clay surface at the pore size larger than 2 nm. Due to this reason, unbalanced adsorption of cations has a high possibility of happening at the surface of clay minerals. Meanwhile, the distribution of water-hydrocarbon molecules is strongly determined by the adsorption of cations. In the balanced cation adsorption, a familiar sandwich structure of water film-hydrocarbon-water film is formed which is also similar to the silica-based nanopores. In the unbalanced cation adsorption, however, water bridges instead of water adsorption films are observed due to the electric field induced by an unbalanced charged surface.

This fundamental study provides a theoretical basis for understanding fluid behavior at the presence of charged clay mineral and can be applied in such as contaminant transport, water purification, transport of ions and charged molecules at the liquid and mineral interfaces, dynamical properties of water molecules at mineral surface, geochemical and biochemical process, and efficient energy-harvesting and energy storage.
BARITE SCALING IN STAGNATION AND FLOW ZONES DURING HYDRAULIC FRACTURING IN MARCELLUS SHALE

Wei Xiong\textsuperscript{1,2}, Johnathan Moore\textsuperscript{1,3}, Mengling Stuckman\textsuperscript{1,4}, Hang Deng\textsuperscript{5}, Dustin Crandall\textsuperscript{1}, Alexandra Hakala\textsuperscript{1}, Christina Lopano\textsuperscript{1}

\textsuperscript{1}National Energy Technology Laboratory, Pittsburgh, PA 15236 and Morgantown, WV 26505; \textsuperscript{2}Oak Ridge Institute of Science and Education, Oak Ridge, TN 37830; \textsuperscript{3}Battelle Research Support Team, Morgantown, WV 26505; \textsuperscript{4}Leidos Research Support Team-National Energy Technology Laboratory, Pittsburgh, PA 15236; \textsuperscript{5}Lawrence Berkeley National Laboratory, Berkeley, CA 94720;

Scaling is a problem that hinders gas production in hydraulically fractured shale reservoirs. The complex fracture passages can lead to local geochemical interactions, resulting in different scaling process spatially due to localized flow conditions. During the shut-in period of hydraulic fracturing, main flow pathways in hydraulic fractures allow localized fluid transport at slow flow rate, while simultaneously near-stagnation zones in the fractures are likely to exist where fluid is trapped. Geochemical reactions can vary under bulk flow and in diffusion-controlled dead ends. Investigating barite scaling in these different flow zones will help to understand the location and extent of scale minerals, thus to better evaluate the impact of scaling on transport pathways in shale gas production. In this study, we designed flow-through experiments with two Marcellus shale cores from the Marcellus Shale Energy and Environmental Laboratory. One core was cut in half, channels along the length of the core were milled into one half, and holes were drilled perpendicular to the channels in the matrix. The channels act as active flow and holes act as stagnation zones. The other core was halved and holes were etched into the matrix at the same locations, but without channels. Proppant was utilized to keep the main flow pathway open. Synthetic produced water was mixed with Monongahela River water as base fluid. Hydraulic fracturing fluid (HFF) chemicals similar with our previous work (Vankeuran et al., 2017) were added. The HFF was injected through the core at 66 °C, 1800 psi core pressure and 2000 psi confining pressure, at 0.02 mL/min (28.8 mL/day) for 28 days. For the core with channels, a thin layer of barite coatings formed in the channels with thicker barite accumulations occurring on the unmilled side across from the holes located on the milled side. This thicker barite coating demonstrates that diffusion-controlled dead-ends promoted barite settling and growth in these zones. For the core without the channels, barite formed on the surface and dead-end holes were filled with proppants. The proppants in the holes were covered with and glued together by barite. The bulk proppants have the potential to block the stagnant zones adjacent to primary flow pathways. This study illustrates that mineral scale can accumulate more readily in diffusion-controlled zones than main flow pathways, implying that the diffusion-controlled zones are potential locations where gas transport pathways may be hindered in shale reservoirs.
SEM maps of the reacted core surface
NANO-TUBULAR CLAY MINERALS OF CHRYSOTILE AND HALLOYSITE AS BARRIER MATERIALS FOR IMMOBILIZING RADIOACTIVE IODINE

Huifang Xu¹, Wenbin Yu¹, ², Eric Roden¹, and Quan Wan²

¹Department of Geoscience, University of Wisconsin-Madison, Madison, WI 53706, USA
²State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou 550081, China

It is challenge to immobilize radioactive iodine in high-level nuclear waste repository, because iodine is very mobile in forms of iodide and iodate ions with -1 charge in groundwater and surface water. Nano-tubular mineral chrysotile (a serpentine group mineral) can adsorb iodide at the wedge shape positions between neighboring chrysotile nanotubes. The adsorbed iodide at the wedge-shaped site form strong bonds with hydrogen on the both sides (Wen et al., 2019). Nano-tubular halloysite (a kaolinite group mineral) can preferentially adsorb iodate on its inner surface covered with OH. Curved halloysite inner surface results in the smaller OH triangle with respect that o flat kaolinite surface, which makes it possible to form tri-dentate binding between the surface OH and three O in the iodate polar pyramid (Wen et al., 2020). Desorption experiments show that the adsorbed iodate cannot be desorbed. However, iodide adsorbed on lizardite and iodate adsorbed on kaolinite can be easily desorbed. Our results indicate that a mineral composite with chrysotile and holloysite can a potential backfill material for immobilizing radioactive iodine in high-level nuclear water repository.

References:

Structure model showing strong bonding site for iodide at the wedge-shaped site.
EFFECTS OF IONIC RADIUS ON ADSORPTION STRUCTURES OF HARD CATIONS ON CLAY MINERALS

Akiko Yamaguchi1,2*, Masahiko Okumura1, and Yoshio Takahashi2

1Center for Computational Science & e-Systems, Japan Atomic Energy Agency; 2Dept. of Earth and Planetary Science, Graduate School of Science, The Univ. of Tokyo

Clay minerals have important roles in environmental behavior of various cations at earth’s surface. For example, cesium is strongly adsorbed on clay minerals by forming an inner-sphere (IS) complex, which causes fixation radiocesium at soil surface after its deposition [1,2]. On the other hand, rare earth elements (REEs) are weakly adsorbed on clay minerals which form outer-sphere (OS) complexes. Therefore, it is easily extracted by ammonium ion solution [3]. As shown above, there are different adsorption structures on clay minerals, although both of cesium and REE are hard cations. However, the origin of this difference is unclear at present.

The purpose of this study was to reveal a primary factor causing the difference. First, extended X-ray absorption fine structure (EXAFS) was systematically applied to various cations, including K+, Rb+, Cs+, Sr2+, Ba2+, Y3+, La3+, and Lu3+, adsorbed on several clay minerals. We found that the cations which have larger and smaller cation radii than Ba2+ form the IS and the OS complexes, respectively. Based on this result, we made a hypothesis that ionic radius is the primary factor in determining the adsorption structure. To confirm this hypothesis, additional X-ray diffraction and adsorption experiments were conducted. Furthermore, we performed numerical simulations for evaluating the adsorption structures of the various cations. We obtained consistent results with our hypothesis. The systematics on the ionic radius is useful for predicting environmental behaviors of other cations for which chemical properties are unknown, such as radium (Ra2+). Based on the systematics, Ra2+, which has a larger ionic radius than Ba2+, is expected to form an IS complex and be fixed on clay minerals.

Distribution of Novel Per- and Polyfluoroalkyl Substances on Montmorillonite

Bei Yan¹, Yanjie Shen², Juan Yao², Xiaoying Yu², Jinxia Liu¹*

¹Department of Civil Engineering, McGill University, Montreal, QC, Canada
²Energy and Environment Directorate, Pacific Northwest National Laboratory (PNNL), Richland, Washington 99354, United States
Corresponding author: jinxia.liu@mcgill.ca

Repeated discharges of aqueous film-forming foams (AFFF) in designated firefighting training areas are closely linked to severe soil and groundwater contamination by per- and polyfluoroalkyl substances (PFAS). Besides the legacy PFAS such as perfluoroalkyl acids, novel non-anionic PFASs have been discovered in AFFF impacted sites. Soil minerals, particularly montmorillonite clays, are hypothesized to play a critical role in the transport and fates of these novel PFAS, but the knowledge remains sparse. In the study, the adsorption behaviors of five novel PFAS, i.e., perfluorooctaneamido ammonium salt (PFOAAmS), perfluorooctaneamido betaine (PFOAB), perfluorooctane sulfonamidoalkyl ammonium salt (PFOSAmS), perfluorooctane sulfonamidoalkyl betaine (PFOSB), and 6:2 fluorotelomer sulfonamidoalkyl betaine (6:2 FTAB), on a source clay (SWy-3, Na-rich Montmorillonite) were explored. The distributions of PFAS on clay and sand surface have been recorded using the time-of-flight secondary ion mass spectroscopy (ToF-SIMS) for the first time. The adsorption capacity of the clay for cationic PFAS is several times higher than sand. The electrostatic interactions between the quaternary ammonium ion (-R₁R₂R₃N⁺) with negatively charged clay layers played a dominant role in adsorption only for selected PFAS. The charge distribution/iso-substitution of Al by Mg of the clay strongly dictated the distribution of PFOAAmS and PFOSAmS, and the hydrophobic interaction among the adsorbed PFAS facilitated the formation of large clay aggregations. The environmental implications of the phenomena are discussed.

Biography

Dr. Bei Yan is a postdoctoral researcher at McGill University. His research focuses on using the combined experimental and computer simulation strategy to elucidate adsorption mechanisms and developing novel remediation materials and processes for water and wastewater treatment.
4D IMAGING REVEALS MECHANISMS OF CLAY-CARBON PROTECTION AND RELEASE

Judy Q. Yang\textsuperscript{1,5}, Xinning Zhang\textsuperscript{2,4}, and Ian C. Bourg\textsuperscript{3,4}, and Howard A. Stone\textsuperscript{1}

\textsuperscript{1}Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544; \textsuperscript{2}Department of Geosciences, Princeton University, Princeton, NJ 08544; \textsuperscript{3}Department of Civil and Environmental Engineering, Princeton University, Princeton, NJ 08544; \textsuperscript{4}Princeton Environmental Institute, Princeton University, Princeton, NJ 08544; \textsuperscript{5}Department of Civil, Environmental, and Geo- Engineering, University of Minnesota, Minneapolis MN 55455

Soil absorbs about 20\% of anthropogenic CO2 emissions annually, and clay is the key carbon-capture material. Although sorption to clay is widely assumed to strongly retard the microbial decomposition of soil organic matter, enhanced degradation of clay-associated organic carbon has been observed under certain conditions. The conditions in which clay inhibits microbial decomposition remain uncertain because the mechanisms of clay-organic carbon interactions are not fully understood. Here we reveal the spatiotemporal dynamics of carbon sorption and release within clay aggregates and the role of enzymatic decomposition by directly imaging a transparent smectite clay on a microfluidic chip. We demonstrate that clay-carbon protection is due to the quasi-irreversible sorption of high molecular-weight sugars within clay aggregates and the exclusion of bacteria from these aggregates. We show that this physically-protected carbon can be enzymatically broken down into fragments that are released into solution. Further, we suggest improvements relevant to soil carbon models.

Figure: 4D imaging of clay and the observed quasi-irreversible sorption and reversible sorption.
Significant amount of literature exists on the mobilization and/or fractionation of rare-earth elements (REE) in sediments and sedimentary rocks. While the REE have long been considered to be immobile during diagenesis, more recent studies provided evidences of their mobilization and fractionation during diagenesis (Lewis et al., 1997; Fulignati et al., 1999; Uysal and Golding, 2003; Honty et al., 2008). Consequently, the REE distribution in sedimentary rocks has been widely used to characterize source compositions of detrital sediments (Taylor and McLennan, 1985) and to trace variations in physico-chemical conditions of fluids and illitization reactions (Clauer and Chaudhuri, 1995; Uysal et al., 2000; Uysal and Golding, 2003). On the other hand, the studies investigating REE mobilization during the illitization process in shale often provided somewhat contradictory conclusions. This may be due to the fact that previous studies used the material that originated from different locations and various geological environments. Moreover, a broad range of size fractions (whole rock, silt or clay separates) was investigated thus adding to the overall uncertainties.

For the purpose of this research four Pennsylvanian shale formations were selected originating from the Anadarko Basin (OK) and covering a 2.1 km depth span (from 2.1 to 4.2 km). Thereupon, three illite-smectite (I-S) fractions (<0.2 µm, <1 µm, <2 µm) were isolated to critically evaluate the effects of illitization on possible REE mobilization and/or fractionation in fine-grained sediment. The study starts from the assumption that authigenic illite-smectite particles concentrated in very fine fractions (<0.2 µm and <1 µm) are the most appropriate to address a potential redistribution of REE inventory triggered by crystal growth mechanism of illite and not by contamination of minerals from other origins. Samples were analyzed for their major-, trace- and REE using the Laser Ablation Inductively Coupled Plasma Mass Spectometer (LA-ICP-MS). The preliminary data has shown that the illitization does not fractionate REE within mineral structures but rather increases their contents in the coarser of the authigenic fraction (<1 µm). The absence of REE fractionation in size fractions strongly suggests that the REE distribution was likely unaffected by the changes related to the crystal growth of illite. Hence, to explain the difference in ∑REE it is suggested that I-S composition and sorption of REE on clay mineral surfaces readily control the REE abundances in different authigenic fractions of illite. The smallest fraction is inferred to contain more smectitic interlayers thus having a direct impact on the total clay particle charge. Conversely, the coarser authigenic fraction is richer in illite and is therefore featured by higher particle charge. It may be concluded that REE abundances, which were documented to decrease from the coarse to fine illite fraction, are essentially controlled by particle nature, composition, and permanent charge.
DIELECTRIC PROPERTIES OF CLAY/ELECTROLYTE INTERFACE AND CLAY INTERLAYERS – IMPLICATIONS FOR SWELLING, AGGREGATION AND SORPTION.

Piotr Zarzycki¹, Benjamin Gilbert¹

¹Energy Geosciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States

The development of hydration layers and electrical double layer at the clay surface is of a primary importance for clay swelling, aggregation, ion exchange and sorption phenomena. Despite decades of studies, we still do not understand how water molecules polarizes near mineral surface, in particular in the presence of the adsorbed electrolyte ions. Although, dielectric relaxation spectroscopy is a unique probe of subtle solvent relaxation phenomena and behavior of water in various states of interactions, spectra interpretation remains problematic.

Here, we show how molecular modeling can provide a unique insight into dielectric signatures of water ordering near the mineral surface, and its implication for the clay-particles aggregation, ion sorption and exchange. We show how molecular modeling can help to unambiguously decompose spectra into individual relaxation modes and relate them to the underlying physical processes of water at the mineral/electrolyte interfaces. By combining molecular modeling and experimental methods, we can explain the effect of crowding and mineral confinement on dielectric, and conductive properties of aqueous solutions. Here, we present the results obtained using classical molecular dynamics for selected swelling and non-swelling clays and carbonate minerals. We conclude that the water dielectric response is governed by the interplay between hydrogen-bond disruption due to ion and surface hydration.

Our results are relevant for understanding the properties of aqueous solutions in contact with mineral surfaces, role of the electrical double layer forces, aggregation, dissolution and precipitation of energy-relevant geological interfaces in the Earth surface and subsurface.
Nanoscale Forces and Nonlinear Transport Behaviors of Geocolloids under Nanoconfinement

Yuanzhong Zhang, Rundong Huang, Xuanlin Du, Sang Bum Kim, and Younjin Min,
Department of Chemical and Environmental Engineering, University of California, Riverside

Abstract

It is known that geocolloids play a major role on the transport and distribution of energy-related contaminants (e.g. naphthalene and cesium etc.) in environment. However, there are many fundamental questions to be answered pertaining to their transport processes and molecular interactions at the nano- and micro-length scales, that are closely related to corresponding relaxation dynamics of colloidal suspension.

Here, monodisperse silica nanoparticles with the radius of ~50 nm were synthesized and selected as model geocolloids. The Surface Forces Apparatus (SFA) was used to measure collective surface forces arising between confining mica surfaces (i.e. model geosurfaces) across colloidal dispersions of silica nanoparticles at varying degrees of confinement as well as dispersant conditions. In the presence of silica nanoparticles in the presence of monovalent ions (10 and 100 mM KCl), the measured forces were purely repulsive on approach and separation; the repulsive forces were long-ranged starting from about up to 500 nm contrasting to the case without silica nanoparticles where the onset of repulsion was less than 10 nm. When silica nanoparticles were dispersed in pure water, the magnitude of onset of repulsion remains constant irrespective of concentration of silica nanoparticles, giving rise to the adhesive instabilities (jumps-out) due to the osmotic pressure effect during separation. When silica nanoparticles were confined to a gap of several colloidal diameters between mica surfaces, a dramatic increase in viscosity of 2-3 orders of magnitude from the bulk was observed, which can be described by the density distribution function and potential mean force characteristics of intermolecular interactions in fluids. Our results provide a picture of the complex colloidal dynamics and interactions between geosurfaces across geocolloidal suspensions, highlighting the impact of nanoconfinement and colloidal stability manipulated by salts.
A large amount of radiological waste is located in the vadose zone at the Hanford Site in southeastern Washington State. Research at Hanford suggests that colloids can be mobilized and potentially transport radionuclides deep into the vadose zone under transient flow. The goal was to quantify in situ colloid mobilization and colloid-facilitated radionuclide transport of sediments at Hanford under field conditions. Experiments were conducted on colloid transport in several 25-foot deep lysimeters, which have been either irrigated with synthetic rainwater to represent the wet, very wet and Chinook (i.e., rapid snowmelt) conditions or non-irrigated to represent natural conditions at Hanford. The ground surface within the irrigated lysimeter is covered to prevent evaporation. Fiberglass wicks were installed at depths of 1, 2, 4 and 7 ft to collect soil solution for colloid analysis. Synthesized 200-nm size EuOHCO₃ colloids were applied to the lysimeters and have characterized their surface and colloid properties. Different-sized polystyrene colloids were also applied as tracer colloids. Solution was collected regularly from the wick samplers and was analyzed for Eu concentrations and particle counts with electron microscopy and energy-dispersive x-ray analysis. The Eu colloids were detected in the deepest wick sampler (7 feet depth) only two and a half months after application of the wicks, while the bulk mass of Eu was still located close to the soil surface. The results indicate that transient infiltration events can cause colloid mobilization and translocation and that colloid-facilitated transport is a likely mechanism for radionuclide transport in near-surface sediments.

Key Words: radionuclide; colloid transport; vadose zone; wick sampler;
HEMATITE MESOCRYSTAL FORMATION THROUGH NEAR INTERFACE NUCLEATION AND ORIENTED AGGREGATION

Guomin Zhu1,2, Maria L. Sushko1, John S. Loring1, Ben Legg1,2, Miao Song1, Jennifer A. Soltis1, Xiaopeng Huang1, Kevin M. Rosso1, and James J. De Yoreo1,2,*

1Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99354, USA. 2Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195, USA.
* Correspondence to: Email: james.deyoreo@pnnl.gov

A diverse class of materials exhibit characteristics of mesocrystals: single crystals constituting distinct nano-sized domains that are atomically aligned. The formation of such structures is often attributed to crystallization through oriented attachment. However, many questions about the fundamental drivers and dynamic progression of this phenomenon remain. And the process become more complexed when coupled with phase transformation. Here we focus on the crystallization of hematite (hm, Fe2O3) mesocrystals from ferrihydrite (fh) nanoparticles. In the oxalate-free solution, the resulting hm crystals are well faceted rhombohedron, while in the presence of oxalate, hm forms nanoporous spindle-shaped mesocrystals. We applied in situ liquid phase TEM with heating temperatures of 80 °C to investigate the formation. We directly observed both the dissolution of fh and the nucleation of new hm particles, which formed within close proximity (~ 1 nm) of the hm/solution interface. Immediately after nucleation, the hm particles attached to the nearby seed to form a hm mesocrystal. Post analyses using EDX mapping and electron diffraction after disassembling the liquid cell confirmed the growth of spindle-shaped hematite during the liquid phase TEM experiments. In addition, we utilized a quasi in situ approach of using indexed TEM grids to cycle samples between the growth reactor and the TEM in order to track the pathway of crystallization. The results were consistent with those of the in situ experiments and confirmed that the fh serves as a buffer and the Hm grow by creation of new particles in the solution near the hm interface. Based on ATR FTIR measurements, ion chromatography and classic DFT calculation we propose that oxalate plays the role of inhibiting classical monomer-by-monomer growth of the hematite particles while promoting the nucleation of new hm particles at the hm/solution interface by modifying the interfacial energy of hm close to the hm/solution interface. In this way, the oxalate ligands bias the growth process away from classical mechanisms and towards oriented attachment.
Multiscale Modelling of Clay Aggregate Behaviour

Hejian Zhu*1, Andrew J. Whittle1, Roland J. Pellenq1,2, Katerina Ioannidou1,3, and Guoping Zhang4

1Massachusetts Institute of Technology, Department of Civil and Environmental Engineering, Cambridge, MA 02139; 2Centre Interdisciplinaire de Nanosciences de Marseilles, Aix-Marseille Université, CNRS, Campus de Luminy, 13288 Marseille Cedex 09, France; 3Laboratoire de Mécanique et Génie Civil, CNRS-Université de Montpellier, 34090 Montpellier, France; 4University of Massachusetts, Department of Civil and Environmental Engineering, Amherst, MA 01003.

Clay is one of the most important industrial material with wide applications in civil and environmental engineering. Understanding the aggregation of clay particles is crucial to a better understanding of clay properties at different length scales. This presentation proposes a multiscale approach. In this approach, inter-particle interaction will be studied at nano-scale through molecular dynamic simulation, from which the potential of mean force (PMF) will be used in meso-scale simulation through coarse-graining technique. Nanoscale and mesoscale simulation results of two types of clays, of which imogolite has tubular primary particles and illite platy particles, will be presented. Imogolite-like materials are potentially useful in medical and material sciences due to its strong monodispersity and controllable diameter. Researchers have studied the chemical composition, atomistic structure, and methods to control the diameter and thermomechanical properties of a single tube. Illite is commonly encountered in geotechnical engineering projects due to its abundance in the earth crust. This study will provide good guidance for both industries. The methodology in general can find its application in many other fields.
Iron oxides are ubiquitous geosorbents regulating the speciation and distribution of heavy metals in water-rock systems. The adsorption processes of heavy metals onto iron oxides that operate in natural systems are complex, with plenty of factors participating or influencing the reactions. Most interesting factors include the coexistent oxyanions which can modify the surface sites of iron oxides and light irradiation that may lead to the change in valence states of heavy metals on semi-conducting iron oxides. In this work, the effects of coexistent oxyanions (sulfate and phosphate) on the adsorption of Cd on ferrihydrite (Fh) and that of light irradiation on the uptake of Cr by hematite (Hem) were studied, respectively. Both coexistent oxyanions remarkably enhanced the removal of Cd by Fh at pH 5. Besides, phosphate is more efficient than sulfate for the long-term immobilization of Cd(II) on Fh, as revealed by desorption experiments. The results of ATR-FTIR spectroscopy indicated that the synergistic adsorption of sulfate and Cd(II) was due to electrostatic interaction and the formation of cation-bridged ternary complexes. In contrast, formation of anion-bridged ternary complexes contributed to the synergistic adsorption of phosphate and Cd(II), in addition to the electrostatic interaction. On the other hand, light irradiation accelerated the oxidation of Cr(III) and reduction of Cr(VI), which were both accompanied by the enhanced uptake of total Cr by Hem at pH ranging ~3 to 5. In the Cr(III) enriched environment, the adsorbed Cr(III) (Cr(III)\text{ad}) could be heterogeneously oxidized to Cr(VI)\text{ad} by the photo-generated holes on Hem; at the same time, aqueous Cr(III) (Cr(III)\text{aq}) could be homogeneously oxidized to highly toxic Cr(VI)\text{aq} by the hydroxyl radicals yielded through interaction between O₂ and the electrons in the valence band of Hem. The produced Cr(VI)\text{ad} on Hem surfaces acted as coexistent anion (similar to the function of phosphate and sulfate) and stimulate further adsorption of Cr(III)\text{aq}, leading to the formation of Cr-riched surface precipitates as detected by TEM. In the Cr(VI) enriched environment, small amounts of Cr(VI) were adsorbed and reduced to Cr(III)\text{ad} by accepting the photo-generated electrons in Hem. The reduction of Cr(VI) was weak, since the available electrons were limited and the produced O₂ and reactive oxygen species would hinder the reduction of Cr(VI).
CONSOLIDATION OF A KAOLINITE SUSPENSION USING A PROTEIN-BASED FLOCCULANT

Yeling Zhu¹, Michael Chae¹, Birendra Adhikari¹, Vinay Khatri¹,², Heather Kaminsky³, Paolo Mussone⁴, and David C. Bressler*¹

¹Biorefining Conversions and Fermentation Laboratory, University of Alberta, Edmonton, AB, Canada T6G 2P5; ²Department of Wood Science, University of British Columbia, Vancouver, BC, Canada V6T 1Z4; ³Centre for Oil Sands Sustainability, Northern Alberta Institute of Technology, Edmonton, AB Canada T5G 0Y2; ⁴School of Sustainable Building and Environmental Management, Northern Alberta Institute of Technology, Edmonton, AB Canada T5G 0Y2

Kaolinite clays in aqueous suspension exist in the form of extremely stable colloidal particles that prevent efficient phase separation. The focus of this study was the conversion of specified risk materials, a biomass byproduct stream from slaughterhouses, into a novel flocculant for settling clay-enriched tailings. The synthesized flocculant was able to adsorb to the surface of kaolinite minerals, which substantially reduced their zeta-potentials and facilitated rapid aggregation. Bench-scale tests using a model clay suspension (4% kaolinite in synthetic process water) showed that the synthesized flocculant enabled settling rates comparable to a commercial flocculant, HPAM, but with a more compact sediment. Overall, our novel protein-based flocculant may provide a solution to fluid tailings from the open-pit mining oil sands industry, as well as other mining and mineral processing industries.
DETERMINING ACTIVE ADSORPTION SITES OF SOIL ORGANIC CARBON ON CLAY MINERAL SURFACE USING ToF-SIMS AND PACA ANALYSIS

Zihua Zhu¹ and Liuqin Hunag²

¹Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99354; ²State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, China.

The heterogenic active adsorption sites on mineral surfaces may harbor critical determination on the protecting capability, preference and efficiency on soil organic carbon (SOC) components. Molecular evidence to show organic behaviors during mineral-microbe-organic interactions is urgently needed to reveal the underlying protecting-releasing mechanism for better prediction on the SOC dynamics. However, such information has been hard to obtain in the complex soil systems. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful surface analysis tool with several unique advantages. For example, it can simultaneously provide elemental, isotopic and molecular information with excellent sensitivity (down to part per million level). More importantly, it is very surface sensitive with an information depth of only about 1-3 nm, making it an exceptional tool to examine subtle chemical changes occurring at the very surface. Therefore, it is very promising to use ToF-SIMS to reveal systematical changes of both SOC and mineral surfaces during mineral-microbe-organic interactions. In this work, ToF-SIMS and principle component analysis (PCA) were used to study the molecular mechanisms of organic preference (e.g., humic substances vs. microbial carbon) by Fe-rich clay mineral (e.g., nontronite NAu-2) during microbial Fe redox processes. Active adsorption sites, which have only been hypothesized or computationally investigated in previous research, were successfully determined by ToF-SIMS data. Such a success indicates a bright future of extensive application of ToF-SIMS and PCA in this field.
COLLOID-MEDIATED TRANSPORT OF ANTIBIOTICS THROUGH CHEMICALLY HETEROGENEOUS POROUS MEDIA

Jie Zhuang*1

1The University of Tennessee, Department of Biosystems Engineering and Soil Sciences, Center for Environmental Biotechnology, Knoxville, TN 37996.

Ciprofloxacin and tetracycline are antibiotics widely used by human and animals, which enter soil through reclaimed water irrigation and biosolid land application. Soil composition, such as soil organic matter, colloids, and metal oxides, may influence their fate and transport behaviors in the subsurface environment. Our experimental studies show that ciprofloxacin cannot break through soil columns regardless of presence and absence of Fe-oxides and humic acids. However, the high adsorption of ciprofloxacin on soil colloids (Kd=10^4-5 L/kg) greatly favors its breakthrough from the soil. This colloid-facilitated effect becomes more significant at lower ionic strength of solution. Compared to ciprofloxacin, tetracycline has a higher mobility in the soil, but colloid-facilitated effect is limited because of its lower adsorption on the soil colloids (Kd=10^3-4 L/kg). The transport of tetracycline is negatively correlated with the contents of Fe-oxides and organic matter in soils. The recovery rates of tetracycline decreased from 35.38% to 11.95% and from 35.38% 0.01% when the proportions of soil surfaces coated by Fe-oxides and humic acids increased from 0 to 50%, respectively. These results show that the mobility of dissolved and colloid-bound tetracycline respond oppositely to the change in solution ionic strength, making the net effect of soil colloids on tetracycline transport vary with soil solution chemistry. This study implies that colloid-mediated interactions of antibiotics with soil surfaces and solution chemistry largely determine the off-site environmental risks of antibiotics.
Interactions of methane (CH₄) with clay minerals under high pressure occur in various geological systems, including unconventional natural gas reservoirs and CH₄ clathrates. CH₄ may be adsorbed on clay minerals’ external surfaces and in the micropores formed by crystallites’ stacking pattern. Under wet conditions and high-pressure, CH₄ forms clathrates in the interlayers of expandable clay minerals. However, smectites’ interlayer accessibility in water-deficient state for CH₄ remained uncertain. The aim of the study was to test whether CH₄ can penetrate and swell smectites’ interlayers under dry conditions.

X-ray diffraction (XRD) experiments were performed under high CH₄ pressure using the Mg-, Ca-, Li-, Cs- and tetramethylammonium (TMA) forms of montmorillonite (MtM) SAz-2 and beidellite SBId-1 (BId), obtained from The Clay Minerals Society Source Clays Repository. The samples were dried and purged with dry nitrogen to decrease the interlayer width. In the monovalent cation-exchanged smectite basal spacing decreased to 12.1 Å (Li-MtM) and 11.2 Å (Cs-MtM), whereas Ca²⁺ and Mg²⁺ cations remained complexed by a few strongly-bound H₂O molecules, acting as pillars for the interlayer. TMA-MtM’s basal space did not change after the drying and remained pillared at 13.8 Å. An increase of the CH₄ pressure up to 60 bar either increased the average basal spacing or had no significant effect (≤ 0.1 Å), but never caused any basal space decrease. Swelling of Mg-MtM was observed for the initial (0 bar CH₄) basal spaces from 11.7 Å to 12.6 Å. For the initial basal space of Mg-MtM as high as 14.1 Å and as low as 10.0 Å for CH₄ pressure increase did not cause the changes in the interlayer width. Mg-BId and Ca-MtM also swelled under high CH₄ pressure, although to lesser extent than Mg-MtM sample. Any of the samples exchanged with a monovalent cation, with d-space < 12.1 Å did not show any swelling, whereas TMA-MtM did not expand despite its interlayer having been already proven to be fully accessible for CH₄. Swelling of Mg-MtM sample was pressure-dependant, as shown in fig. 1, and reversible when CH₄ pressure dropped.

Monte Carlo (MC) simulations were used to calculate free energy of smectite swelling. As interpreted from MC simulations, under CH₄ is pressure, smectite’s basal spacing is controlled by the energetic factor, whereas entropy and mechanical work were minor contributors. Based on swelling free energy calculated from MC simulations for Mg-MtM, basal spacing increased from ~11.9 Å to ~12.2 Å under 80 bar of CH₄, but no swelling was observed for Cs-MtM. The results of experiments and MC simulations jointly prove that CH₄ enters the interlayers of Mg- and Ca-smectites when they are pillared by hydrated cations, and causes the smectite swelling.

This study was financed by National Science Centre, Poland, grant no. 2017/25/N/ST10/02034
AN INVESTIGATION INTO THE EFFECTS OF ALUMINUM SUBSTITUTION AND AGING UNDER AEROBIC CONDITIONS ON THE PHYSICOCHEMICAL PROPERTIES OF FERRIHYDRITE

Sean Zigah
Szigah1@gsu.edu

Sean Zigah1, Brianne Martin2, Carolyn I. Pearce3, Kevin Rosso3, Nadine Kabengi1,2

1 Department of Geosciences, Georgia State University, Atlanta, GA, United States
2 Department of Chemistry, Georgia State University, Atlanta, GA, United States
3 Pacific Northwest National Lab, Richland, WA, United States

The work will identify the effects of Al incorporation and aging under aerobic conditions on the physicochemical properties of ferrihydrite (Fh). Fh is an environmentally prevalent Fe(III) mineral that plays an active role in several geochemical processes such as redox reactions, and the fate and transport of contaminants in aqueous and terrestrial systems1. In natural environments, Fh often co-precipitates in the presence of impurities, particularly Al, and forms Al-bearing phases that can incorporate up to 20 to 30 mole % Al (%-Al Fh)2. However, the sites of Al incorporation into Fh’s structure remain uncertain. This meticulous investigation into the impact of Al in Fh will shed light on the location of Al. We hypothesize that the Al3+ substitutes into the Fe1 octahedral position based on the Michel Fh structural model3.

Two sets of approx. 28 and 16-month old samples of 0, 12, and 24 mol % AlFh were studied. The surface charge reactivity was probed using flow microcalorimetry (FMC). The heats of exchange (Qexch in mJ/mg) of two anionic probes, chloride (Cl-) and nitrate (NO3-), were obtained. The transformations of Fh into more crystalline phases and their properties were investigated using semi-quantitative X-ray diffraction (SQXRD), X-ray absorption spectroscopy (XAS) and X-ray magnetic dichroism spectroscopy (XMCD).

For both sets of aged Fh samples, the energies of Cl/NO3 exchange in mJ/mg, aQexch, followed the following trend: aQexch 0-%-AlFh < aQexch 24%-AlFh < aQexch 12%-AlFh. However, Qexch obtained immediately following synthesis, iQexch, followed iQexch 0 %-%-AlFh < iQexch 12%-AlFh < iQexch 24%-AlFh. Goethite (GH) and hematite (HT) were the phase transformation products identified and analyzed using SQXRD. Al content retards the crystallization of as Fh ages. XRD data also showed that there was an increase in the HT:GH ratio with increasing age for the 0%-AlFh samples. The 12%-AlFh samples did not show any change in crystallinity, while the 24%-AlFh samples did appear to have minor crystallinity. The lack of phase transformation in the 12% AlFh further supports the lack of reduction in surface reactivity observed by FMC. XAS and XMCD showed that Al incorporation increases the ratio of tetrahedrally coordinated Fe3+ to octahedral Fe3+, potentially suggesting that Al3+ occupies the surface octahedral position.

Taken all together, the results of this work showcase how the combined effects of aging and Al-incorporation affects the overall reactivity of Fh and AlFh, and provides experimental constraints to modeling efforts to predict contaminant transport behavior under environmentally relevant conditions.

References:

XVII ICC
İstanbul 2021
12-16 JULY