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Annual Meeting
Held on the Campus of the University of Illinois at Urbana-Champaign
October 6–10, 2013

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1988–1989 sigh

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2010 Jose M. Serratosa
2011 Sridhar Komarneni
2012 Akahiko Yamagishi
2013 Stephen Guggenheim

AWARDS

Marilyn and Sturges W. Bailey Distinguished Member 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
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1996 Victor A. Drits
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2002 Gerhard Lugaly
2004 Benny K. G. Theng
2005 M. Jeff Wilson
2006 Frederick J. Wicks
2008 Norbert Clauer
2009 Joseph W. Stucki
2010 Jose M. Serratosa
2011 Sridhar Komarneni
2012 Akahiko Yamagishi
2013 Stephen Guggenheim
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 Środon
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. McCurry
2012 Jeffrey E. Pox
2013 George E. Christidis

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 Baronne
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 Maneau
2004 Maria F. Brigatti
2005 Maria F. Brigatti
2006 Robert J. Gilkes
2007 Lynda B. Williams
2008 Hailiang Dong
2009 Paul A. Schroeder
2010 Toshihiro Kogure
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Jackson Awardees

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. McCurry
2012 Jeffrey E. Pox
2013 George E. Christidis
Pioneer in Clay Science Award

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 Hayden H. Murray
2011 Glenn A. Waychunas
2013 Thomas J. Pinnavaia

CITATION OF SPECIAL RECOGNITION

1984 Richards A. Rowland
1984 Ada Swineford
1994 Kenneth M. Towe
1996 Don Scafe
2003 William D. Johns

EDITORS OF CLAYS AND CLAY MINERALS

1952 J. A. Pash and M. D. Turner
1953 Ada Swineford and Norma Plummer
1954 W. O. Milligan
1955–1961 Ada Swineford
1962–1964 William F. Bradley
1964–1969 Sturgis W. Bailey
1970–1972 Max M. Mortland
1975–1978 Richards A. Rowland
1979–1990 Frederick A. Mumpton
1999–2000 Stephen Guggenheim
2000–2007 Derek C. Bain
2008–Present Joseph W. Stucki
INTRODUCTION

THE 50TH ANNIVERSARY ANNUAL MEETING OF THE CLAY MINERALS SOCIETY, HELD OCTOBER 6–10, 2013, AT THE UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN, ILLINOIS, USA

The University of Illinois is an ideal location for this special anniversary meeting because it was the academic and professional home of Professor Ralph E. Grim, who was a professor in the Department of Geology from 1948 to 1967 and a research scientist at the Illinois State Geological Survey for 17 years before that. He was one of the founding fathers of clay mineralogy and of The Clay Minerals Society. A new historic marker was recently placed on the west outside wall of the Natural History Building commemorating Professor Grim and his pioneering work, including applications to geology, soil science, civil engineering, and mineral resources. He published many important scientific journal articles, wrote several textbooks, supervised many graduate students, and received numerous awards for his important contributions to science, engineering, and society. He also studied and named the clay mineral illite, which is the second most abundant sedimentary mineral after quartz! Read more about the life and career of Dr. Grim below.

The primary purpose of The Clay Minerals Society (CMS) is to stimulate research in all aspects of clay science and technology and to widely disseminate the research findings. Through its conferences and publications (Clays and Clay Minerals, CMS Workshop Lectures), CMS provides frequent opportunities for information sharing and inter-disciplinary collaborations. The Society cordially invites colleagues from all branches of science and from all countries of the world who study and are interested in clays and clay technology to join in the conferences of CMS and to publish their work in our journal.

RALPH E. GRIM
1902–1989
Clay Mineralogy

Ralph Early Grim was born February 25, 1902, in Reading, Pennsylvania. He entered Yale in 1920 and received a B.A. in geology in 1924. His professors at Yale thought that pursuing a Ph.D. in clay minerals wasn’t too promising a path, so he took a job in 1929 as an assistant professor at the University of Mississippi with a joint appointment as Assistant State Geologist. His report on the bentonites of Mississippi, entitled The Eocene Sediments of Mississippi, led to a Ph.D. from Iowa State University.

He was hired by Illinois State Geological Survey Chief Morris M. Leighton as a petrographer in 1931 and was promoted to Principal Geologist of the Geology Group and Head of the new Clay Resources and Clay Mineral Technology Section in 1945. In 1948, Grim resigned as a principal geologist at the Survey and became a research professor of geology at the University of Illinois. From his professorship, he continued to serve as Head of the Clay Section until 1958. He retired from the University of Illinois as Professor Emeritus in 1967.

Ralph Grim is justly called the “Father of Clay Mineralogy,” and his 60-year career and many honors are impossible even to summarize in this short biography. He could simultaneously perform mundane testing on low-cost geological and mineral resource samples, employ new basic research methods to these samples, and find the unifying fundamental concepts that made it possible to generalize and apply results in a way that had great impact in Survey programs, soil science, and civil engineering. Each of his Survey publications and his three textbooks illustrate this approach. Grim was notable at society meetings where he often rose to ask a speaker whether he or she had thought about how some new...
fundamental insight might be used to create products or processes of value to society—usually leaving the speaker at a loss for words and helping out with a few of his own ideas. Especially, the two editions of Clay Mineralogy and his Applied Clay Mineralogy remain standard texts today. His book with Necip Guven on bentonites also has received wide praise. Grim’s work at the Survey was so widely recognized that his office and laboratories were the only ones located on the building’s first floor so that Chief Leighton could easily direct visitors’ attention to the famous scientist’s research facilities.

He was editor of the Journal of Sedimentary Geology, a founder and the first Distinguished Member of the Clay Mineral Society and a Roebling Medal winner from the Mineralogical Society of America. He was an honorary member of the National Academy of Sciences, Arts, and Letters and Fellow of the Geological Society of America, the American Ceramic Society, and the Society of Economic Paleontologists and Mineralogists. He also was named Fellow by several international societies, and he received the only gold medal ever awarded by the Clay Mineral Society of Spain, and the Medal of the Ordre Nationale and Designated Chevalier of the Ordre Nationale of the Republic of Ivory Coast (1973).

He was given an honorary Ph.D. from the University of Illinois in 1984, and he received a posthumous citation by the Illinois House of Representatives.

Honored by Haydn Murry and James Kirkpatrick.

Citation contributed by Randall E. Hughes.

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**Informal BBQ at Stucki’s home. RSVP to jstucki@illinois.edu for directions and instructions.**

**Welcome Reception & Student Welcome**

**Editorial Board Dinner**
<table>
<thead>
<tr>
<th>Time/Room</th>
<th>October 8</th>
<th>October 9</th>
<th>October 10</th>
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<tbody>
<tr>
<td><strong>Tuesday</strong></td>
<td><strong>Wednesday</strong></td>
<td><strong>Thursday</strong></td>
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<tr>
<td><strong>Social Program</strong></td>
<td><strong>Illini A</strong></td>
<td><strong>Illini C</strong></td>
<td><strong>Pine</strong></td>
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<tr>
<td>8:00</td>
<td>Bailey Award Lecture</td>
<td>Brindley Lecture</td>
<td>Pioneer Lecture</td>
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<td>Redox I</td>
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<td>Zeolite Posters Up</td>
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<td>Redox I</td>
<td>Gen III</td>
<td>Zeolite Posters Up</td>
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<tr>
<td>8:40</td>
<td>Lunch On Your Own (CMS Nomenclature Committee—Ballroom)</td>
<td>Lunch On Your Own (CMS Past Presidents’ Luncheon—Colonial Room)</td>
<td>Isotopes</td>
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<tr>
<td>9:00</td>
<td>Redox II</td>
<td>Gen IV</td>
<td>Enviro Posters Up</td>
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<td>Break—Illini Room B</td>
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<td>Enviro Posters Up</td>
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<td>9:30</td>
<td>Authors at Posters</td>
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<td>Conference Banquet</td>
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<tr>
<td>9:40</td>
<td>Informal “The Friends (and enemies) of Illite/Smectite”</td>
<td>Assemble at Registration Desk</td>
<td>Informal BBQ at Stucki’s home. RSVP to <a href="mailto:jstucki@illinois.edu">jstucki@illinois.edu</a> for directions and instructions.</td>
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**Key for Session Abbreviations on next page**
KEY FOR SESSION ABBREVIATIONS

Barriers: Clay Barrier Technologies for Landfills and Mining
Organizers: Will P. Gates and William J. Likos

CO2: CO2 Sequestration
Organizers: Andreas Busch and Eugene S. Ilton

Enviro: Modified Clays for Environmental Applications
Organizers: Yael Mishael and Hongping He

F & S: Ferrihydrite and Schwertmannite
Organizers: Rob Fitzpatrick and Huifang Xu

Frac: Clay Minerals in Petroleum Reservoirs and Hydraulic Fracturing
Organizers: Joan E. Crockett, Shane K. Butler, and Stephen P. Altaner

Gen: General Sessions
Organizers: Michael F. Aldersley, David L. Bish, F. Javier Huertas, and Jana Madejová

History: Some Intellectual Genealogies: Honoring Those Who Came Before Us
Organizer: Duane M. Moore

illite: illite: The Big Picture
Organizers: Georg H. Grathoff and Jan Środoń

ISCM: Industrial and Specialty Clay Minerals
Organizers: Marc Herpy, William F. Moll, and Haydn H. Murray

Isotopes: Clays and Isotopes
Organizer: Fred J. Longstaffe

MSCM: Molecular Studies of Clay Minerals and Related Structures
Organizers: Randall T. Cygan and Jeffery A. Greathouse

Nano: Structural Characterization of Lamellar Compounds and Their Nanocomposites
Organizers: Gary J. Beall, Bruno Larson, and Doug M. McCarty

Organizers: Reiner Dohrmann and Patrik Sellin

Redox: Iron Redox Processes
Organizers: Molly M. McGuire and Alanah Fitch

Zeolites: Evolving Applications of Natural Molecular-sieve Zeolites
Organizers: Steven M. Kuznicki, Tetyana Kuznicki, and Albana Zeko
## Program

### Friday, October 4

<table>
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<tr>
<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>6:00–10:00 pm</td>
<td>Executive Committee Meeting: Illini Union Colonial Room</td>
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### Saturday, October 5

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<th>Time</th>
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<tr>
<td>8:00 am–5:00 pm</td>
<td>CMS Council Meeting: Illini Room C</td>
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<tr>
<td>8:00 am–5:00 pm</td>
<td>Workshop on Advanced Applications of Synchrotron Radiation in Clay Science, Illini Room A</td>
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<tr>
<td>6:00 pm–8:00 pm</td>
<td>Informal BBQ at Stucki's Home. All are invited, but please RSVP to <a href="mailto:jstucki@illinois.edu">jstucki@illinois.edu</a> to get directions and further instructions.</td>
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### Sunday, October 6

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<th>Time</th>
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<tr>
<td>6:00–9:00 pm</td>
<td>Registration in Front of Illini Rooms, Main Floor West Corridor</td>
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<td>7:45 am–6:00 pm</td>
<td>Field Trip to Starved Rock and Matthiessen State Parks. Meet in the Illini Union North Lobby, facing the circle drive.</td>
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<td>6:30–9:00 pm</td>
<td>Welcome Reception and Student Welcome, Illini Room B</td>
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### Monday, October 7

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<th>Time</th>
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<td>7:30 am–5:00 pm</td>
<td>Registration in Front of Illini Rooms, Main Floor West Corridor</td>
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<td>8:00 am–5:00 pm</td>
<td>Social Program: Amish Country. Meet in the Illini Union North Lobby, facing the circle drive.</td>
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### MORNING, Monday, October 7

#### Illini Room A

**Plenary Session**

- **8:00–8:10** Introductory remarks, Joseph W. Stucki, Chair
- **8:10–8:20** Introductory remarks, Peter Komadel, CMS President
- **8:20–8:30** Introduction of the 2013 Marion L. & Chrystie M. Jackson Mid-Career Clay Scientist Award Recipient
  - Haydn H. Murray, Indiana University
- **8:30–9:10** George E. Christidis*: SMECTITE HETEROGENEITY IN BENTONITES: THE KEY TO INTERPRET THE UNIQUE PHYSICAL AND CHEMICAL PROPERTIES OF THESE MATERIALS (MARION L. & CHRYSTIE M. JACKSON MID-CAREER CLAY SCIENTIST AWARD LECTURE)
**ILLINI ROOM A**  
**Clay Minerals in Petroleum Reservoirs and Hydraulic Fracturing**  
Organizers: Joan E. Crockett, Shane K. Butler, and Stephen P. Altaner  


9:40–10:00 Tomasz Topór*, Arkadiusz Derkowski, and Douglas K. McCarty: POROSITY AND GAS SHALE FORMATION DIAGNOSIS  

10:00–10:20 Coffee break  


10:40–11:00 Joan Crockett*, Maria Mastalerz, and Stephen Altaner: IMPORTANCE OF CLAY MINERALOGY AND GEOCHEMISTRY IN THE PRE-EMERGENT LIQUIDS-FROM-SHALE PLAY IN THE NEW ALBANY SHALE (DEVONIAN-MISSISSIPPIAN), ILLINOIS BASIN  

11:00–11:20 Eric Daniels*: THE IMPORTANCE OF CLAYS AND SHALE PROPERTIES FOR SHALE RESERVOIR HYDRAULIC STIMULATION AND GROUNDWATER PROTECTION  


11:40–12:00 Randall Hughes* and Beverly Seyler: DIFFERENCES IN PORE-FILLING CLAY MINERAL COMPOSITIONS IN ILLINOIS RESERVOIRS AND THEIR IMPACT ON RECOVERY OF OIL  

**ILLINI ROOM C**  
**Molecular Studies of Clay Minerals and Related Structures. I**  
Organizers: Randall T. Cygan and Jeffery A. Greathouse  


9:40–10:00 Benjamin Rotenberg*, Amish J. Patel, and David Chandler: MOLECULAR EXPLANATION FOR WHY TALC SURFACES CAN BE BOTH HYDROPHILIC AND HYDROPHOBIC  

10:00–10:20 Coffee break  


10:40–11:00 B. Grégoire*, C. Carteret, V. Erastova, H.C. Greenwell, and D. Fraser: LAYERED DOUBLE HYDROXIDES AS NANOREACTORS FOR PREBIOTIC CHEMISTRY  


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11:20–11:40 Michael Holmboe* and Ian C. Bourg: THE TEMPERATURE-DEPENDENCE OF SOLUTE DIFFUSION IN SMECTITES: COMPARING EXPERIMENTS AND MOLECULAR DYNAMICS SIMULATIONS

11:40–12:00 Hendrik Henz*: CLAY MINERALS AND CEMENT MINERALS—MOLECULAR AND INTERFACIAL PROPERTIES IN MODEL AND EXPERIMENT

**PINE ROOM**


Organizers: Reiner Dohrmann and Patrik Sellin

9:20–10:00 Olivier Leupin* and Patrik Sellin: THE USE OF CLAY IN RADIOACTIVE WASTE DISPOSAL—A REVIEW OF THE DIFFERENT APPLICATIONS

10:00–10:20 Coffee break

10:20–10:40 Patrik Sellin* and Olivier Leupin: ALTERATION OF CLAYS IN ENGINEERED BARRIERS FOR NUCLEAR WASTE REPOSITORIES—WHAT ARE THE ISSUES?

10:40–11:00 Reiner Dohrmann*, Six Olsson, Stephan Kaufhold, and Patrik Sellin: CEC METHODS USED FOR THE STUDY OF SOILS, CLAYS, AND BENTONITE BARRIERS AND EC PROCESSES IN THE FIRST PACKAGE OF THE ALTERNATIVE BUFFER MATERIAL TEST, SWEDEN

11:00–11:20 Daniel Svensson*: EARLY OBSERVATIONS IN A LARGE SCALE 6½ YEAR IRON-BENTONITE FIELD EXPERIMENT (ABM2) AT ÄSPÖ HARD ROCK LABORATORY, SWEDEN

11:20–11:40 Ian C. Bourg*, Michael Holmboe, Carl Steefel, and Garrson Sposito: ADSORPTION, DIFFUSION, AND PORE MICROSTRUCTURE IN ENGINEERED CLAY BARRIERS FOR RADIOACTIVE WASTE STORAGE

11:40–12:00 Erin L. Hunter*, James M. Tinjum, and Craig H. Benson: INFLUENCE OF MINERALOGY ON RADIONUCLIDE SORPTION CAPACITY IN BARRIER SOILS

**ROOM 407**

### General Session. I

Organizers: Michael F. Aldersley, David L. Bish, F. Javier Huertas, and Jana Madejová

9:20–9:40 Sayako Inouë* and Toshihiro Kogure: STRUCTURES OF CHLORITE/SERPENTINE MINERALS IN TOYOHA GEOTHERMAL SYSTEM, SOUTHWESTERN HOKKAIDO, JAPAN

9:40–10:00 Sandra C. Londono* and Lynda B. Williams: EVALUATING THE ROLE OF ZETA POTENTIAL IN A NATURAL ANTI-BACTERIAL CLAY FROM THE COLOMBIAN AMAZON

10:00–10:20 Coffee break


10:40–11:00 Michael F. Aldersley*, Prakash C. Joshi, and James P. Ferris: THE MONTMORILLONITE CATALYZED SYNTHESIS OF RNA DIMERS

11:00–11:20 Mohammad Hadi Mohammad*, Hossein Faghhihian, and Ahmad Zia Yaltahi: PRODUCTION OF LINEAL ALKYLBENZENE WITH MODIFIED NATURAL BENTONITE
PROGRAM | MONDAY, OCTOBER 7

11:20–11:40 Abhy Kadakia* and David L. Bish: THE EFFECTS OF STEAM ON THE SURFACE PROPERTIES OF PALYGORSKITE: IMPLICATIONS FOR PALYGORSKITE-WATER INTERACTIONS

11:40–12:00 Xiaoxue Yang*, Anhuai Lu, Yan Li, Yun Zhu, Haoran Wang, and Hongrui Ding: THE EFFECT OF A BACILLUS MUCILAGINOSUS STRAIN ON THE STRUCTURE OF MONTMORILLONITE

NOON, MONDAY, OCTOBER 7

12:00–1:20 Lunch break—on your own
12:00–1:20 Sustaining Members’ Luncheon (by invitation), Colonial Room

AFTERNOON, MONDAY, OCTOBER 7

ILLINI ROOM A Industrial and Specialty Clay Minerals. I
Organizers: Marc Herpfer, William F. Moll, and Haydn H. Murray

1:20–1:40 Jessica Elzea Kogel: APPLIED CLAY SCIENCE—HAVE WE LOST OUR WAY?

1:40–2:00 Charles R. Landis* and Ryan P. Collins: SOME RECENT EFFORTS IN NEW PRODUCT DIFFERENTIATION FOR FRESHWATER DRILLING FLUIDS: THINKING DIFFERENT SIMULTANEOUSLY

2:00–2:20 Damon D. Jackson and James R. O'Brien*: INDUSTRIAL-SCALE PURIFICATION OF KAOLIN USING A CONDUCTION-COOLED SUPERCONDUCTING HIGH-GRADIENT MAGNETIC SEPARATOR

2:20–2:40 Prakash B. Malla*: KAOLIN: PRODUCT INNOVATION AND APPLICATIONS

2:40–3:00 Huitang Zhou*: A UNIQUE APPLICATION OF NATURALLY MIXED PALYGORSKITE AND MONTMORILLONITE (PALY-MONT) CLAY

3:00–3:20 Coffee break

3:20–3:40 Wouter L. Ijdo*: Hectorite Clay—A UNIQUE, MULTI PURPOSE RHEOLOGICAL ADDITIVE

3:40–4:00 Don A. Anschutz, David Guerta, Robert J. Pruett*, and Chris Stephenson: CERAMIC PROPPANTS MANUFACTURED FOR HYDRAULIC FRACTURING USING GEORGIA KAOLIN

4:00–4:20 Christopher Greissing*: FEDERAL LEGISLATIVE AND REGULATORY UPDATE

4:20–4:40 Bob Goss* and Marc Herpfer: HOW DOES ONE PROFITABLY SUCK AND CLING (OR HOW TO SELL HOLES)?
ILLINI ROOM C

**Molecular Studies of Clay Minerals and Related Structures. II**

Organizers: Randall T. Cygan and Jeffery A. Greathouse

1:20–1:40
H. Christopher Greenwell*, James Suter, Richard L. Anderson, and Peter V. Coveney: EVALUATING THE SWELLING AND EXFOLIATION OF TREATED CLAY MINERALS THROUGH COMPUTER SIMULATION

1:40–2:00
Brice F. Ngouana W* and Andrey G. Kalinichev: ADSORPTION AND MOBILITY OF CESIUM AND STRONTIUM ON MONTMORILLONITE CLAY SURFACES

2:00–2:20
Stephanie L. Teich McGoldrick*, Gregg T. Beckham, Jeffery A. Greathouse, and Randall T. Cygan: HETEROGENEOUS NUCLEATION OF METHANE HYDRATES IN THE PRESENCE OF CLAY MINERAL SURFACES

2:20–2:40
Paul Fenter*: OBSERVING THE INTERACTIONS OF IONS WITH MUSCOVITE-WATER INTERFACES USING X-RAYS

2:40–3:00
Lonia Friedlander*, Gilles Frapper, Timothy Gocht, and Artem Oganov: A ‘CLUSTER’ COMPUTATIONAL MODELING METHOD TO EXPLORE THE EFFECTS OF METEOR IMPACTS ON CLAY MINERAL SPECTROSCOPY

3:00–3:20 Coffee break

3:20–3:40
Cliff T. Johnston*, Kiran Rana, Bushra Khan, Hui Li, Cun Liu, Brian J. Teppen, and Stephen A. Boyd: MOLECULAR SPECTROSCOPY AND MODELING OF DIOXIN AND POLYAROMATIC HYDROCARBON INTERACTIONS WITH CLAY MINERALS

3:40–4:00
C. Ignacio Sainz-Díaz*, Cristina Luga, Elba Ortiz, and Elizabeth Escamilla: INTERACTIONS BETWEEN ORGANICS AND WATER MOLECULES WITH SILICATE SURFACE BY THEORETICAL ATOMIC METHOD

4:00–4:20
Christian Detellier* and Gustave Kenne Dedzo: FUNCTIONAL ORGANO-KAOLINITE NANOHYBRID MATERIALS

PINE ROOM

**Alteration and Cation Exchange Processes in Clays, Soils, and Engineered Clay Barriers for Radioactive Waste Disposal. II**

Organizers: Reiner Dohrmann and Patrik Sellin

1:20–1:40
Rainer Dähn*, Erich Wieland, Philippe Schaub, Maria Marques, and Bart Baeyens: UPTAKE AND ALTERATION PROCESSES IN OPALINUS CLAY: AN X-RAY ABSORPTION AND MICRO-X-RAY-DIFFRACTION STUDY

1:40–2:00

2:00–2:20
R. K. Dubey*: BEARING OF THERMAL STRESS ON MECHANICAL STABILITY AND ITS IMPUPLICATION IN ASSESSING THE POSSIBILITY OF RADIOACTIVE WASTE DISPOSAL IN ARGILITE OF VINDHYAN SUPERGROUP, INDIA

XIX
PROGRAM | MONDAY, OCTOBER 7

ROOM 407

General Session. II
Organizers: Michael F. Aldersley, David L. Bish, F. Javier Huertas, and Jana Madejová

1:20–1:40

1:40–2:00
Jana Madejová*, Helena Pálková, and Ľuboš Jankovič: INFRARED STUDY OF THE INTERACTION OF PYRIDINE WITH ACID-TREATED MONTMORILLONITE

2:00–2:20
Peter Komade*, Lubo Jančovič, Jana Madejová, Janka Hrácová, Daniela Jočhe-Moliková, and Ivan Chodák: ORGANOPHILIC MODIFIERS AND PROPERTIES OF RUBBER NANOCOMPOSITES

2:20–2:40
Connie I. Constan*: CERAMIC RESOURCE SELECTION AND SOCIAL VIOLENCE IN THE GALLINA CULTURE AREA OF NORTHERN NEW MEXICO

2:40–3:00

3:00–3:20
Coffee break

3:20–3:40
Jonathan E. Seppala* and Gale A. Holmes: CLAY COMPOSITIONS AS BALLISTIC WITNESS MATERIALS. TIME, TEMPERATURE, AND HISTORY DEPENDENT MATERIAL PROPERTIES

3:40–4:00
Ana L. Barrientos Vélazquez* and Youjun Deng: MINERALOGY VARIATIONS IN CENTRAL TEXAS BENTONITES DUE TO LOCAL HYDROLOGY INFLUENCES

4:00–4:20
Jennifer L. McKay and Fred J. Longstaffe*: TRACKING CYCLIC STEAM INJECTION IN OIL SANDS USING OXYGEN AND HYDROGEN ISOOTOPIC COMPOSITIONS OF CLAY MINERALS

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4:20–4:40 Michael Plötze*: WINNING THE 6TH REYNOLDS CUP–AN EDUCATED GUESS OR MORE!
4:40–5:00 Emmanuel J. Ajidahun* and Rufus T. Ajayi: GEOCHEMICAL STUDIES OF REGOLITH TREND IN MOKURO ITAGUNMODI IN IFE ILESA SCHIST BELT OF SOUTHWESTERN NIGERIA

EVENING, MONDAY, OCTOBER 7

6:00– Editorial Board Meeting and Dinner. Meet in the Illini Union North Lobby, facing the circle drive.

TUESDAY, OCTOBER 8

7:30 am–5:00 pm Registration in Front of Illini Rooms, Main Floor West Corridor
8 am–5 pm Social Program: Lincoln Sites Tour. Meet in the Illini Union North Lobby, facing the circle drive.

MORNING, TUESDAY, OCTOBER 8

ILLINI ROOM A

Plenary Session
8:00–8:05 Introductory announcements, Joseph W. Stucki, Chair
8:05–8:10 Greetings from SSSA, Carolyn Olson
8:10–8:20 Introduction of the Marilyn & Sturges W. Bailey Distinguished Member Award Recipient
John F. Rakovan, Miami University, Oxford, Ohio
8:20–9:05 Stephen Guggenheim* and A. F. Koster van Groos: NEW X-RAY ENVIRONMENTAL INSTRUMENTATION FOR STUDYING SOLIDS IN SOLID-LIQUID-GAS SYSTEMS UNDER CONFINING PRESSURES AT ELEVATED TEMPERATURES (BAILEY AWARD LECTURE)

Technical Sessions

ILLINI ROOM A

Iron Redox Processes. I
Organizers: Molly M. McGuire and Alanah Fitch
9:40–10:00 Christopher A. Gorski*, Laura E. Klupfel, Andreas Voegelin, Michael Sander, and Thomas B. Hiddes: INFLUENCE OF SMECTITE MINERALOGY ON MEASURED REDOX PROPERTIES: A COMBINED ELECTROCHEMICAL AND SPECTROSCOPIC STUDY
10:00–10:20 Coffee Break
10:20–10:40 Anke Neumann, Tyler L. Olson, Weiqiang Li, Brian L. Beard, Clark M. Johnson, Kevin Rosso, Vitaly Alexandrov, and Michelle M. Scherer*: REDOX REACTIONS BETWEEN AQUEOUS Fe(II) AND STRUCTURAL Fe(III) IN CLAY MINERALS: A NEW CONCEPTUAL FRAMEWORK
10:40–11:00 Linduo Zhao*, Hailiang Dong, Ravi Kukkadapu, Abinash Agrawal, Deng Liu, Jing Zhang, and Richard E. Edelmann: BIOLOGICAL OXIDATION OF IRON(II) IN MICROBIALLY REDUCED NONTRONITE COUPLED WITH NITRATE REDUCTION BY PSEUDOGULBENKIANIA SP. STRAIN 2002

TECHNICAL SESSIONS

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11:00–11:20 Sheldon K. Su, Martin Pentrák*, Linda Pentráková, Adi Radian, Yael Mishael, and Joseph W. Stucki: OXIDATION OF IRON(II) BY NITRATE IN ABIOTICALLY REDUCED SMECTITE

11:20–11:40 Alannah Fitch* and Thomas Nelson: ALTERATIONS IN QUINONE AQUEOUS ELECTROCHEMISTRY ASSOCIATED WITH MONTMORILLONITE CLAY

11:40–12:00 Janice L. Bishop* and Will P. Gates: VARIATION IN SMECTITE OH BAND POSITION WITH CATION CHEMISTRY: ANALYSIS OF VIBRATIONAL BANDS IN SPECTRA OF BEIDELITE, MONTMORILLONITE, NONTRONITE, AND HECTORITE

ILLINI ROOM B
Poster Presentations
7:30 am–5:15 pm Poster Presentations Setup
5:30–7:00 pm Authors Present at Poster Presentations

ILLINI ROOM C
General Session. III
Organizers: Michael F. Aldersley, David L. Bish, F. Javier Huertas, and Jana Madejová

9:20–9:40 Hongping He*, Tian Li, Qi Tao, and Tianhu Chen: ALUMINUM ION OCCUPANCY IN THE STRUCTURE OF SYNTHETIC SAPONITES: EFFECT ON CRYSTALLINITY

9:40–10:00 Mathias H. Koster* and H. Albert Gigu: BORON IN SMECTITE FROM CALCIUM AND SODIUM BENTONITE DEPOSITS

10:00–10:20 Coffee break


10:40–11:00 Michael A. Velbel*, Eric K. Tomui, and Michael E. Zolensky: REPLACEMENT OF OLIVINE BY SERPENTINE IN THE QUEEN ALEXANDRA RANGE 93005 CARBONACEOUS CHONDRITE (CM2) REACTANT-PRODUCT COMPOSITIONAL RELATIONS AND SOVOLUMETRIC CONSTRAINTS ON REACTION STOICHIOMETRY AND ELEMENTAL MOBILITY DURING AQUEOUS ALTERATION

11:00–11:20 Jeffrey E. Post*, Cara M. Santelli, and Michael A. Velbel*: PRESERVING A LEGACY WHILE PRESERVING A COLLECTION: A PROPOSED CMS 50TH ANNIVERSARY PROJECT


PINE ROOM
Evolving Applications of Natural Molecular-sieve Zeolites
Organizers: Steven M. Kuznicki, Tetyana Kuznicki, and Albana Zeke

9:20–9:40 Tetyana Kuznicki, Daniel B. Kuznicki, and Steven M. Kuznicki*: ADVANCES IN MOLECULAR SIEVES: NEW POTENTIAL FOR UTILIZING THE PROPERTIES OF MINERAL NATURAL Zeolites

9:40–10:00 Ian Wu, James A. Sawada, Sayed Alireza Hosseinizadeh-Hejazi, Paul Svenson, WeiZhu An*, Tetyana Kuznicki, and Steven M. Kuznicki: NATURAL SODALITE MEMBRANES FOR SELECTIVE HYDROGEN SEPARATIONS

10:00–10:20 Coffee break
10:20–10:40 Weizhu An*, Xiaoxia Zhou, Xin Liu, Pei Chan, and Steven M. Kuznicki: NATURAL ZEOLITE CLINOPTILOLITE-PHOSPHATE COMPOSITE MEMBRANES FOR WATER DESALINATION

10:40–11:00 Weizhu An*, Omar Zarro, Paul Swenson, and Steven M. Kuznicki: NATURAL CLINOPTILOLITE AND ITS PHOSPHATE COMPOSITE MEMBRANES FOR H₂ SEPARATION FROM CO₂

11:00–11:20 Lan Wu* and Steven M. Kuznicki: SYNTHESIS AND CHARACTERIZATION OF CHABAZITE ANALOG FROM DELAMINATED METAKAOLIN WITH HIGH CRYSTALLINITY AND LOW Si/Al RATIO

11:20–11:40 Narasimhan Loganathan*, Pascal Boulet, Bogdan Kuchta, Oliver Schaef, and Renaud Denoyel: ADSORPTION AND ENERGETICS OF PROTEIN BOUND UREMIC TOXIN IN THREE DIFFERENT ZEOLITIC SYSTEMS—A COMPUTATIONAL MONTE CARLO STUDY

11:40–12:00 Sayed Alireza Hosseinzadeh Hejazi*, James A. Sawada, and Steven M. Kuznicki: CHARACTERIZATION OF NATURAL ZEOLITE MOLECULAR SIEVES USING ZERO-LENGTH COLUMN CHROMATOGRAPHY TECHNIQUE

NOON, TUESDAY, OCTOBER 8

12:00–1:20 Lunch break—on your own

12:00–1:20 CMS Nomenclature Committee (by invitation), Ballroom

AFTERNOON, TUESDAY, OCTOBER 8

ILLINI ROOM A Iron Redox Processes. II

Organizers: Molly M. McGuire and Alanah Fitch

1:20–1:40 Chelsea Neil*, Young-Shin Jun, and Jeffrey Y. Yang: IRON OXIDATION AND PHASE TRANSFORMATION DURING ARSENOPYRITE DISSOLUTION INDUCED BY MANAGED AQUIFER RECHARGE

1:40–2:00 Tae-hee Koo*, Toshihiro Kogure, Jae-hoon Kim, and Jin-wook Kim: THE STRUCTURAL AND CHEMICAL MODIFICATION OF NONTRONITE ASSOCIATED WITH MICROBIAL Fe(III) REDUCTION UNDER VARIOUS REDOX CONDITIONS: INDICATORS OF “ILLITIZATION”


2:20–2:40 Alanah Fisch* and Anna Weiss: ALTERATIONS IN 2,6-DISULFONATE ANTHRAQUINONE AQUEOUS ELECTROCHEMISTRY ASSOCIATED WITH MONTMORILLOCNITE CLAY

3:00–3:20 Coffee break

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3:00–3:20 Coffee break
ILINI ROOM A  
**Industrial and Specialty Clay Minerals. II**  
Organizers: Marc Herpfer, William F. Moll, and Haydn H. Murray  
3:20–3:40 Ian D. R. Mackinnon* and Graeme J. Millar: **PRACTICAL APPLICATIONS FOR CLAY-DERIVED ZEOLITE N: AN AMMONIUM-SELECTIVE ION EXCHANGER FOR INDUSTRY USE**  
3:40–4:00 William J. Miles*: **BENTONITE COMMODITY MARKET TRENDS FOR TWO DECADES**  
4:00–4:20 William J. Miles*: **ARMAGOSA VALLEY SEPIOLITE MINERALOGY AND MARKETS**

ILINI ROOM B  
**Poster Presentations**  
7:30 am–5:15 pm Poster Presentations Setup  
5:30–7:00 pm Authors Present at Poster Presentations

ILINI ROOM C  
**General Session. IV**  
Organizers: Michael F. Aldersley, David L. Bish, F. Javier Huertas, and Jana Madejová  
1:40–2:00 Gary P. Tomaino* and William F. Moll: **WHAT WE HAVE LEARNED ABOUT OPAL: IDENTIFICATION/MISIDENTIFICATION, QUANTIFICATION, AND REGULATION**  
2:00–2:20 Claudia Belviso, Francesco Cavalcante, F. Javier Huertas, Luca Medici, Ashille Palm, Piero Ragine, and Saveno Fiore*: **TRACE ELEMENTS MOBILITY IN THE CLAY FRACTION OF MARINE SEDIMENTS**  
3:00–3:20 Coffee Break

ILINI ROOM C  
**Molecular Studies of Clay Minerals and Related Structures. III**  
Organizers: Randall T. Cygan and Jeffery A. Greathouse  
3:20–3:40 Narasimhan Loganathan and Andrey G. Kalinichev*: **MOLECULAR DYNAMICS SIMULATION OF Cs+ ION ADSORPTION AT THE HYDRATED MUSCOVITE SURFACE–INTERFACIAL STRUCTURE AND ADSORPTION ENERGY PROFILES**  
3:40–4:00 Xiandong Liu*, Xiancai Lu, Michel Sprik, Jun Cheng, Evert Jan Meijer, and Rucheng Wang: **UNDERSTANDING ACID-BASE CHEMISTRY OF CLAY MINERALS USING FIRST PRINCIPLE MOLECULAR DYNAMICS**

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XXIV
Marimuthu Krishnan, Moumita Saharay, and R. James Kirkpatrick*: MOLECULAR DYNAMICS MODELING OF CO2 AND POLY(ETHYLENE GLYCO) IN MONTMORILLONITE: THE INTERLAYER STRUCTURE OF CLAY-POLYMER COMPOSITES AND THE INCORPORATION OF CO2

PINE ROOM  Modified Clays for Environmental Applications
Organizers: Yael Mishael and Hongping He

1:20–1:40 Runliang Zhu*, Qingze Chen, Jianxi Zhu, Qi Tao, and Hongping He: AN EFFECTIVE METHOD FOR ENHANCING THE ADSORPTION CAPACITY OF TMA MODIFIED MONTMORILLONITE

1:40–2:00 Jakub Matusik* and Anna Wcislo: EQUILIBRIUM AND KINETIC STUDY OF HEAVY METALS SORPTION ON GRAFTED HALLOYSITE

2:00–2:20 Selina I. Omonnhenle* and Ian J. Shannon: CLAY DERIVED MATERIALS FOR ENVIRONMENTAL MANAGEMENT

2:20–2:40 Linda Pentráková*, Martin Penticr, Kai Su, Adi Radian, Yael Mishael, and Joseph W. Stucki: NITRATE REDUCTION BY REDOX-MODIFIED SMECTITES EXCHANGED WITH NATURALLY OCCURRING POLYMERIC CATIONS

2:40–3:00 Hagay Kohay*, Avital Izbitsky, and Yael Michael: DEVELOPING AN EFFICIENT POLYMER-MINERAL SORBENT FOR FILTRATION OF DICLOFENAC IN THE PRESENCE OF DISSOLVED ORGANIC MATTER

3:00–3:20 Coffee break

3:20–3:40 Georg H. Grathoff*, Jan Dietel, Marko Bertmer, Katja Emmerich, and Laurence N. Warr: GEOPOLYMER CEMENTS FROM EOCENE ILLITE/SMECTITE RICH FRIEDLAND CLAY, NE GERMANY, TO SEAL BOREHOLES

3:40–4:00 Giorgio Ryvó*, Omer Mor, and Maya Samuel: ARE METACHROMASY AND PHOTO-STABILIZATION OF ADSORBED DYES RELATED?

4:00–4:20 Jianxi Zhu*, Hongping He, Jingming Wei, Yanhong Qing, and Lingya Ma: CHARACTERIZATION OF ZWITTERIONIC SURFACTANTS MODIFIED ORGANO-MONTMORILLONITES AND THE INTERCALATION MECHANISM


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Poster Session

Illini Room B
Poster Presentations
7:30 am – 5:15 pm Poster Presentations Setup
5:30 – 7:00 pm Authors Present at Poster Presentations

Alteration and Cation Exchange Processes in Clays, Soils, and Engineered Clay Barriers for Radioactive Waste Disposal

Clays and Isotopes
2 Austin Boles*, Halim Mutlu, Tonguc Uysal, Laurence War; and Ben van der Pluijm: CHARACTERIZATION OF CLAY GOUGE FROM THE NORTH ANATOLIAN FAULT (TURKEY)
3 John Harper* and Paul A. Schroeder: ANOXIC CONDITIONS WITHIN THE SMOKY HILL CHALK MEMBER OF THE NIOBARA FORMATION AND ITS EFFECT ON ORGANIC AND INORGANIC C-N ASSEMBLAGES

CO₂ Sequestration
4 Miao Zhang*, Christopher J. Spiers, Sander M. de Jong, Andreas Busch, and Rick Wentink: SWELLING STRESS DEVELOPMENT IN CONFINED SMECTITE AGGREGATES UPON EXPOSURE TO CO₂

Ferrihydrite and Schwertmannite
5 Yuji Arata* and Allison R. Vandevoort: X-RAY ABSORPTION SPECTROSCOPIC INVESTIGATION OF IONIC SILVER Sorption MECHANISMS AT THE GOETHITE-WATER INTERFACE

General Session
6 Dong Liu, Peng Yuan*, Hongmei Liu, and Hongping He: DETERMINATION OF THE SOLID ACIDITY OF MONTMORILLONITE BASED ON SINGLE NH₃ ADSORPTION SYSTEM
7 Peng Yuan*, Daoyong Tan, Faiza Annabi-Bergaya, and Dong Liu: ORGANOSILANE MODIFICATION OF TUBULAR HALLOYTÉS FOR THE LOADING AND CONTROLLED RELEASE OF IBUPROFEN
9 M. Elena Ramos and F. Javier Huertas*: ADSORPTION OF LACTATE AND CITRATE ON MONTMORILLONITE
10 J. H. Car*, G. D. Zhang, and J. L. Li: CLAY MINERALOGY OF SOILS FROM DEIXING PORPHYRY COPPER ORE FIELD IN JIANGXI PROVINCE, CHINA
11 Simone Patrícia Araúna da Paza, Rômulo Simões Angélica, and Rômulo A. Machewa da Silva: INTERLAYER SPECIES CHARACTERIZATION OF SMECTITES BY LASER LIGHT DIFFRACTION TECHNIQUE: AN INDIRECT EVALUATION
26 Eun-Ju Kim* and Yoon-Seok Chang: SULFIDE MINERALS-COATED IRON NANOPARTICLES AND THEIR ENVIRONMENTAL APPLICATIONS: CONTAMINANT REACTIVITY AND BIOCOMPATIBILITY
27 Michael Holmboe*, Karin Norrfors, Susanna Wold, and Mats Jonsson: INFLUENCE OF Y-RADIATION ON MONTMORILLONITE: EFFECTS ON COLLOID STABILITY, RADIONUCLIDE RETENTION, AND REACTIVITY TOWARDS H₂O₂

Industrial and Specialty Clay Minerals
23 Anja M. Schleicher*, Ben A. van der Pluijm, and Laurence N. Warr: CLAY MINERALS IN THE SAN ANDREAS FAULT: LESSONS LEARNED FROM ROCKS OF THE SAN ANDREAS FAULT OBSERVATORY AT DEPTH (SAFOD) DRILLHOLE
24 Qinfu Liu*, Yinmin Zhang, and Hongfei Cheng: MECHANICAL AND GAS BARRIER PROPERTIES OF RUBBER/KAOLIN NANOCOMPOSITES
25 Hongfei Cheng* and Qinfu Liu: HIGH TEMPERATURE PHASE TRANSITION OF KAOLINITE INTERCALATED BY POTASSIUM ACETATE

Iron Redox Processes
26 Eun-Ju Kim* and Yoon-Seok Chang: SULFIDE MINERALS-COATED IRON NANOPARTICLES AND THEIR ENVIRONMENTAL APPLICATIONS: CONTAMINANT REACTIVITY AND BIOCOMPATIBILITY
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**Modified Clays for Environmental Applications**

28 Giovanna D. Calabria*, Mirian C. Shinzato, and Fernando B. Faria: PRODUCTION OF ZINC-ZEOLITE FROM THERMAL AND CHEMICAL TREATMENTS

29 Jakub Matusik* and Lucyna Matykowska: CHROMATE AND ARSENATE REMOVAL BY KAOLINITE INTERCALATED WITH AMMONIUM SALTS

30 Chun-Chun Hsu* and Youjun Deng: MODIFY SMECTITES TO ENHANCE THEIR ADSORPTION CAPACITIES FOR ZEARALENONE

31 Pingxiao Wu* and Zhujian Huang: ROLES OF CLAY MINERALS IN THE ORIGIN OF LIFE

32 Chun-Chun Hsu* and Youjun Deng: MODIFY SMECTITES TO ENHANCE THEIR ADSORPTION CAPACITIES FOR ZEARALENONE

33 Valéria Bizovská, Ľuboš Jankovič, and Jana Madejová: INTERCALATION OF OCTYLAMMONIUM CATIONS INTO MONTMORILLONITE

**Molecular Studies of Clay Minerals and Related Structures**

34 Brennan O. Ferguson*, Bruce Arey, Tamas Varga, Alice Dobnallkova, R. James Kirkpatrick, and Geoffrey M. Bowers: X-DIFFRACTATION, HELIUM ION AND ELECTRON MICROSCOPY OF SMECTITE-NATURAL ORGANIC MATTER COMPOSITES

35 Florence T. Ling*, Peter J. Heaney, and Jeffrey E. Post: SORPTION OF CONTAMINANT LEAD WITH TRICLINIC AND HEXAGONAL BIRNESITE

**Structural Characterization of Lamellar Compounds and their Nanocomposites**

36 Eleanor Bakker, Zane Prüse, and George E. Christidis*: CESIUM SATURATION: AN ALTERNATIVE APPROACH TO IDENTIFY HETEROGENEITY OF SMECTITES

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**EVERNING, TUESDAY, OCTOBER 8**

8:00– Informal “The Friends (and enemies) of illite/smectite”—assemble at Registration Desk

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**WEDNESDAY, OCTOBER 9**

7:30 am–5:00 pm Registration in Front of Illini Rooms, Main Floor West Corridor

**MORNING, WEDNESDAY, OCTOBER 9**

**ILLINI ROOM A**

Plenary Session

8:00–8:10 Introductory announcements, Joseph W. Stucki, Chair

8:10–8:20 Introduction of the George W. Brindley Lecture Recipient

R. James Kirkpatrick, Michigan State University

8:20–9:05 Andrey G. Kalinichev: TACKLING THE NANOSCALE STRUCTURAL AND COMPOSITIONAL DIVERSITY OF CLAY-WATER INTERFACES IN MOLECULAR SIMULATIONS: RECENT PROGRESS, CHALLENGES, AND OPPORTUNITIES (GEORGE W. BRINDLEY LECTURE)
## TECHNICAL SESSIONS

### ILLINI ROOM A

#### CO₂ Sequestration
Organizers: Andreas Busch and Eugene S. Ilton

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### ILLINI ROOM C

#### Some Intellectual Genealogies: Honoring Those Who Came Before Us. I
Organizer: Duane M. Moore

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### ILLINI ROOM A

#### CO₂ Sequestration
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|------------|-------------------------------------------------------------------
| PINE ROOM  | Organizers: Will P. Gates and William J. Likos                   |
|            | 9:40–10:00 Rebecca McWatters*, Will Gates, Abdelmalek Bouazza, Daniel Wilkins, Greg Hince, Jan Snape, Daniel Jones, and R. Kerry Rowe: GEOSYNTHETIC CLAY LINERS EMPLOYED IN BARRIER SYSTEMS DESIGNED TO CONTAIN HYDROCARBON-CONTAMINATED SOIL IN ANTARCTICA |
|            | 10:00–10:20 Coffee Break                                          |
|            | 10:20–10:40 Will P. Gates* and Abdelmalek Bouazza: PROSPECTS FOR GEOSYNTHETIC CLAY LINER APPLICATIONS IN MINING AND INDUSTRIAL FACILITIES |
|            | 10:40–11:00 Andras Fehervaran*, Antonio F. Patti, Terence W. Turney, Abdelmalek Bouazza, and Will P Gates: GLYCEROL CARBONATE-BENTONITE COMPLEXES FOR ENHANCED CONTAINMENT OF HYPERSONAL LEACHATES |
|            | 11:00–11:20 Faith M. Zang*, William J. Likos, and Craig H. Benson: EFFECTS OF DESICCATION CYCLING AND CATION EXCHANGE ON HYDRAULIC CONDUCTIVITY OF GEOSYNTHETIC CLAY LINERS |
|            | 11:20–11:40 Melissa Setz*, Amara Meier, Sabrina Bradshaw, and Craig H. Benson: EFFECT OF AMMONIUM ON THE HYDRAULIC CONDUCTIVITY OF GEOSYNTHETIC CLAY LINERS |
|            | 11:40–12:00 Kuo Tian*, Erin L. Hunter, Jiannan Chen, Craig H. Benson, and James M. Tinjum: HYDRAULIC CONDUCTIVITY OF GEOSYNTHETIC CLAY LINERS TO LOW-LEVEL RADIOACTIVE WASTE LEACHATE |

| ROOM 407   | Program: Structural Characterization of Lamellar Compounds and their Nanocomposites. I  
| Organizers: Gary J. Beall, Bruno Lanson, and Dougal M. McCarty |
|            | 9:20–9:40 Chengxiang Li*, Huifang Xu, Rucheng Wang, and Hromi Konishi: STUDY OF UNUSUAL BLACK TALC ORES IN GUANGFENG COUNTY, JIANGXI PROVINCE, CHINA |
|            | 9:40–10:00 Katja Emmerich*, Rainer Schuhmann, and Annett Steudel: KINETICS OF DEHYDROXYLATION OF CS-VACANT MONTMORILLONITES AT 540 AND 700 °C AND SPONTANEOUS REHYDROXYLATION |
|            | 10:00–10:20 Coffee break                                          |
|            | 10:20–10:40 Sylvain Grangeon, Bruno Lanson*, Julien Guilhermet, Anne-Claire Gaillot, Martine Lanson, and Alain Manceau: Zn SORPTION MODIFIES DYNAMICALLY THE LAYER AND INTERLAYER STRUCTURE OF VERNADITE |
|            | 10:40–11:00 Reinhard Kleeberg* and Kristian Ufer: THE RIETVELD PROGRAM BGMN—A TOOL USEFUL IN STRUCTURE AND PHASE ANALYSIS OF CLAYS |
|            | 11:00–11:20 Baptiste Dazas, Eric Ferrage, and Bruno Lanson*: INTERLAYER STRUCTURE OF TRIHYDRATED (3W) MONTMORILLONITE |

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NOON, WEDNESDAY, OCTOBER 9
12:00–1:20 Lunch break—on your own
12:00–1:20 CMS Past Presidents’ Luncheon (by invitation), Colonial Room

AFTERNOON, WEDNESDAY, OCTOBER 9

ILLINI ROOM A
CO2 Sequestration
Organizers: Andreas Busch and Eugene S. Ilton
1:40–2:00 Edesio Miranda-Barbosa*: FROM EMPIRICAL METHODS TO MODELING, HOW TO MEASURE THE SEALING CAPACITY OF CAPROCKS.
2:00–2:20 Gernot Rother*, Eugene S. Ilton, Elizabeth G. Krukowski, and Robert J. Bodnar: MONTMORILLONITE INTERACTIONS WITH SUPERCRITICAL CO2: NEUTRON SCATTERING AND EXCESS SORPTION
3:00–3:20 Coffee break
5:00–5:30 CMS ANNUAL BUSINESS MEETING: ILLINI ROOM A; EVERYONE IS WELCOME

ILLINI ROOM C
Some Intellectual Genealogies: Honoring Those Who Came Before Us. II
Organizer: Duane M. Moore
1:20–1:40 Bruce Velde: JOHN HOWER: AN UNUSUAL MENTOR AND FORMIDABLE SCIENTIST
1:40–2:00 Paul A. Schroeder: INTELLECTUAL CLAY SCIENCE GENEALOGY OF PAUL A. SCHROEDER
2:00–2:20 Sridhar Komarneni: LAYER CHARGE DECREASE AND OSMOTIC SWELLING MECHANISMS LEARNED UNDER THE GUIDANCE OF JACKSON ON CLAYS LED TO DESIGNER MATERIALS AT PENN STATE
2:20–2:40 Joseph W. Studki: THE LEGACY OF JOE L. WHITE, A FRIEND AND COLLEAGUE TO ALL HE MET
2:40–3:00 Charles B. Roth: PHILIP F. LOW: A DISTINGUISHED SOIL AND CLAY PHYSICAL CHEMIST, AND PERSONAL COMMENT ABOUT C. E. MARSHALL: CLAY MINERALOGIST AND COLLOID CHEMIST

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3:40–4:00 Douglas K. McCarty: VICTOR DRITS, CLAY SCIENCE PIONEER
5:00–5:30 CMS ANNUAL BUSINESS MEETING: LINNI ROOM A; EVERYONE IS WELCOME

PINE ROOM

Clay Barrier Technologies for Landfills and Mining. II
Organizers: Will P. Gates and William J. Likos
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1:40–2:00 M. Victoria Villar*: LONG-TERM BENTONITE HYDRAULIC CONDUCTIVITY EVOLUTION UNDER LOW HYDRAULIC GRADIENTS
3:00–3:20 Coffee break
3:40–4:00 Xiaoli Wang* and Reinhard Kleeberg: XRD ANALYSIS OF STRUCTURAL PARAMETERS OF DIOCTAHEDRAL SMECTITES BY THE RIETVELD METHOD
5:00–5:30 CMS ANNUAL BUSINESS MEETING: LINNI ROOM A; EVERYONE IS WELCOME

ROOM 407

Structural Characterization of Lamellar Compounds and their Nanocomposites. II
Organizers: Gary J. Beall, Bruno Lanson, and Dougal M. McCarty
1:40–2:00 George E. Christidis* and Eleni Koutsopoulou: A NEW APPROACH TO IDENTIFY TROIOCTAHEDRAL SMECTITES WITH X-RAY DIFFRACTION
2:00–2:20 Jeffrey E. Post* and Peter J. Heaney: TIME-RESOLVED SYNCHROTRON X-RAY DIFFRACTION STUDY OF DEHYDRATION BEHAVIORS OF PHYLLOMANGANATES
2:20–2:40 Kideok D. Kwon*, Keith Refson, and Garrison Sposito: DECONVOLUTION OF TRANSITION-METAL SUBSTITUTION AND INTERCALATION EFFECTS ON LAYER-TYPE IRON MONOSULFIDE (MACKINAWITE) STRUCTURE
3:00–3:20 Coffee break
3:40–4:00 Xiaoli Wang* and Reinhard Kleeberg: XRD ANALYSIS OF STRUCTURAL PARAMETERS OF DIOCTAHEDRAL SMECTITES BY THE RIETVELD METHOD
5:00–5:30 CMS ANNUAL BUSINESS MEETING: LINNI ROOM A; EVERYONE IS WELCOME
THURSDAY, OCTOBER 10

7:30 am–1:00 pm  Registration in Front of Illini Rooms, Main Floor West Corridor

Entertainment from The Other Guys

MORNING, THURSDAY, OCTOBER 10

ILLINI ROOM A  Plenary Session

8:00–8:10  Introductory announcements, Joseph W. Stucki, Chair

8:10–8:20  Introduction of the Pioneer in Clay Science Recipient

Joseph W. Stucki, University of Illinois at Urbana-Champaign

8:20–9:05  Thomas J. Pinnavaia: SILICATE INTERCALATION CHEMISTRY: A FORTY YEAR ODYSSEY
(PIONEER IN CLAY SCIENCE LECTURE)

TECHNICAL SESSIONS

ILLINI ROOM A  Clays and Isotopes

Organizer: Fred J. Longstaffe

9:20–10:00  Samuel M. Savin*: CLAYS AND ISOTOPES: HALF A CENTURY OF NEW QUESTIONS AND NEW ANSWERS

10:00–10:20  Lynda B. Williams* and Richard L. Hervig: UNCONVENTIONAL ISOTOPES IN UNCONVENTIONAL OIL SHALE

10:20–10:40  Coffee Break

10:40–11:00  Fred J. Longstaffe* and Richard J. Léveillé: OXYGEN, HYDROGEN, AND CARBON ISOTOPIC SYSTEMATICS OF KAUAI KEROLITE AND ITS ORGANIC SUBSTRATE

11:00–11:20  Arkadiusz (Arek) Derkowski*, Marek Szczerba, Jan Środoń, and Michał Banaś: RADIOGENIC AR RETENTION DURING SOLID-STATE GLAUCONITE AND ILLITE TRANSFORMATION


11:40–12:00  Ian C. Bourg*, Michael Holmboe, John N. Chrisensen, and Garrison Sposito: ISOTOPIC FRACTIONATION BY DIFFUSION IN CLAY INTERLAYER NANOPORES

12:00–12:20  H. Albert Gidl*, Adrian M. Hall, Karin Ebert, and Anthony E. Fallick: HOT AND COOL KAOULINS OF THE FENNOSCANDIAN SHIELD
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<td>Paul A. Schroeder* and Jason C. Austin: CARBON AND OXYGEN ISOTOPES IN PEDOGENIC GIBBSITE: AN EMERGING RESOURCE FOR UNDERSTANDING SOIL FORMING AND TRANSPORT PROCESSES</td>
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<td>12:40–1:00</td>
<td>Jennifer Huggett*, Fred Longstaffe, David Wray, and Jacob Aduenti: CHARACTERISATION OF GLAUCONY FROM THE SHALLOW MARINE UPNOR FORMATION, LONDON BASIN</td>
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**PROGRAM | THURSDAY, OCTOBER 10**

### Illite: The Big Picture

**Organizers:** Georg H. Grathoff and Jan Środoń

**ROOM 407**

**Ferrihydrite and Schwertmannite**

**Organizers:** Rob Fitzpatrick and Huifang Xu

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<td>Jessica Ray*, Benjamin Gilbert, and Young-Shin Jun: DRYING-INDUCED AGGREGATION AND PHASE TRANSFORMATION OF IRON OXIDE NANO PARTICLES: IN SITU AND EX SITU PROPERTIES GOVERNED BY FORMATION CONDITIONS</td>
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<td>Young-Shin Jun*, Yandi Hu, Chelsea W. Nei, and Byeongdu Lee: AN IMPROVED UNDERSTANDING OF IRON (HYDRO)OXIDE FORMATION ON ENVIRONMENTALLY ABUNDANT MINERALS</td>
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11:00–11:20 Haleigh Howe*, Lev Spivak-Birndorf, Derrick Newkirk, and Laura Wasylenki: STABLE NI ISOTOPE FRACTIONATION IN SYSTEMS RELEVANT TO BANDED IRON FORMATIONS
11:20–11:40 Aaron Thompson*, Viktork Tishchenko, Christof Meile, Michelle Scherer, Tim Pasakarnis, and Jared Wilmoth: Fe2+ CATALYZED IRON ATOM EXCHANGE IN SOILS FROM THE LUQUILLO CRITICAL ZONE OBSERVATORY
11:40–12:00 Huifang Xu*, Hiromi Konishi, and Eric E. Roden: CRYSTAL STRUCTURES AND DOMAIN STRUCTURES OF FERRIHYDRITE: DIRECT OBSERVATION USING Z-CONTRAST IMAGING METHOD

AFTERNOON, THURSDAY, OCTOBER 10
1:00–5:00 Field trip to Morrow Plots, Urbana Moraine, and Fithian Illite. Meet in the Illini Union North Lobby, facing the circle drive

EVENING, THURSDAY, OCTOBER 10
6:00 pm–8:00 pm Informal BBQ at Stucki's Home. All are invited, but please RSVP to jstucki@illinois.edu to get directions and further instructions.

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GEOCHEMICAL STUDIES OF THE REGOLITH TREND IN MOKURO ITAGUNMODI IN IFE ILESA SCHIST BELT OF SOUTHWESTERN NIGERIA

Emmanuel J. Ajidahun* and Rufus T. Ajayi

The geochemistry of regolith overlying basement rocks in Mokuro-Itagunmodi area along selected road-cut sections was investigated with a view to determining the mineralogy, elemental concentrations and their distribution patterns in relation to the bedrock, and possible mineralization.

Elemental concentrations were determined with Energy Dispersive X—Ray Fluorescence (ED-XRF) analytical technique while mineralogical constituents were also determined using the X-Ray Diffraction (XRD) technique. In addition, Petrographic studies of bedrock sample were carried out using the petrographic microscope.

The results of petrographic studies showed that tremolite-anthophyllite schist and amphibolite constitute the main lithologies in the study area. The concentration of Al₂O₃ ranged between 23 wt % and 25 wt % whilst Fe₂O₃ ranged between 22 wt % and 30 wt % in the mottled zone indicating a bauxitic laterite. In comparison with the parent rocks, the regolith revealed significant depletion in SiO₂, CaO, Na₂O, K₂O and MgO whilst Al₂O₃, Fe₂O₃, TiO₂, MnO, Cr, Cu, V and Cu were relatively enriched. The overall distribution patterns suggested that vertical dispersion played significant role during the weathering of these rocks. Furthermore, the association of Cr, Ni, Cu, V, Zn suggested strong mafic-ultramafic influence whilst the strong and significant relationships of Fe and Mn with As, Co, Cu, Ni and Zn (r² ranged between 0.44 and 0.92 at p ≤ 0.01) indicated a redistribution of potential pathfinder elements into oxides of Fe and Mn resulting from adsorption and co-precipitation in the surficial environments. The major minerals in the regolith are kaolinite, quartz, chlorite, goethite, rutile, chromite, ilite, smectite and montmorillonite. Kaolinite, quartz, chlorite and goethite had mean relative proportions of 35.68 %, 29.95 %, 16.32 % and 12.02 %, respectively. The relatively high proportion of kaolinite resulted from conversion of chlorite and montmorillonite due to well drained environment while the absence of gibbsite indicated the early stage of weathering in the area.

The element associations and distribution patterns reflect strong mafic-ultramafic influence, however, the effect of heterogeneous bedrock could not be ruled out. Furthermore, the clay mineral distribution implied that early stage of weathering in a well drained environment was achieved. In terms of exploration application, the relatively high Ni and As enrichment probably indicate disseminated nickeliferous sulphide and gold mineralization.

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Elemental concentrations were determined with Energy Dispersive X—Ray Fluorescence (ED-XRF) analytical technique while mineralogical constituents were also determined using the X-Ray Diffraction (XRD) technique. In addition, Petrographic studies of bedrock sample were carried out using the petrographic microscope.

The results of petrographic studies showed that tremolite-anthophyllite schist and amphibolite constitute the main lithologies in the study area. The concentration of Al₂O₃ ranged between 23 wt % and 25 wt % whilst Fe₂O₃ ranged between 22 wt % and 30 wt % in the mottled zone indicating a bauxitic laterite. In comparison with the parent rocks, the regolith revealed significant depletion in SiO₂, CaO, Na₂O, K₂O and MgO whilst Al₂O₃, Fe₂O₃, TiO₂, MnO, Cr, Cu, V and Cu were relatively enriched. The overall distribution patterns suggested that vertical dispersion played significant role during the weathering of these rocks. Furthermore, the association of Cr, Ni, Cu, V, Zn suggested strong mafic-ultramafic influence whilst the strong and significant relationships of Fe and Mn with As, Co, Cu, Ni and Zn (r² ranged between 0.44 and 0.92 at p ≤ 0.01) indicated a redistribution of potential pathfinder elements into oxides of Fe and Mn resulting from adsorption and co-precipitation in the surficial environments. The major minerals in the regolith are kaolinite, quartz, chlorite, goethite, rutile, chromite, ilite, smectite and montmorillonite. Kaolinite, quartz, chlorite and goethite had mean relative proportions of 35.68 %, 29.95 %, 16.32 % and 12.02 %, respectively. The relatively high proportion of kaolinite resulted from conversion of chlorite and montmorillonite due to well drained environment while the absence of gibbsite indicated the early stage of weathering in the area.

The element associations and distribution patterns reflect strong mafic-ultramafic influence, however, the effect of heterogeneous bedrock could not be ruled out. Furthermore, the clay mineral distribution implied that early stage of weathering in a well drained environment was achieved. In terms of exploration application, the relatively high Ni and As enrichment probably indicate disseminated nickeliferous sulphide and gold mineralization.
REMOVAL OF AFLATOXIN BY SMECTITE FROM SIMULATED AND REAL FERMENTATION SOLUTIONS DURING BIOFUEL PRODUCTION

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Bentonite clays have long been used as additives in aflatoxin contaminated corn to reduce its toxicity. With increasing demand for sustainable energy, about 34% of the U.S. corn is now being used for biofuel production. To reduce wastage of corn, the biofuel industry should be an ideal place to accept the aflatoxin contaminated corn. However, during fermentation process for ethanol production, the aflatoxin become concentrated up to three times in the byproduct of the matrices known as dried distiller’s grain with soluable (DDGS), which are extensively used for livestock consumption.

The objective of the current research is to test the efficiency of smectites in removing aflatoxins from the fermentation solution so that the goals of minimizing the toxicological effects of aflatoxinB1 (AfB1) to both human and animal, and of maximizing the profitability of the corn growers, animal and biofuel industry can be achieved.

Four calcium bentonites from Mississippi and Alabama were investigated for their aflatoxinB1 adsorption characteristics after screening some physical and chemical properties. Their mineralogy were evaluated by X-ray diffraction, scanning electron microscope, Fourier transform infrared, and transmission electron microscope. AflatoxinB1 (AfB1) adsorption isotherms were conducted on these clays. Ethanol and sugar in fermentation solutions are the two major potential competing compounds for the adsorption sites on smectites with aflatoxin. Both ethanol and sugar can access the interlayer space of smectites as indicated by the literature. We conducted aflatoxin adsorption experiments in with the simulated fermentations which contained up to the upper limit values in real fermentation solutions. Real fermentation solution was collected from a local ethanol plant. Aflatoxin will be spiked into the real fermentation solution to investigate the effect of other fermentation matrix on smectite’s adsorption efficacy for aflatoxins.

The mineralogy of the samples proved that all the bentonites had smectite as a predominant mineral associated with other minerals like quartz, pyrites, calcites, feldspars, etc. For aflatoxin adsorption experiments, calcium saturated clays of <2µm were used. The experiments showed that all the bentonites were good adsorbents for AfB1. Higher adsorption capacity e.g., 8.6 mol/kg (almost 19% of the weight) for aflatoxin was found in one Mississippi bentonite. The aflatoxin adsorption isotherms in the simulated fermentation solutions suggested that ethanol and glucose had very little effects on smectites’ adsorption for AfB1. Compared with adsorption in solutions free of these two compounds, more than 90% of the clay’s adsorption capacity for the aflatoxin have been preserved even with higher amounts of ethanol (up to 20% of the volume of the solution) and glucose (up to 10% of the weight of the solution).

The preliminary results suggested that bentonites were still effective adsorbents for mycotoxins during biofuel production. We are extending our research by analyzing the clay’s efficiency to bind AfB1 in contaminated real fermentation solutions by HPLC method. The results will be reported at the conference.
THE MONTMORILLONITE CATALYZED SYNTHESIS OF RNA DIMERS
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A synthesis has been developed providing nucleotide dimers comprising natural or unnatural nucleoside residues. A ribonucleoside 5¢-phosphorimidazolide is added to a nucleoside adsorbed on montmorillonite at neutral pH with the absence of protecting groups. Approximately 30% of the imidazolide is converted into each 2¢-5¢ dimer and 3¢-5¢ dimer with the rest hydrolyzed to the 5¢-monophosphate.

Experiments with many combinations have suggested the limits to which this method may be applied, including heterochiral and chimeric syntheses. This greener chemistry has enabled the synthesis of dimers from activated nucleotides themselves, activated nucleotides with nucleosides, and activated nucleotides with nucleotide 5¢-monophosphates. Both homo- and heterochiral combinations of reagents have been tried.

The montmorillonite catalyzed oligomerization of 5¢-activated nucleotides leads to oligomers up to 50 residues in length (Huang and Ferris, 2007) using the excellent catalyst Volclay®. However, all oligomers must necessarily begin as dimers, so we considered it important to study in detail the formation of these products under prebiotic conditions. Then a meaningful comparison could be drawn between our syntheses and the formation of long oligomers that is part of our studies of the origins of life. In the synthesis of trimers from these dimers, we looked for alternative synthetic methods via a 5¢-phosphate dimer with activated nucleotides as well as 5¢-hydroxy nucleotide dimers with the same reactant.

The method has shown promise in targeting trimer synthesis and the procedure lends itself to the development of combinatorial libraries. The use of enzymatic hydrolysis has played a crucial role in this work, facilitating product identity across the spectrum of products prepared. The yields of the corresponding homochiral and heterochiral dimers from A and U will require careful modeling of the reactants in their interactions with both the clay and one another to locate the source of the similarities and differences.

The lack of reactivity of arabino- and xylo-nucleosides also poses interesting structural, modeling, and origins of life issues. Results with clays that catalyze long oligomer formation only poorly reveal that they too catalyze these dimer syntheses albeit less well than Volclay®.

This research was supported by NASA Astrobiology Institute grant NNA09DA80A.

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NATURAL ZEOLITE CLINOPTILOLITE-PHOSPHATE COMPOSITE MEMBRANES FOR WATER DESALINATION

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Natural zeolite clinoptilolite membranes directly sectioned from the rock deposit (Mt. Kobau and Manery Creek area of British Columbia, Canada) show intrinsic molecular sieve characteristics for selective separations of water and hydrated cations. Although almost complete removal of cations was observed with these dense rock membranes the associated low water flux limited their practical applications. Novel natural zeolite clinoptilolite-based phosphate composite membranes were prepared by dry pressing of mixed powdered materials followed by high temperature autoclave steaming at 150 °C. Figure 1 shows the preparation procedure for natural clinoptilolite phosphate composite membranes used in this study.

Performance of these natural clinoptilolite phosphate composite membranes in water desalination was examined in a cross flow membrane water treatment system with different levels of salinity. Water desalination through the prepared natural clinoptilolite phosphate membranes were measured in a temperature range of 25~95°C and feed side pressure of 1 atm. Cation concentrations (Na, K, Ca and Mg ions) and conductivities of both feed and permeate streams were analysed by AA (Atomic Absorption) and with a conductivity meter (Accumet Excel XL20). Significant reduction of conductivities in the permeate stream was observed at all temperatures studied. Water flux of approximately 20 kg m⁻² h⁻¹ and high desalination of over 98% removal of Na⁺ were obtained with the new composite membranes at 95°C (Figure 2), which is nearly 10 time higher than that of natural zeolite rock membranes. Introducing phosphate into the composite membranes not only provided strong chemical bonding between natural zeolite particles but might have created a chemically favourable interface between zeolite crystals facilitating the desalination process. The technical progress of making natural zeolite membranes from rock sheets into composite natural zeolite membranes will be reported. The potential of moving from an experimental proof-of-concept stage into a commercially valuable membrane technology for various industrial applications will also be discussed.

Figure 1. Preparation procedure for natural clinoptilolite phosphate composite membranes.
Figure 2. Cation concentration in feed and permeate streams at 95°C.
NATURAL CLINOPTILOLITE AND ITS PHOSPHATE COMPOSITE MEMBRANES FOR H₂ SEPARATION FROM CO₂

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Clinoptilolite is one of the most abundant natural zeolites in the world. Its intrinsic framework crystalline structure results in two-dimensional intersecting channels with apertures of 4.4 x 7.6 Å and 4.7 x 4.1 Å. The strong dependence of surface properties and channel sizes on the type, size and chemical properties of the entrained cations allow for possible surface modification and size tuning of the clinoptilolite materials which make them suitable for selective gas separation at high temperatures. Hydrogen separation is vital for the “Hydrogen economy” and its separation from CO₂ has been the focus of current research. Gas permeance and H₂/CO₂ separation through membrane discs made directly from natural clinoptilolite (St. Cloud Mining Inc, New Mexico, USA) and its powder-phosphate composite were evaluated. Natural clinoptilolite phosphate composite membranes were prepared by hydraulic press of commercial clinoptilolite powder with phosphate components, followed by high temperature steaming at 150 °C to 250 °C (Figure 1). XRD analysis of the composite membrane sample showed characteristic patterns of clinoptilolite and formed phosphate.

High hydrogen permeances of 6×10⁻⁷ mol m⁻²s⁻¹Pa⁻¹ and ideal H₂/CO₂ selectivities of 11.7 and 9.5 were observed at room temperature for the sliced natural clinoptilolite mineral aggregates and the lab prepared clinoptilolite powder-phosphate composite membranes, respectively (Figure 2). The hydrogen permselective results from the natural clinoptilolite membranes demonstrate the characteristic zeolitic properties of molecular sieves. The observed high H₂ permeances and H₂/CO₂ selectivities from clinoptilolite-phosphate composite membranes show great potential for natural materials based membrane technology in high temperature hydrogen separations.

Figure 1. Typical natural clinoptilolite phosphate membranes prepared by dry pressing and high temperature steaming.
Figure 2. Single gas hydrogen and CO₂ permeances through a natural clinoptilolite composite membrane at 25 °C.

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FE-CLAY COMPOSITE AS A CATALYST IN THE REACTION OF 2-PROPANOL IN THE GAS PHASE: EVALUATION OF ACID AND REDOX ACTIVE SITES

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Pillarization is an alternative process for catalyst preparation. In general, active species are introduced in the interlayer space of 2:1 type clays, modifying the clay propeties increasing both porosity and thermal stability. Pillaring with iron is interesting since the resulting active species can be active either as acid or redox catalyst depending upon reaction conditions. 2-propanol is a versatile molecule and it can be transformed into important raw products for the industry employing catalytic processes—such as propene and propanone. The former is mostly used for polymer manufacturing and propanone is utilized in the production of paints, plastics and pharmacs. There are two mechanism pathways when 2-propanol interact with a catalyst: if acid sites are prominent the reaction proceeds in the direction of the dehydration product propene. Conversely, the presence of redox sites produces the oxidation product, propanone. In this work, 2-propanol was used as model molecule for evaluation of active sites of a Fe-clay composite. A Brazilian clay (Brasgel) in suspension was mixed with an iron nitrate solution pre-hydrolyzed by sodium carbonate. The material was washed and dried at 60°C overnight following a subsequent calcination at 500°C for 3 h. The raw clay and the Fe-clay composite were characterized by Mössbauer spectroscopy, temperature programmed reduction (TPR), infrared spectroscopy and powder x-ray diffraction (XRD). The catalytic and sites activities were evaluated by the reaction of 2-propanol in the gaseous phase. The reaction was performed by heating the catalyst in an oven from 40°C to 640°C in a quartz tube. A nitrogen stream (30 mL min⁻¹) saturated with 2-propanol vapors (0°C) was introduced in a reactor fixed bed containing 50 mg of the tested material. All products were analyzed by GC (FID detector) and the conversion was calculated using the initial chromatographic peak area of 2-propanol. The selectivity was evaluated by propanone to propene ratios. The raw clay was dominated by a 2:1-type clay as major phase and a poor crystalline goethite (α-FeOOH). After pillaring, the basal space disappeared indicating a collapse in the structure or even the filling of the clay galleries with hematite. In fact, TPR results indicated a profile which is distinguished from the raw clay and also from pure hematite. These differences could be attributed to the different accessibility hydrogen diffusion rates in the resulting structure, indicating that iron is irregularly distributed in the material. Catalytic activity shows that propene is the principal product with a 50% of yield(selectivity of 60%). The first derivative of the conversion rate as function of the temperature indicated that the material is active at relatively low temperature (140°C). Propanone, on the other hand, was formed in a yield of less than 1%. The presence of propene as the main product of 2-propanol indicated that acid sites are more active than redox sites in our working reaction conditions.
CERAMIC PROPPANTS MANUFACTURED FOR HYDRAULIC FRACTURING USING GEORGIA KAOLIN

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Ceramic proppants are a component of completion fluids used in hydraulic fracturing by the petroleum and natural gas industries. Ceramic proppants are used in place of sand and resin-coated sand in conventional and unconventional oil and gas reservoirs where high conductivity needs to be maintained for well production. Ceramic media give high conductivity because of their high strength, uniform particle geometry, and resistance to thermal and chemical degradation.

Kaolin in the southeastern United States extends along the Fall Line from near Lexington, South Carolina; through Wrens, Macon and Andersonville, Georgia; to near Eufala, Alabama. The State of Georgia accounts for the largest total volume of kaolin production in the USA, and the World, for applications such as ceramics, refractories, pigments, and functional additives. Georgia kaolin is mined from sedimentary deposits that are late Cretaceous and early Tertiary in age. The diverse provenance and depositional environment of Georgia sedimentary kaolin results in deposits having a diverse range of chemistry and particle size, which benefit the many uses of Georgia kaolin including as a raw material for ceramic proppants. This presentation will describe features of kaolin-based ceramic proppants produced from sedimentary kaolin deposits mined in Georgia.
In recent years, concerns of silver toxicity have been raised due to popular applications of silver nanoparticles to many consumer products as an antimicrobial agent. As silver nanoparticles enter the environment, there is a great risk for silver to adversely affect human and ecological health. Understanding the fate and transport of silver in aquatic-terrestrial environments becomes critical in regulating its use and assessing the risk. Recent investigations have shown the important silver nanoparticle interactions with soil components: 1) unusually high sorption capacity of silver nanoparticles in soils, 2) phase transformation (e.g., complexation with humic substances and sulfidation) of silver nanoparticles in aqueous systems and or minerals, and 3) the ligand complexation and ligand/proton promoted dissolution of silver nanoparticles. It is evident that sorption of ionic silver and silver nanoparticles in soils and sediments is becoming increasingly important since such geochemical process can suppress/enhance the bioavailability. While our previous investigation examined the interaction of silver nanoparticles in soils, this study focuses on the sorption mechanisms of ionic silver in a common soil mineral, goethite, using experimental geochemistry (e.g., batch sorption experiments and zeta potential measurements) and synchrotron based X-ray techniques (e.g., X-ray absorption spectroscopy).
Characterization of smectite heterogeneity is a complex process and has several analytical constraints. The heterogeneity pertains mainly to the layer charge and charge localization (octahedral vs tetrahedral). Identification of smectite compositional characteristics is important for most industrial applications. Hence several classification schemes of smectites have been proposed, based on their crystal chemical and thermal properties. XRD is has been used for the determination of layer charge and charge heterogeneity. Moreover, application of special treatments such as the Hoffman-Klemmen effect provides a fast tool for distinction of beidellite from montmorillonite.

The purpose of this work is the application of an alternative approach for the characterization of smectite heterogeneity, based on Cs-saturation and glycerol solvation of the clay fractions and examination by XRD. The method was applied to a series of natural dioctahedral smectites of variable layer charge and charge localization (montmorillonites, beidelites and nontronites), and to a series of dioctahedral smectites based on SAz-2 smectite, with gradually reduced layer charge via the Greene-Kelly test. Glycerol solvation was performed at 60 °C and 100 °C for 20-48 h to evaluate the influence of kinetics on the saturation.

The XRD traces of the Cs-smectites are controlled both by the magnitude of the layer charge and charge localization. Montmorillonites with high layer charge form single layer glycerol complexes up to 48 h of glycerol solvation. Gradual decrease of layer charge yields 2 layer complexes. The low charge Wyoming montmorillonites form single layer complexes at 20 h solvation time and mixtures of single and 2-layer complexes with increasing solvation time. This heterogeneity is partially attributed to the charge localization i.e to the tetrahedral. However, SWy-1 montmorillonite displays a greater proportion of single layer complexes than 2-layer complexes, which cannot be attributed only to charge localization. Cs-SAz-2 montmorillonites with reduced layer charge display hysteresis, since they form greater number of single layer glycerol complexes than their natural counterparts with comparable layer charge.

In Al-rich smectites with tetrahedral charge, the type glycerol complexes formed is controlled by the magnitude of the layer charge. High charge beidelites form single layer complexes regardless of the duration of glycerol solvation, whereas their low charge counterparts form mixtures of single and 2-layer complexes at long solvation times. Nontronites and ferruginous montmorillonites form single layer complexes at short solvation cycles which in cases may evolve to mixtures of single and 2-layer complexes at long solvation cycles. The proposed approach is sensitive in identifying charge heterogeneity especially in low charge montmorillonites, which is not usually detected with conventional analytical methods.
MINERALOGY VARIATIONS IN CENTRAL TEXAS BENTONITES DUE TO LOCAL HYDROLOGY INFLUENCES

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Bentonites in Central Texas occur in the narrow Eocene deposit parallel to the coast line. Despite their much younger age than the more widely distributed bentonites in the Northwest states such as Montana and Wyoming, the bentonites in Central Texas are generally Ca-bentonites, showed more variations in mineralogy compositions. The local bentonite industry has classified the clays to different groups according to their color (white, blue, yellow, brown) and “hardness” (soft vs. hard). These categories are the results of differences in the redox chemistry, iron oxide content, occurrence of iron in smectite structures, and abundance of cementing opaline silica.

The mineralogy composition differences are often an indication of varied hydrological processes occurred on a local scale. Due to the importance of the mineralogy on the selection of industry processing procedures, their ultimate commercial applications, and as an indicator of the geological processes, both the industry and the scientific communities have dedicated significant efforts to study the sources, deposition, transportation, and mineral transformation in the bentonite deposit. Unfortunately, most reports from the early studies were not published in scientific journals, and there were many unsettled arguments about the origin and the geochemical processes in the deposits. The objective of this study was to reveal these geological and geochemical processes occurred in the Central Texas bentonites based on mineral composition variations.

Texas bentonite deposits of Jackson group (Eocene epoch) have been studied by many researchers. Deposits of Helms, Clark-Kennard and Dubose, Magdalene Johnson, and Miller in Gonzales and Fayette counties, Texas were selected in this study. Three groups can be distinguished among these deposits: 1) the northeast Miller deposit is characterized by brown yellowish clays, 2) the center deposits (Helms, Clark-Kennard, Magdalene Johnson, Dubose pits) by white clays, and 3) the southwest HW Jonson deposit by white grey clays.

From the Miller deposit three samples were analyzed: yellow clay, brown clay and mudstone. A hard and soft white clay samples were collected from the Clark pit piles. Yellowish jarosite precipitates were observed in this deposit. The Helm pit had an ash layer (divided to upper ash layer and lower ash layer), a bentonite, and a black material sample. Extensive red, orange, and black coatings have been observed along the cracks of bentonite clays in the Helm bentonite. The Kennard pit was adjacent to the Clark pit, but the clays were blue in color. One ash and one bentonite sample were collected. The Magdalene Jonson pit was adjacent to the Clark pit and had similar white bentonite. Distinct stratification was observed in the HW Johnson pit: a blue layer of deposit was sandwiched between two white bentonite deposits, and the blue layer dipped toward the Northeast direction. The samples were air dried, ground, and fractionated for mineral identification of the sand, silt, and clay fractions using X-ray diffraction and electron microscopes.

Preliminary results of the mineralogical composition showed that the bentonite in the Helms deposit was dominated by montmorillonite with opal-cristobalite. The ash layer below this bentonite bed showed montmorillonite, quartz and feldspars but lack of opal. In this deposit, substantial accumulation of manganese oxides occurs in potholes at the bottom of the bentonite layer. The XRD patterns indicated the presence of smectite, halloysite, bimessite, feldspar, and quartz. The Clark—Kennard, Dubos deposits were believed as the same deposit but with different redox chemistry. The two white bentonites from the Clark pit differed in the amount of opal-cristobalite, which was present only in the hard white clay. The volcanic ash of the Kennard pit contained also smectite, suggesting weathering of the ash. It also contained minor amounts of mica, gypsum, feldspars and quartz, suggesting minor influence of later sedimentary processes, and the oxidation of pyrite in the sample. The Dubose sediments contained montmorillonite, gypsum, opal, iron in smectite structures, and abundance of cementing opaline silica.
quartz, and feldspars. There were differences in the pH values of these four deposits. The Helms samples had a pH value ~6, followed by Helms with a pH of 5, Clark and Dubose had a pH of ~4, and the Kennard samples had the lowest pH value of 3. The difference of the pH was mainly due to the oxidation of pyrite in the samples. The blues clays contained more pyrite and they are more acidic.

The mudstone and brown clay in the Miller deposit were similar in their mineralogy. Montmorillonite was the most abundant mineral in the clay fraction. Compared with the bentonites from other deposits, the bentonites in Miller deposit contained much more quartz, feldspars, mica, and kaolinite due to alluvial processes. The yellow clay sample had higher clay content. In the HW Johnson deposit there were three well defined bentonite layers. The upper white clay layer was dominant by smectite and opal with minor amounts of quartz and feldspars. The middle blue clay composition was similar but pyrite was also present. In the low white clay layer opal was not present but clinoptilolite was observed in the silt fraction.

The differences in the deposits and among the strata of the same deposit suggested that the local geological processes and hydrology had determinative roles in the mineralogical and chemical compositions of the deposits and the structural cation compositions of the smectites in the deposits. Ash to bentonite transformation rate, occurrence of redox sensitive minerals either as dispersed phases in the matrix or as coatings were affected by the local hydrology, which in turn, might have been determined by the landscape and the permeability of both overlay and underneath materials.
ABSTRACTS

TRACE ELEMENTS MOBILITY IN THE CLAY FRACTION OF MARINE SEDIMENTS
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The distribution of trace elements in soils is mostly controlled by bedrock geochemistry but some trace elements, mainly heavy metals, are also introduced in the environment by several anthropogenic sources. It is therefore of paramount relevance to establish background elemental concentrations of heavy metals for assessing possible exotic inputs as well as an intrinsic potential toxicity of some lithologies.

A proper risk assessment, and the formulation of effective remediation strategies, cannot leave aside the elemental mobility and bioavailability. As a matter of fact, toxicity of metals strongly depends on their geochemical forms and on sediment forming minerals. Among minerals, clay sized phases play the most important role on the fate and distribution of trace elements. In this study a set of 100 samples of marine clay sediments coming from 5 different locations, formations, and stratigraphic position was investigated to determine concentrations and geochemical mobility of seventeen elements (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sn, Ti, V, Zn) considered important in Italian legislation. Al, Fe, Mn and K were also measured.

The samples were investigated for their granulometric, mineralogical and chemical compositions. Mineralogical compositions of whole sample and clay size fraction have been determined by powder X-ray diffractrion. Their major element content has been measured by X-ray fluorescence spectrometry. The trace element mobility was assessed on the finer fraction (less than 4 microns) by the BCR sequential extraction procedure based on 4 steps to extract: i) exchangeable elements; ii) reducible fraction (mainly related to Fe and Mn oxides); iii) elements bounded to organic matter (oxidizable); iv) and residual elements (in silicates and other resistant minerals). Trace elements concentrations have been measured by inductively coupled plasma mass spectrometry.

As to be expected, the mineralogical composition varies in dependence of the stratigraphic position and age. Whole samples are composed mainly of phyllolites, carboanates, quartz and feldspars. Minor minerals are pyrite, goethite, hematite, (gypsum). Minerals forming clay fraction are interstratified phases (I/S and Chl/S), kaolinite, illite, chlorite, quartz and feldspars. Goethite, hematite, pyrite and gypsum are in very little amounts. Several trace minerals (REE phosphates, apatite, zircon, monazite, metal oxides, etc.) were identified by scanning electron microscopy.

Major elements content agrees well with the mineralogical composition for both whole sample and clay fraction. Trace elements concentrations vary largely in the extracting solutions (up to 2 order of magnitude). Percentages of leached trace elements range from 5% to 18% of their total concentration. Hg concentrations are undetectable or negligible.

The amount of trace elements associated with the most mobile fraction is low and higher amounts were measured for Cd (8%) and for Co, Se, Ni, Pb (2-3%). Cobalt (16%), Te (13%), Cu (10%) and Cu, Cd, Be, Ni (8%) are significantly associated with the oxidisable metal fraction. Higher amount of elements are removed by the 3rd step (elements associated with the organic matter). Cd and Se (14%), Pb (10%), Ni and Mo (9%), Co (6%). The sum of the average values for the 3 steps gets to the following order of elemental mobility: Cd >> Co >> Se >> Ni >> Te >> Cu >> Pb >> Be >> Mo >> Zn >> As >> V >> Ti >> Cr >> Sb >> Sn.

Statistical analyses indicate relationships between concentrations and age and stratigraphic position thus suggesting a possible influence of the diageneric degree on the elemental mobility. High mobility of some hazardous elements should be considered when clays are employed for human uses, environmental controls and risk assessment.
Recent studies have shown that smectite interlayer spacings expand upon contact with CO2 at elevated pressures (Gesting et al. 2012a; 2012b; Bton et al., 2012; Loring et al., 2012; Rother et al., 2013). This swelling of smectites caused by exposure to CO2 could affect cap rocks of CO2 storage sites. The expansion is kinetically fast, occurs at CO2 pressures as low as 1 MPa and is completed at about 8 MPa. The kinetics and magnitude vary for different interlayer cations. For all examined interlayer cations (Na, K and Ca), the magnitude depends on the initial hydration state. Maximal expansion is observed for hydration states at which not all cations are fully hydrated. Dry as well as monolayer and bilayer hydrated smectites show minimal to no expansion. In-situ ATR-FTR and 13C NMR revealed the presence of linear CO2 molecules that were rotationally constrained by possibly more than one interlayer surface, cation, or water binding mode. No carbonate or bicarbonate species were identified (Loring et al., 2012). This is contradicted by Hur et al. (2013) and Romanov (2013), who did observe irreversible intercalation of carbonate species into montmorillonite, using DRIFTS and XPS. De Jong et al. (2012) report CO2 induced swelling pressures around 10 MPa from uniaxial tests on montmorillonite.

The aim of the presented study is to further elucidate the mechanism of CO2 induced swelling of montmorillonites and to check the effect of CO2 on other clay minerals.

Neutron diffraction experiments were performed on the BIODIFF instrument at FRMII in Garsching (Germany). Wyoming montmorillonite (SWy-2, CMS) and BED montmorillonite (commercial bentonite) exchanged with Na, Ca and Cu-Trien at relative humidities of 0, 11 and 33% D2O, as well as a commercially available kaolinite and a finely milled muscovite were analysed in a high-pressure cell. A transmission geometry was used and diffraction patterns were collected with a cylindrical 2D detector (3-120° 2theta, wavelength of 2.68Å). All samples were evacuated in the measurement cell prior to measurement. Patterns were recorded sequentially at 0, 30, 60, 90, 120, 150, 180 and 0 bar CO2 pressure, 318K, over a period of 2h per pressure step.

The neutron diffraction results confirm the expansion of the d(001) spacings of Ca and Na exchanged smectites equilibrated at 11% and 33% RH. The swelling does not increase above 60 bar. The shift to lower angles of the basal spacings is associated with a broadening of their reflections. Higher order basal reflections are shifted rationally, suggesting the presumed intercalation does not produce mixed layering. The expansion was observed to be reversible, although an increase of the intensity of the 00l reflections was recorded in some of the evacuated samples after CO2 exposure. The Cu-Trien exchanged samples showed a remarkable decrease in intensity of the basal reflection upon charging with CO2, but no shift of the d(00l). Cu-Trien is a charged metal-organic complex, which, in solution, exchanges the interlayer cations in smectites. Cu-Trien exchanged smectites are free of interlayer water; since the complex is not hydrated. These diffraction measurements confirm that the interlayer water performs a crucial role in the CO2 induced expansion. The d(001) spacings of the analysed kaolinite and muscovite samples did not change upon exposure to CO2, but an increase of the intensity of the basal reflections was observed. Further data treatment is required for the interpretation of these results. Rietveld clay structures are being fitted to the diffraction patterns to quantify the observed changes of d-spacings. Structure refinements will be done to verify if the presumed CO2 intercalation only affects the interlayer spacing. Diffraction patterns extracted at different eta angles will be compared to analyse sample textures. The latter

References

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is required to quantify the effect of gas pressure induced preferential orientation on the relative intensities of the 00l versus hkl reflections/bands.

Supercritical (318 K, 0-25 MPa) excess CO₂ sorption measurements were performed on the clay samples used for neutron diffraction, by means of a high-precision manometric apparatus. Samples were dried in-situ in vacuum at 473 K for >24 h, prior to measurement. Water vapor equilibrated samples were filled into the measurement cells in a glove box at the corresponding conditions. Precision of the measurements was assessed from repetitions and proved good. All recorded isotherms reach maxima between 7 and 10 MPa. At higher pressures a steep drop of the excess sorbed amounts is observed. All samples, except for the smectites equilibrated at 33% RH, yield negative excess sorption at pressures above 15 MPa. Desorption isotherms are consistently lower than adsorption isotherms. The maxima of the smectite isotherms are higher for the samples equilibrated with 33% RH (0.5 mmol/g) than for 11% RH (0.4 mmol/g), while the 11% RH and dry smectite isotherms are similar. All smectite isotherms are convex upwards in the pressure range below their maximum. Muscovite isotherms are slightly convex upwards but almost linear, while the kaolinite isotherms are concave upwards. The latter implies a weakly sorbing surface in which cooperative interactions are important (IUPAC type III). The maximal excess sorption values for kaolinite (0.6 mmol/g) and muscovite (0.35 mmol/g) are only slightly lower than for smectites, despite their considerably smaller N₂ BET surfaces. Expansion of the d(001) spacings of the clay samples during sorption analysis, due to the exposure to CO₂, would result in a drop of the isotherms to lower excess values, only if the interlayer space is not accessible to sorbate. The observed decrease of the isotherms is at considerably higher pressures than the initiation of expansion as observed with other techniques. Since also kaolinite and muscovite samples yielded negative excess sorption at high pressures, a low density of the sorbed CO₂ phase on clay surfaces should be considered.
George W. Brindley was born in Stoke-on-Trent, England, on June 19, 1905. He had an impeccable pedigree, receiving his M.Sc. in 1928 from the Bragg school in Manchester University and his Ph.D. from Leeds University in 1933. Dr. Brindley (as he was known to virtually all who addressed him) then worked in the Physics Department at Leeds, alongside R.W. James, where he undoubtedly honed his talents in X-ray scattering. Much of his early work at Leeds is still used in the X-ray diffraction field, particularly his treatment of microabsorption. His early work on the relationships between X-ray powder diffraction peak shapes and crystallite size, strain, and disorder also remains valid and is still cited. Dr. Brindley gradually (and accidentally) moved into the field of clay mineralogy, and his 1946 papers on the crystal structure of kaolinite with K. Robinson remain some of his major achievements. Although kaolinite has been studied by a myriad of investigators, the structural details contained in his 1946 papers remain unchallenged and largely unimproved after over 65 years. I can still recall the day he gave me (with much fanfare) a signed copy of one of his last reprints of his 1946 Mineralogical Magazine paper on the structure of kaolinite. His monograph Crystal Structures of Clay Minerals and their X-ray Identification also remains one of the primary references in clay mineralogy, and it is difficult to imagine this reference ever being supplanted.

Dr. Brindley had a reputation as an excellent teacher, and he was an outstanding, albeit quite demanding, mentor. Although he retired the year before I arrived as a graduate student at Penn State, he continued to arrive at work at eight and depart at five, Monday through Friday, and he typically worked Saturday morning. He demanded at least the same of his students, and I was given special dispensation to arrive at nine AM only because I worked each evening until ten or eleven PM. Dr. Brindley was well known as an international ambassador, and many of his students and research associates were international (Figure 1). Perhaps as a result, Dr. Brindley was accustomed to having his students work all year with little or no vacation. During my first semester when I mentioned a trip home for Thanksgiving, we almost parted ways, and I again needed special dispensation to take a few days off for Thanksgiving and Christmas holidays. His students and postdocs at that time had unprecedented access to him, as he focused all of his efforts on research and was always available to chat. He came to the lab, which doubled as student office space, every day promptly at 10 AM for coffee, and we typically chatted for half an hour about clay minerals or politics. He also prepared tea in the lab every afternoon, but he usually enjoyed this in his office just across the hall.

Dr. Brindley loved to talk about field work, often joking that he did it field work in museums. It was there that he obtained many of the fine specimens that he studied over the years, often writing multiple articles on milligram-sized samples. Although he tried to convince me to begin work as a graduate student early, forgoing field camp, I persevered and enjoyed this important capstone experience. But Dr. Brindley did enjoy collecting in the field, and we visited western North Carolina and Riddle, Oregon, to examine some important Ni-phylllosilicate localities. It was during those trips that I first heard him say that there is a Ph.D. thesis in every rock. The longer I work in the field of mineralogy, the more I realize this is true. A Ph.D. thesis is not just a collection of research results; it is also a reflection of the skills, experiences, and passion of the student who created it. A Ph.D. thesis is a statement of the student’s capabilities and potential for future research. It is a testament to the student’s dedication and hard work. It is a celebration of the student’s accomplishments and a preview of what is to come. A Ph.D. thesis is a product of the student’s intellect, creativity, and perseverance.

Figure 1: Dr. Brindley (center), with (from left) Sridhar Komarneni, David Bish, Zoran Maksimovic, and Shoji Yamanaka, circa 1976 in Dr. Brindley’s lab at Penn State.
more I appreciate those words. Whether in the field or in the lab, Dr. Brindley’s attention to detail served him well and made him one of the pre-eminent clay mineralogists of the twentieth century. He applied the same physics that he studied as a graduate student to the fine-grained minerals that are central to our scientific society. And his fundamental understanding of diffraction physics and mathematics allowed him to tackle problems on which we still work. It was a fortunate day indeed for our science when Dr. Brindley was first introduced to clay minerals.
Beidellite $\text{Al}_2\text{OH}$ 4580 2.183

The OH combination (stretching plus bending) band near 2.17-2.32 µm is diagnostic for phyllosilicate detection in remote sensing studies. We present analyses of a large collection of smectites with variable cation chemistries for ground-truthing of smectite detection on the Earth and Mars. The OH band centers are compared with the cation (Si, Al, Fe, and Mg) compositions within octahedral and tetrahedral sites in order to (i) determine their effects on the spectral signatures and (ii) make specific smectite detections from remote sensing. Variations in this band have been studied previously for Al- and Fe-bearing dioctahedral smectites (e.g., Bishop et al., 2002; Gates et al., 2005) and for Al-smectites with varying degrees of Al substitution in the tetrahedral sites (Bishop et al., 2011).

Near-infrared (NIR) reflectance spectra exhibit trends in the OH combination band center depending on the abundance of Al, Fe, and Mg (Figure 1, Table 1). Reflectance and transmittance spectra of the mid-IR fundamental OH stretching and bending vibrational bands are under study as well and will be compared with the NIR reflectance bands in order to assess contributions to the NIR bands from multiple cations. For example, montmorillonite/SWy-1 contains some Fe and Mg cations that broaden the band near 2.21 µm, while SAz-1 contains substantial Mg substitution and low Fe substitution for Al resulting in a narrower band closer to 2.22 µm. In addition to the characteristic nontronite band near 2.29 µm, SWy-1 has a weaker band near 2.24 µm due to AlFeOH sites. An Fe/Mg-smectite from Flagstaff Hill, Calif. exhibits a doublet feature near 2.29 and 2.32 µm consistent with FeOH and MgOH clusters, rather than a disrupted dioctahedral/trioctahedral mixed layer system. The strong apparent correlation of the combination band with cation composition for smectites could extend the use of remote sensing for detailed compositional and geochemical analyses on Earth and other planets.

Table 1. Band Centers for the OH Combination Absorption in Reflectance Spectra of Selected Smectites from Figure 1.

<table>
<thead>
<tr>
<th>Smectite</th>
<th>Wavenumber (cm$^{-1}$)</th>
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<tbody>
<tr>
<td>Beidellite</td>
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Clay minerals modified with organic surfactants have received great attention during past decades because of their use as fillers in clay-polymer nanocomposites. While the intercalation of long chain alkylammonium cations into smectites has been extensively studied, detailed investigation of octylammonium cations has been reported seldom. The objective of the present work was to examine the effect of size and loading amount of dioctylammonium (2C8) and tetraoctylammonium (4C8) cations on the arrangement of surfactants within montmorillonite interlayers. The reason to concentrate on 2C8 and 4C8 assay first was that they were isomers with frequently used surfactants with 1C16 and 2C16 chains in both research and industry. The extent of further study with 1C8 and 3C8 is connected with the promising results achieved with 2C8 and 4C8 and reported in this abstract.

Less than 2 μm fraction of JP montmorillonite (Jelíňová Porok, Slovakia) saturated with Na+ cations and dioctylammonium and tetraoctylammonium salts were used for organoclays preparation. The concentration of organic cations varied from 0.2 to 2.0 mmol.g−1 or between 20 % and 200 % of the CEC of montmorillonite. The carbon analysis revealed gradual, almost linear increase in the quantity of the intercalated surfactant with increasing amount used. The highest content of 172 % and 196 % of CEC was found for 2C8 and 4C8 cations, respectively, at 2.0 mmol.g−1 of the cation used for preparation and suggesting that in addition to organic cations the molecules of the 2C8 and 4C8 salts were co-adsorbed to montmorillonite interlayers and/or outer surfaces. The thickness of the organic phase depended on the cation used and its loading. The d001 value of 2C8-montmorillonite showed consecutive creation of monolayers (1.29–1.37 nm at 0.2–0.4 mmol.g−1 loading), bilayers (1.74–1.87 nm at 0.6–1.2 mmol.g−1) and paraffin (2.32 nm at 1.4–2.0 mmol.g−1) arrangement. For 4C8-montmorillonite the d001 value increased to 2.48 nm at 1.0 mmol.g−1 loading corresponding to paraffin configuration. The content of the intercalated surfactants was followed by IR spectroscopy in the CH stretching (3000–2800 cm−1) and the first overtones (2νCH, 5900–5500 cm−1) regions. The areas of the CH3 and CH2 bands, reflecting the quantity of the adsorbed surfactant, showed good correlation with the values obtained from the carbon analysis. The νCH and 2νCH regions were also used to probe the ordering of the intercalated cations because the positions of the CH2 bands were sensitive to the conformational changes of the hydrocarbon chains. With the increasing amount of the 2C8 and 4C8 cations the νCH and 2νCH bands were shifted to lower wavenumbers. While for 2C8 cation the marked change of the position appeared at 0.6 mmol.g−1 loading, continual changes were observed for 4C8 cation. Downward shift indicated increasing number of all-trans conformers with the alkyl chains in more ordered structure. These findings are of high importance for the preparation of organo-montmorillonite hybrids with less common surfactants not investigated so far in detail for utilization in clay-polymer nanocomposites.
CHARACTERIZATION OF CLAY GOUGE FROM THE NORTH ANATOLIAN FAULT (TURKEY)

Austin Boles1*, Halim Mutlu2, Tonguc Uysal3, Laurence Warr4, and Ben van der Pluijm1

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Field sampling of multiple surface locations along the trace of the North Anatolian Fault Zone (Turkey) has yielded clay-rich fault gouge. Clay gouge has been proposed as an explanation for weak fault behavior on the San Andreas Fault and has the potential to date the timing of fault-related neomineralization as well as identify the source of mineralizing fluids. X-ray Diffraction (XRD) of oriented bulk samples identified six of eight locations with the occurrence of clay minerals. The <2 µm grain size of these samples was further separated into 4 size fractions for detailed characterization. XRD measurements of these size fractions were conducted on oriented and random-powder mounts. Illite or i/S is present in 4 of 6 samples; chlorite or chlorite-smectite is present in all samples; pure smectite is present in 4 samples; and kaolinite is present in multiple samples. Samples containing illite were selected for quantitative XRD analysis, and prepared for stable isotopic analysis and Ar-dating. Characterization of each size fraction of these samples by WiLDFiRE modeling constrains illite polytypism and relative amounts, which range from 0-70% 1Md illite. Based on prior work, we infer that the low-temperature 1Md illite polytype grew within the fault zone, in equilibrium with a fluid that was active during deformation. X-ray Texture Goniometry (XTG) of thick sections of gouge shows weak fabric development, with m.r.d. values ranging from 2-2.2, which further supports in situ growth of clays. Samples will be processed for Ar-radiometric and O/H isotopic analysis that will constrain the timing of clay growth and the fluid source for neomineralization during deformation, respectively. We hypothesize for the NAF that meteoric water infiltrated along a dynamically evolving fracture network, resulting in the production of illitic clays that would locally promote creep behavior.

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Quartz overgrowth cement typically is the most important control on reservoir quality in quartzose sandstones that have experienced high thermal exposures. In such sandstones vast improvements in reservoir quality occur where authigenic grain coating chlorite has inhibited the nucleation of quartz overgrowths. It is the chlorite distribution, and not its volume, that is the critical control on its effectiveness for preserving reservoir quality as illustrated in Figure 1.

We have developed a model that attempts to predict both the volume abundance and coat coverage of authigenic chlorite that forms from the alteration of volcanic rock fragments (VRFs). Although chlorite forms from a number of mechanisms, sandstones with VRFs and associated authigenic chlorite are found throughout the world in reservoirs of diverse ages and depositional settings.

To build a predictive model we need to consider how VRFs alter to form chlorite, the spatial distribution of the chlorite as the reaction proceeds, and properties of the chlorite as it forms. We have improved our understanding of these factors by conducting a series of high temperature experiments as well as by examining natural samples. Our experiments were conducted using hydrothermal reactors with two component mixtures of quartz grains and andesite, pyroxenite, or volcanic glass. We also measured chlorite abundance, grain coverage, and thickness together with the volumes of unaltered, replaced, and dissolved VRFs in sandstones from five datasets.

The model simulates VRF dissolution and chlorite formation from the time of deposition to the present day. Input parameters include the depositional volume abundances and types of VRFs, the partitioning of chlorite between replacement and cement, the nominal chlorite thickness, and the kinetics of dissolution for each VRF type. The model simulates the pore wall area available for chlorite growth while accounting for the grain size distribution and the impact of compaction and cementation. Model output through geologic time includes chlorite cement and replacement abundances, the amount of VRF replacement and dissolution, the grain coat coverage, and the average coat thickness. The model is coupled with models of sandbox compaction, quartz cementation, plagioclase albitionization, and other mechanisms.
diagenetic processes as well as with models of bulk physical properties including porosity, permeability, mineralogy, chemical composition, and elastic bulk and shear moduli.

We have tested the model on five datasets with fairly well developed grain coating chlorite. In our initial tests we were reasonably successful in reproducing the measured grain coat coverage in most samples but tend to overpredict the secondary porosity resulting from VRF dissolution (Figure 2). The overestimate in VRF dissolution may reflect the compactional loss of dissolution pores or indicate additional sources for the chlorite mass including, for instance, alteration of in situ or interbedded detrital clay.
ISOTOPIC FRACTIONATION BY DIFFUSION IN CLAY INTERLAYER NANOPORES
Ian C. Bourg*, Michael Holmboe1,2, John N. Christensen1, and Garrison Sposito1,3
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Experimental and molecular dynamics (MD) simulation results have shown that aqueous solutes (metals, halides, noble gases, methane, CO2) undergo kinetic isotope fractionation during diffusion in liquid water according to the inverse power law $D \propto m^{-b}$ with $b = 0$ to 0.2 (Schloemer and Krooss, 2004; Richter et al., 2006; Bourg and Sposito, 2007, 2008; Bourg et al., 2010; Zeebe, 2011). The experimental database suggests that this kinetic isotope effect may be enhanced in nanoporous media such as clay barriers or reverse osmosis membranes (Fritz, 1992; Pernaton et al., 1996). Here, we present MD simulations that use well tested methodologies for simulating diffusion in clay interlayers (Holmboe and Bourg, in prep) to probe the kinetic isotope fractionation of methane, CO2, and Li+ in clay interlayers and in bulk liquid water: Our preliminary results confirm that kinetic isotope fractionation by diffusion in clay interlayer nanopores differs significantly from kinetic isotope fractionation by diffusion in bulk liquid water.

Figure 1: Isotopic fractionation power law exponent $b$ of aqueous solutes, plotted as a function of solute radius. Most of the data were obtained for diffusion in liquid water (Schloemer and Krooss, 2004; Richter et al., 2006; Bourg and Sposito, 2007, 2008; Bourg et al., 2010). The arrows show the enhancement of the kinetic isotope effect for solutes diffusing in water-filled nanopores (Fritz, 1992; Pernaton et al., 1996).

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Figure 1: Isotopic fractionation power law exponent $b$ of aqueous solutes, plotted as a function of solute radius. Most of the data were obtained for diffusion in liquid water (Schloemer and Krooss, 2004; Richter et al., 2006; Bourg and Sposito, 2007, 2008; Bourg et al., 2010). The arrows show the enhancement of the kinetic isotope effect for solutes diffusing in water-filled nanopores (Fritz, 1992; Pernaton et al., 1996).
Adsorption, diffusion, and pore microstructure in clay interlayer nanopores play key roles in determining the performance of engineered clay barriers proposed for use in the storage of high-level radioactive waste. These processes are strongly coupled at the molecular scale and on larger scales. For example, adsorption modulates the speciation of solutes in clay barriers, which influences the mobility of solutes and the swelling pressure (and thus microstructure) of the argillaceous medium. The microstructure, in turn, influences adsorption selectivity and solute diffusion coefficients. The resulting feedback loop between adsorption, diffusion, and pore microstructure may significantly influence the performance of engineered clay barriers. Here, we discuss these feedbacks based on our studies of the ion exchange selectivity of clays (Bourg and Sposito, 2011a,b), solute diffusion in clay nanopores (Bourg et al., 2006, 2007, 2008; Bourg and Sposito, 2010, 2011b; Holmboe and Bourg, in preparation), and clay microstructure (Holmboe et al., 2012).
IMPACT OF NATURAL ORGANIC MATTER ON SMECTITE-H₂O INTERFACIAL STRUCTURE AND DYNAMICS—INSIGHTS FROM NMR

Geoffrey M. Bowers*1, Brennan O. Ferguson1, and R. James Kirkpatrick2

1Division of Chemistry, Alfred University, Alfred, NY, 14802, USA; 2College of Natural Science, Michigan State University, East Lansing, MI, 48824, USA

Molecular-scale processes at mineral-water interfaces play crucial roles with respect to our energy future and the well-being of the environment. For example, carbon sequestration via mineralization in deep saline aquifers, the photocatalytic decomposition of H₂O at mineral surfaces for low-energy H₂ generation, the use of mineral analogs in Li⁺ batteries, and the fate and transport rates of organic and inorganic contaminants in the environment all depend critically on the behavior of ions and H₂O at interfaces. In each of these examples, our ability to predict and control these phenomena depends on our understanding of fundamental molecular-scale behavior at mineral-water interfaces.

Significant progress has been made in understanding molecular-scale behavior in hydrated smectite systems due to advances in neutron scattering, nuclear magnetic resonance (NMR), and molecular modeling (see references in Bowers et al. 2011 and Bowers et al. 2013). However, natural organic matter (NOM) is also known to play important roles in metal ion sorption and transport, and NOM is often found associated with minerals in the soils and suspended colloids in natural waters. The impact of NOM on the interfacial dynamics of ions and H₂O in hydrated mineral systems has yet to be explored in great detail. Though some studies have been published examining metal binding structures at NOM-mineral interfaces, we are unaware of any molecular-scale spectroscopic investigations of alkaline and alkaline earth metal binding sites/structures in these more complex clay-NOM systems. Thus, a critical missing piece in our understanding of inorganic and organic contaminant transport in the environment is understanding of the binding structure, diffusion rates, and the chemical mechanisms of motion and binding underlying the structure and dynamics in smectite-H₂O-NOM systems.

In this talk, we will discuss the ways in which the presence of natural organic matter modifies the interfacial structure and dynamics in smectite-H₂O systems using multi-nuclear (¹⁷Na and ⁴⁰Ca) solid-state nuclear magnetic resonance (⁴₀NMR) spectroscopy. For both Na⁺- and Ca²⁺-hectorite (a low-Fe smectite with octahedral Li⁺ for Mg²⁺ charge development) coated with various fractions of Suwanee River NOM, we observe different cation resonances depending on the system H₂O content. At 43% R.H. (dominantly two-layers hydrates for both clays) the Na⁺ environment observed for Na-hectorite-NOM is broader and appears at lower resonance frequency than that observed for the clay without NOM at all temperatures between -100 and +20°C, whereas the Ca²⁺ environment in Ca-hectorite-NOM is quite similar to the clay without NOM (a relatively narrow peak broader than Ca²⁺ in pure aqueous solution appearing at 0 ± 3 ppm). In the presence of excess H₂O, both clay-NOM systems show a narrow resonance representing a mobile cation environment and a second, broader peak that is similar to that for the low-H₂O samples. For Ca²⁺, both peaks in the paste sample and the single peak in the low-H₂O case shift to more positive resonance frequency and broaden with decreasing temperature, matching our observations for Ca-hectorite without NOM. The changes in resonance frequency suggest that the strength of the interactions between the cations and their coordinating species weaken with increasing temperature. The line narrowing indicates that the resonances are influenced by dynamic behavior (e.g., diffusion/hopping of the cation between sites or exchange of the H₂O molecules within or in and out of the cation coordination sphere). None of the resonances are as narrow as in a pure solution, showing that all the Na⁺ and Ca²⁺ are proximity restricted regardless of the hydration state. The results also show that a fraction of both cations remains accessible to moisture despite the NOM coatings.

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In this talk, we will discuss the ways in which the presence of natural organic matter modifies the interfacial structure and dynamics in smectite-H₂O systems using multi-nuclear (¹⁷Na and ⁴⁰Ca) solid-state nuclear magnetic resonance (⁴₀NMR) spectroscopy. For both Na⁺- and Ca²⁺-hectorite (a low-Fe smectite with octahedral Li⁺ for Mg²⁺ charge development) coated with various fractions of Suwanee River NOM, we observe different cation resonances depending on the system H₂O content. At 43% R.H. (dominantly two-layers hydrates for both clays) the Na⁺ environment observed for Na-hectorite-NOM is broader and appears at lower resonance frequency than that observed for the clay without NOM at all temperatures between -100 and +20°C, whereas the Ca²⁺ environment in Ca-hectorite-NOM is quite similar to the clay without NOM (a relatively narrow peak broader than Ca²⁺ in pure aqueous solution appearing at 0 ± 3 ppm). In the presence of excess H₂O, both clay-NOM systems show a narrow resonance representing a mobile cation environment and a second, broader peak that is similar to that for the low-H₂O samples. For Ca²⁺, both peaks in the paste sample and the single peak in the low-H₂O case shift to more positive resonance frequency and broaden with decreasing temperature, matching our observations for Ca-hectorite without NOM. The changes in resonance frequency suggest that the strength of the interactions between the cations and their coordinating species weaken with increasing temperature. The line narrowing indicates that the resonances are influenced by dynamic behavior (e.g., diffusion/hopping of the cation between sites or exchange of the H₂O molecules within or in and out of the cation coordination sphere). None of the resonances are as narrow as in a pure solution, showing that all the Na⁺ and Ca²⁺ are proximity restricted regardless of the hydration state. The results also show that a fraction of both cations remains accessible to moisture despite the NOM coatings.
ORGANIC-INORGANIC HYBRIDS HAVING A TALC-LIKE STRUCTURE: SYNTHESIS, CHARACTERIZATION AND APPLICATIONS AS FILLERS FOR POLYMERS

Jocelyne Brendlé1, Marie-Hélène Tuillier2, Jean-Christophe Gallego1, Marion Lacaud1, Véronique Bounor-Legaré3, Mohamed Bahlou3, Claire Marichal1, Severinne Rigolet1, and Marc Reinholdt4

1Equipe Matériaux à Porosité Contrôlée (MPC), Institut de Science des Matériaux de Mulhouse, CNRS UMR 7361, Université de Haute-Alsace, 68093 Mulhouse Cedex, France;
2Equipe Mécanique Matériaux et Procédés de Fabrication (MMPP), Laboratoire de Physique, Mécanique, Textile (LPMT, EA 4365, conventionnée au CNRS), Université de Haute Alsace, 68093 Mulhouse Cedex, France;
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4Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS UMR 7285–Université de Poitiers, 86022 Poitiers Cedex, France

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2:1 phyllosilicates and especially smectites, display interesting adsorptive and ion-exchange properties, thermal and chemical stability, swellability in polar solvents, and ability to orient to form films. They are thus widely investigated in several fields and in particular in the clay-polymer nanocomposites one. In order to enhance the compatibility between clays and polymers, a treatment has to be performed to render the clay organophilic. This can be achieved by intercalation of organic moieties within the interlayer galleries, via grafting through sol-gel process, by direct synthesis under hydrothermal conditions or sol-gel process.

In this study we focused on the one pot sol-gel synthesis of organic-inorganic talc like hybrids (TLH) having the following chemical formula: Mg3(RSi)4O8(OH)2 (where R stands for the organic part) starting from organotrialkoxysilanes having different functionalities (phenethyl(PE), phenylaminoethyl(PAM), diethyolphosphatoethyl(DEP)) and an ethanolic solution of magnesium salts. The key parameters governing the synthesis were finely tuned for each system. It was shown that low temperature (20-90°C) and short aging times (~1day) lead to the formation of lamellar structure as confirmed by X-Ray diffraction. The chemical formula of the obtained materials were determined by X-Ray fluorescence spectrometry and thermogravimetric analysis. The stability of the Si-C bond was checked by iRTF 13C and 29Si NMR reveal a lower Mg-Mg orbital overlap in hybrids materials than in MgO. The EXAFS analysis emphasises also a deviation from the regular Mg octahedral coordination in talc-like hybrids. Two different Mg-O distances were indeed identified and the shorter one is found to be significantly higher than predicted in the theoretical talc structure. Finally, applications of the different materials as new nanofillers for polymers has been achieved through in situ polymerization of polyethylene (in the presence of PE-TLH and PAM-TLH) and by melt intercalation for polypropylene-DEP-TLH composites.
CLAY MINERALOGY OF SOILS FROM DEXING PORPHYRY COPPER ORE FIELD IN JIANGXI PROVINCE, CHINA

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Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing, 100037, China
*caih_cags@163.com

Dexing porphyry copper ore field is the largest openpit copper ore field in Asia, located in Jiangxi Province in the central China. Its ecological environmental pollution draws the attention of the public. Clay mineralogical study of soil is essential in investigating and evaluating the ecological environment, also in controlling the environmental pollution. So the clay minerals of soils from Dexing mining environment should provide scientific basis for environmental study of polymetallic sulfide deposits.

The samples are collected from Tongchang mining area, one of three main mines in Dexing porphyry copper ore field, including surface soils in the mine waste dump and tailing reservoirs; surface and submerged soils in Dawu River Basin; bottom sediments in Dawu River. Soil minerals are determined by quantitative X-ray powder diffraction (XRD) analysis, with an average content of 38.9% clay minerals and 61.1% nonclay minerals. The clay mineral assemblage is mainly characterized by illite, kaolinite, chlorite, muscovite/vermiculite and illite/smectite mixed-layer mineral (Table 1).

The results showed that these soils in Dexing mining area are rich in illites, belonging to latarite in the initial stage (kaolinitization stage) according to their clay mineral assemblage. A large number of illites formed in weathering and depotaissication of some aluminosilicate minerals (feldspar, muscovite etc.) suggested relatively weak weathering. But soils of different area have different clay mineral assemblage: illite–chlorite is the main clay mineral association of soils in the mine waste dumps, soils of Dawu River basin and the tailing reservoirs are respectively mainly with illite–kaolinite and illite–kaolinite–chlorite association. In the vertical soil profile, surface soils focus on illite whose content is much higher than other clay minerals, but submerged soils have relatively homogeneous clay mineral composition.

The clay minerals play an important role in the migration, transformation and stabilization of heavy metals in soil environment. The species and amount of clay minerals in soils are closely related with environmental heavy metal contamination. The main pollution sources in Dexing area are acid mine wastewater and alkaline wastewater from ore dressing. The major heavy metal elements in soils and water are Cu, Zn, Pb, Hg and As. The contents of Cu, Pb, Zn and Hg in surface soils are higher than those in deep soils, just because the surface soils contain rich illite which is a kind of clay mineral with strong copper, zinc, lead and mercury adsorption capacity. While, the content of As in surface soils is lower than that of deep soils, because of relatively high content of chloride and kaolinite in deep soils. The arsenic adsorption capacity of chloride and kaolinite is greater than that of the other clay minerals.

Table 1. X-ray diffraction analysis data of the clay minerals in soil of Dexing mining area

| Sample No. | Location | Depth (cm) | illite | kaolinite | chlorite | muscovite/vermiculite | illite/smectite
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The structure of zeolite allows cation exchange between the intracrystalline spaces; however, it is limited by the diameter of the pores of this mineral. There are many technological processes to improve some mineral properties, as those related to the ion exchange. In the case of clinoptilolite, the cation exchange with zinc salts is not effective due to its low affinity for this metal. The objective of this research is to improve the retention of zinc in the clinoptilolite structure using zinc solutions and the molten zinc process. The zinc has bactericidal properties and within the zeolite structure can be used as a filter media. To increase the amount of zinc retained in the zeolite structure some tests were performed.

The experiments were carried out in batch tests using different concentrations of zinc in solution (10 to 1100 mg L⁻¹) at ambient temperature (25°C). For these tests, 1 g of natural zeolite (ZN) and zeolite samples preheated at 300°C (Z300) were added to 5 mL of each solution, for a period of 42 h. Afterwards, these samples were filtered and washed with distilled water, and the resulting solutions were chemically analyzed spectrophotometrically. The analysis of the effect of concentration on metal removal indicated that almost 100% of Zn²⁺ (97.4%) was retained by ZN and 90.4% by Z300. In both cases, the removal capacity decreased with increasing of the concentrations of Zn²⁺ in solution – due to the saturation of the exchanging sites of the clinoptilolite. Nevertheless the concentration of the retained zinc in the mineral structure of ZN increased with the zinc concentration (reaching a maximum value of 2.9 mg g⁻¹ at 1000 mg L⁻¹ of zinc). To 2.300 samples, at the same concentration (1000 mg L⁻¹) the adsorbed zinc was 3.4 mg g⁻¹ and at 1400 mg L⁻¹ was 4.1 mg g⁻¹. X-ray fluorescence analysis indicated that ZN (obtained at 1000 mg L⁻¹ treatment) retained 2% of ZnO and Z300 (treated by 1400 mg g⁻¹ of zinc in solution) 5%.

A molten exchange of ZnCl₂ method was also performed with the clinoptilolite (1:1) where the mixture was heated at 380°C for 4 h in a muffle furnace. After the molten process, the sample was washed with distilled water and dried at 110 °C and analyzed by the X-ray fluorescence technique. The result indicated the presence of almost 15% of ZnO in this clinoptilolite sample.

The experimental data confirmed that the clinoptilolite can retain more zinc when treated by the molten ZnCl₂ process than those with zinc in solution.
The "ignimbrite Orvieto-Bagnoregio" (iOB) is an assemblage of Quaternary pyroclastic flows that stretches over a wide area located 80 km NNW of Rome. In detail it is constituted by two main silica under-saturated pyroclastic flows often bearing chabazite and phillipsite. Despite the comprehensive commercial and petrographic knowledge of this rock, no studies have concentrated specifically on understanding the process(es) that led to zeolitization of the flows. Previous research generally focused on the crystal-chemistry of zeolites (and sometime of glass) and the extent of zeolitization through the formation. Because authigenic processes can be strongly influenced by local conditions, detailed sampling is required to detect small chemical-mineralogical variations that otherwise would be missed. The aim of this work is to formulate a zeolitization model that is consistent with the detailed vertical mineralogical variations of the iOB. After a preliminary survey and study all over the iOB cropping area, the best exposed section was sampled on a face of the Palombara quarry (Viterbo province). The section presents two facies belonging to a single pyroclastic flow, grey and poorly consolidated at the bottom and yellow-orange and lithified at the top. The change in color is sharp and occurs along an irregular, sub-horizontal surface. On the quarrying front, a climber has collected nineteen samples, one per meter, along a vertical line. X-ray diffraction analyses detected zeolites only in the yellow-orange facies. The lowest zeolite content was recorded at the top (13 wt.%), and zeolite content never exceeded 40 wt.% (avg. 34 wt.%). Chabazite always prevails over phillipsite (avg. 29 and 4 wt.% respectively). The feldspar content in the yellow facies is greater than in the grey one (avg. 43 wt.% vs. 34 wt.%), whereas volcanic glass is more abundant in the latter (avg.: 17 wt.% vs. 66 wt.%). Chemical analyses by X-ray Fluorescence and atomic absorption spectroscopy revealed Na and K loss in the yellow-orange facies compared with the grey facies, whereas Ca, Mg and Sr showed a gain. Na loss increased from the top to the middle of the zeolitized section, where the strongest loss was recorded. Ca and Sr gains, as well as the Na loss, were correlated with zeolite content along the section: R²=0.8 (both Ca and Sr) and R²=0.9 (Na). Determination of Fe³⁺/Fe²⁺ ratios demonstrated that the different color of the two facies is linked to the higher iron oxidation in the yellow-orange facies. Scanning electron microscope (SEM) observations revealed the sequence of crystallization of the secondary phases in the yellow-orange facies: authigenic K-feldspar → chabazite → phillipsite (Fig.1).

Energy dispersive spectroscopy (EDS) analyses of primary feldspars, authigenic K-feldspars, and volcanic glass showed only minor variations in chemical composition that were not related to stratigraphic position. On the contrary, chabazite and phillipsite revealed a distinct chemical variability linked to the stratigraphy, with zeolites in the central part of the yellow facies being poorer in sodium.
Our data indicate that authigenic processes have been more intense in the central portion of the section, which is consistent with secondary mineralization governed by the progressive cooling of a pyroclastic flow. The base of the flow was not altered because it was quickly cooled by the substrate, giving the grey facies. The original top of the flow deposit, directly exposed to the air, also cooled quickly, acting—as did the bottom of the unit—as a thermal insulator for the core of the deposit. In the hottest section, the phonolitic glass initially began to react forming K-feldspar, leaving an excess of Ca and Na available. Decrease in the $aK^+/aCa^{++}$ ratio, the percolation of water, and progressive cooling resulted in conditions favorable for chabazite nucleation. As chabazite formation consumes more Ca than K, its formation continued until the $aK^+/aCa^{++}$ ratio became favorable for phillipsite nucleation. Secondary mineralization ceased when the unit cooled, as indirectly demonstrated by the significant amount of residual unaltered glass in the zeolitized facies. Only later was the original top of the flow deposit progressively eroded because it was un lithified.

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Chemical evolution of solutes in brines associated with hydrocarbon productions have been explained in terms of model reactions of waters with some common silicate minerals (such as clay minerals, feldspars, and micas) and calcium-magnesium carbonate minerals. These models have failed far short of linking any part of the brine chemistry to hydrocarbon production. Our study of rare earth elements (REEs) in several brines from illite-rich Devonian Woodford Shale in northern Oklahoma points out that existing models must find a way to include the role of diagenesis-catagenesis of organic matter as a means of providing some significant amount of solutes to oil-associated brines. The total REE contents of the brines analyzed ranged from about 0.14 ppb to about 0.57 ppb. The PAAS-normalized distribution patterns of the REEs in each of these brines had some common features which included: Ce negative anomaly, enrichment of the middle rare earth elements (MREEs), Eu positive anomaly, and enrichment of the heavy rare earth elements (HREEs). When taken in conjunction with their K/Rb ratios (which are often far above the average K/Rb ratios of feldspar and clay mineral, and micas), their very high U/Th ratios, and their presence in organic-rich shale rocks containing abundant phosphate nodules, the REE signatures of the brines bear some mark of these solutes, as perhaps several others, having come from organic matter source in these shales.
Geosynthetic clay liners (GCL) are used as an alternative to compacted clay barriers in disposal facilities for coal combustion products (CCPs). GCLs consist of a thin layer of bentonite clay (5~10 mm) sandwiched between two geotextiles and sometimes laminated to a geomembrane. The efficacy of a GCL is controlled by the hydraulic conductivity of the bentonite, which is comprised primarily of the clay mineral montmorillonite. The species and valence of the cations on the surface of the montmorillonite mineral strongly affect behavior of bentonite and the hydraulic conductivity of GCLs. The sodium (Na⁺) cation is the primary cation bound to the surface of the bentonite in most GCLs. Thus, the bentonite in GCLs often is referred to as Na-bentonite. The Na on the mineral surface is exchangeable and can be replaced by other cations in water contacting a GCL.

In this study, the effect of CCP leachates on the swelling of bentonite and the hydraulic conductivity of GCLs was evaluated systematically. CCP leachates for testing were identified from a database of chemical properties of leachates from CCP disposal facilities in the US. Five CCP leachates were identified for testing that represent different conditions in CCP disposal facilities. Five commercially available GCLs were used for testing: two conventional Na-bentonite GCLs (CS and GS), two polymer-modified bentonite GCLs (CR and GR), and one GCL with a bentonite-polymer nano-composite (BPN).

Synthetic leachates were prepared that represent the primary cations and anions in the five CCP leachates: (i) typical CCP leachate, (ii) strongly divalent cation fly ash leachate, (iii) flue gas desulfurization (FGD) residual leachate, (iv) high cation concentration leachate, and (v) trona ash leachate. These leachates were characterized by their ionic strength (I) and relative abundance of the different cation species (RMD) in solution:
where $M_m$ is the total molarity of monovalent cations and $M_d$ is the total molarity of polyvalent cations in the solution. The relationship between $\lambda$ and RMD for the leachates in the CCP disposal facility database is shown in Fig. 1 (base units in M).

Hydraulic conductivity tests were conducted on the GCLs by direct permeation with CCP leachate. All tests were conducted using flexible-wall permeameters at 20 kPa effective stress and an average hydraulic gradient of 190. Results of the hydraulic conductivity tests are summarized in Fig. 2. All of the GCLs had low hydraulic conductivity ($<10^{-10}$ m/s) to typical CCP leachate, The GCLs with BPN and one of the GCLs with polymer-modified bentonite (GR) had very low hydraulic conductivity ($<10^{-11}$ m/s) to all leachates. The GCLs with conventional Na-bentonite (CS and GS) and one of the GCLs with polymer-modified bentonite (CR) had high hydraulic conductivity ($>10^{-7}$ m/s) to trona leachate. Hydraulic conductivities to the high ionic strength, FGD, and strongly divalent cation leachates (shown as low RMD in Fig. 2) varied between GCLs in a non-systematic manner.
The kaolinite intercalation and its application in polymer-based functional composites have attracted great interest, both in industry and in academic fields, since they frequently exhibit remarkable improvements in materials properties compared with the virgin polymer or conventional micro and macro-composites (Gardolinski & Lagaly, 2005). The intercalation can increase the usability of kaolinite. This is due to intercalation can improve the particle size and whiteness or brightness of kaolinite. Therefore, its intercalation complexes are widely used in the fabrication of paper, paints and inks, rubber and plastic, fiberglass, cracking catalysts, cosmetics, medicines, etc. (Franco et al., 2004; Cheng et al., 2010c).

Potassium acetate (KAc) has been shown to readily intercalate within the kaolinite structure (Cheng et al., 2010a). Also of significant interest regarding the kaolinite-KAc complex is its thermal behavior and decomposition (Benazzouz & Zaoui, 2012). This is because heating treatment of intercalated kaolinite is necessary for its further application, especially in the field of plastic and rubber industry.

A systematic study on the thermal decomposition of the kaolinite–KAc complex using XRD was made by the authors (Cheng et al., 2012). Upon heating the complex to 200 °C and cooling back to room temperature in nitrogen atmosphere, two diffraction peaks appeared at 1.168 and 0.972 nm, and the 1.41 nm reflection was missing. Upon exposure to air for 1 min phases were observed with d(001) spacings of 1.41, 1.16, 0.99, 0.89, and 0.86 nm. The 1.41 nm phase corresponds to the fully expanded kaolinite, and the 1.16 and 0.98 nm phases correspond to the two expanded phases of the 200 °C pattern. The two expanded phases at 0.89 and 0.86 nm may correspond to the formation of a hydrated kaolinite.

Our recent finding (Cheng et al., 2010b) showed that the peak intensity of the expanded phase of the kaolinite–KAc intercalation complex decreased with heating above 300 °C, and the basal spacing reduced to 1.19 nm at 350 °C and 0.715 nm at 400°C. The XRD patterns of the kaolinite–KAc intercalation complex reveal that the intercalation complex has completed the dehydroxylation at below 500 °C (Fig 1). At 600°C, the reflections of the intercalation complex and kaolinite disappear and new products are formed. According the standard ICDD reference pattern, it is indicated that the sample has completed the dehydroxylation at below 500 °C (Fig. 1).
that the chemical substance KHCO₃ is present. As the temperature of the system is raised, a small amount of K₂CO₃ is formed at 700 °C by the thermal decomposition of KHCO₃. At the same time, the water and carbon dioxide are released from the complex. The formation of K₂SiO₃, the structure of which is very similar to that of kaliophilite, is observed at a rather low temperature (700 °C). At 800 °C, a new compound (K₂Al₃SiO₈), the structure of which is the same as natrolite, is observed with the reduction by elemental carbon of K₂CO₃. At 900 °C and 1000 °C, the formation of potassium aluminum silicate (K₄Al₂Si₂O₇) is observed. It can be observed a considerable amount of K₃AlO₃ forms in this intercalation complex sample until about 1100 °C. It is concluded that the whole process for the high temperature phase transition of kaolinite-potassium acetate intercalation complex can be mostly described by reactions:

It is concluded that the new chemical formed may be due to: 1) The potassium can decrease the melting point of chemical substance when potassium takes part in the chemical reaction with the raise of temperature. 2) The potassium ion fits into the ditrigonal holes of the oxygen-surface of kaolinite, and it can not be deintercalated from the interlayer. Therefore, the potassium ion exists as a chemical substance that is present at the start of a chemical reaction, resulting in the new chemical substance to appear with the raised of temperature.
SMECTITE HETEROGENEITY IN BENTONITES: THE KEY TO INTERPRET THE UNIQUE PHYSICAL AND CHEMICAL PROPERTIES OF THESE MATERIALS

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Bentonites are industrial clays which consist predominantly of smectite regardless of the mode of origin and have important physical and chemical properties that are dictated by this mineral. They usually but not always form at the expense of volcanic glass. Systematic research over the past 25 years has revealed several important features of the bentonite genesis and has contributed to understanding of the variations in physical and chemical properties, which characterize these clays. Genesis of smectites via alteration of volcanic follows the Ostwald step rule: The system preferentially forms the phase with the fastest precipitation rate, not the most stable phase. Metastable intermediate reaction products have simple structures and form more rapidly than thermodynamically stable minerals. These intermediate phases are often amorphous gels. Smectites transform to more stable minerals with increasing temperature namely illite or chlorite via mixed layer phases. The formation of smectite instead of zeolites during alteration of volcanic glass is facilitated by loss of alkalis in open systems and a high Mg-activity. The frequent presence of zeolites in bentonites indicates the existence of “hydrologically quasi-closed domains” during alteration.

The lack of thermodynamic stability during the formation of bentonites yields considerable heterogeneity in smectites, which pertains mainly to the layer charge and charge localization (octahedral vs tetrahedral). Detailed work by our team has shown that this heterogeneity occurs within the micrometer scale and reflects the existence of microenvironmental heterogeneity. However, the chemistry of the parent rock also controls the crystal chemical characteristics of smectites (Christidis, 2008). The discovery of the compositional heterogeneity renders important the identification of smectite content and the unexpected outcome of alkali-activation, a common industrial practice in most bentonites. The heterogeneity of smectite layer charge is of economic and geologic importance, because it strongly affects key smectite properties such as swelling, cation exchange capacity and ion exchange selectivity as well as rheological properties.

Recent approaches in assessment of bentonites include the distribution of smectite layer charge in bentonite deposits, the charge of smectite fundamental particles and the identification of trioctahedral smectites (Christidis & Eber, 2003; Christidis & Huff, 2009; Christidis & Koutrouposou, 2013). The distribution of smectite layer charge in bentonites has contributed to understand the variability of physical and chemical properties in large deposits with comparable smectite content and the unexpected outcome of alkali-activation, a common industrial practice in most bentonites. Also the concept of fundamental particle charge has helped us explain the smectite-water properties, such as viscosity and swelling (Pratzkalis et al., 2010). This is of particular importance for the industry because the properties of smectite suspensions are controlled by particles not by unit cells. Future developments of these approaches include the influence of the fundamental particle charge on the hydrophobicity of the smectite surfaces and the influence of layer charge on the production of organophilic bentonites. Finally, the proposed approach for identification of trioctahedral smectites (naponite, stevensite and hectorite) is based on the thermal behavior of the various smectites and their different characteristics when they are saturated with cations of low hydration energy such as Cs and K (Christidis & Koutrouposou, 2013). The method has been extended recently to dioctahedral smectites and the first results are indeed promising (Bakker et al., 2013).

In summary, our systematic work on bentonites from various places, suggests that understanding of the physical properties of these clays requires shift from observation in the macro-scale to investigation of the smectite characteristics in the micro-scale. Recent advances on bentonite research by several workers including our team have shown that this approach is rational and feasible.

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In summary, our systematic work on bentonites from various places, suggests that understanding of the physical properties of these clays requires shift from observation in the macro-scale to investigation of the smectite characteristics in the micro-scale. Recent advances on bentonite research by several workers including our team have shown that this approach is rational and feasible.
A NEW APPROACH TO IDENTIFY TRIOCTAHEDRAL SMECTITVES WITH X-RAY DIFFRACTION

George E. Christidis* and Eleni Koutsopoulou

Characterization of smectitic clays is a major task for appraisal of bentonite resources. Due to their abundance in most commercial bentonite deposits, dioctahedral smectites have been studied extensively in terms of characterization. Hence, determination of layer charge and charge heterogeneity (Hoffmann-Klemmen effect) are well known routine characterization methods for dioctahedral smectites. In contrast, laboratory methods for routine characterization of trioctahedral smectites are not currently available. In this context, a new approach for identification of trioctahedral smectites, saponite, stevensite and hectorite is proposed. The method is based on the differences in the XRD traces of the three smectites after a) heating at 500°C for 90 min and b) glycerol solvation of the Cs-forms of the smectites for 20 h. After heating at 500°C i.e. well below the dehydroxylation temperature of the three smectites, saponite and hectorite re-expand upon EG solvation whereas stevensite layers totally collapse, forming kerolite-type layers. Hence stevensite is the only smectite, which undergoes phase transformation prior to dehydroxylation. Saponite, hectorite and the kerolite-like phase dehydroxylate at ~800°C.

Upon Cs-saturation and glycerol solvation saponite forms one layer- and hectorite two-layer complexes. Cs-stevensite displays evidence of random interstratification between one- and two-layer glycerol complexes and gradually forms two-layer glycerol complexes at prolonged solvation. In contrast, Cs saturation and ethylene glycol (EG) solvation yields two-layer EG complexes, rendering identification of the individual trioctahedral smectites impossible. Except for the individual Mg-smectite types, the proposed method may be used to identify compositional heterogeneity that exists in the smectites. Furthermore, it is useful in identifying the individual trioctahedral Mg-smectites when present in mixtures and in detecting interstratified layers of different Mg-trioctahedral smectites. Application of this approach revealed that the SYnL-1 laponite (CMS Source Clay Project) is not homogeneous but consists of hectorite, stevensite and mixed layer hectorite/stevensite layers and that the Mg-trioctahedral smectites in Vicalvaro Basin, Spain and the Amargosa Valley, Nevada, USA, are mixtures of saponite and stevensite. Also, the saponite from lizard peninsula, Cornwall, is compositionally heterogeneous, consisting of layers with variable charge.
CERAMIC RESOURCE SELECTION AND SOCIAL VIOLENCE IN THE GALLINA CULTURE AREA OF NORTHERN NEW MEXICO

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My research examines the relationship between social violence and ceramic resource procurement. Do people in middle-range societies alter resource use in response to conflict? Specifically, does social strife influence the distance to which potters in middle-range societies will travel to collect ceramic resources? This work builds on a technological choice theoretical framework. Technological choice studies examine the choices made by artisans during the production sequence. These choices can create variability in the final product, or conversely a more standardized form. A holistic approach to raw material selection incorporates both materials science work on the physical characteristics of objects and investigation of the cultural and social situation in which the items were produced. Focusing on societies in conflict requires understanding of both the potters’ materials and their cultural setting.

Distance and quality are primary elements in clay selection. Clay is heavy, so for many potters distance is the determining factor in clay selection. Dean Arnold estimated procurement thresholds using worldwide ethnographic data from 111 traditional societies. He found that for both clays and tempers, people prefer to travel only one kilometer, but they will go up to four kilometers if necessary. These thresholds were the basis for the field component of my research.

Pottery production occurred throughout the Pre-Columbian American Southwest under conditions of pervasive conflict in the 13th century A.D. The Gallina culture area is an ideal location for investigating resource procurement and social violence in northwestern New Mexico. Conflict in this area is evidenced by defensive architecture, such as towers and cliff houses, burned structures with human remains, and human remains with embedded projectile points and skull trauma. Two sites in the Gallina culture area were chosen, one with a defensive setting and architecture the other with an open site plan and no defensive structures. Ceramics from each of the sites and the clay resources in proximity to the sites were examined to see if conflict affected resource selection.

In this research, X-ray diffraction (XRD) determined the clay mineralogy of ceramic matrices and the collected natural clays, petrography identified the aplastic mineralogy of the pottery sherds and collected clay samples, and inductively coupled plasma-mass spectrometry (ICP-MS) provided the chemistry of the ceramic matrices and the natural clays. Numerous field and laboratory characterizations provided more information about the qualities of the available clays, and the ceramics themselves. The combined results of the laboratory tests, mineralogical studies, and chemical comparisons indicate that Gallina potters did not alter their resource selection in response to social violence.

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ABSTRACTS

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IMPORTANCE OF CLAY MINERALOGY AND GEOCHEMISTRY IN THE PRE-EMERGENT LIQUIDS-FROM-SHALE PLAY IN THE NEW ALBANY SHALE (DEVONIAN-MISSISSIPPICIAN), ILLINOIS BASIN

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The New Albany Shale (NAS) (Devonian-Mississippian), source rock for an estimated 95% or more of Illinois Basin oil and gas, remains a pre-emergent unconventional resource play in the Illinois Basin. This is attributed to several factors, such as concerns about reservoir quality, geochemical and mineralogical characteristics of the shale over the maturation trend, and suitability of the shale as an in-situ liquids play. The integration of a wide range of geologic, bulk sample mineralogical, clay mineralogical and geochemical information may be important in all aspects of the potential play development, from regional analysis to targeting, geo-steering, and well completion strategies in individual lateral wells. Thickness, lateral distribution, organic richness, and oil window maturity distribution parameters for the NAS are generally known to be favorable in many areas in the Illinois Basin. But questions remain about key geochemical and geological factors that are likely to be important to successful development of the play. Bulk sample and clay mineralogical characteristics as well as their role in developing targeting strategies in the shale are not well-understood in the NAS across the basin, yet they are thought to be critical in future play development. Porosity, permeability, reservoir pressure, natural fractures and brittle versus ductile characteristics are likely to be intimately associated with the bulk sample and clay mineralogy of the shale. Certain NAS samples in the Illinois Basin show a decreasing percentage of clay minerals from about 50% to less than 30% with increasing thermal maturity (above vitrinite reflectance values of 0.65%), yet other thermally mature samples (with calculated Ro > 0.65%) have a higher percentage of clay minerals around 40%. For the Barnett and Marcellus gas shales, it has been suggested that successful in-situ shale plays contain less than 40% clay, lending to uncertainties in evaluation of promising shale reservoir criteria for a liquids-from-shale play in NAS. We will present new and currently available bulk sample and clay mineralogical data of NAS from wells over a range of thermal maturity zones, discuss the implications for potential development of the play, and suggest directions for future research.
The inorganic nanocarrier, Layered Double Hydroxide (LDH), containing the anionic form of mefenamic acid (Mef), a non-steroidal anti-inflammatory drug was characterized by chemical analysis, powder X-ray diffraction (PXRD), thermal analysis (TGA-DTG) and vibrational spectroscopy (FT-IR and FT-Raman) which were supported by Density Functional Theory in order to assist the experimental data. In order to assess the cytotoxic effects, hemolytic assays were performed for mefenamic acid and LDH-Mef and, finally, pharmacological evaluation was carried out to study the differences on anti-inflammatory and anti-nociceptive activities evoked by mefenamic acid after intercalation in LDH.

The interlayer distance, \(d_{003}\) value (2.06 nm), and the enamate anion dimension achieved by DFT calculation (about 1.1 x 0.7 x 0.7 nm), suggests a bilayer arrangement of the guest species in the interlayer space (Figure 1). The chemical composition of LDH-Mef, \([\text{Mg}_2\text{Al}(\text{OH})_6]\) \((\text{C}_9\text{H}_8\text{NO}_2)_{0.55}\text{Cl}_{0.45}\cdot 2\text{H}_2\text{O})\), was proposed according to the elemental analysis (CHN) data, metals contents and the percentage of \(\text{H}_2\text{O}\) (obtained from TGA curve). The amount of the organic species present in 100 g of LDH-Mef is 33 g. The physico-chemical characterization showed the integrity of the molecule after the intercalation process.

The pharmacological effects of LDH-Mef compared to Mef and the LDH were evaluated by hemolytic, anti-inflammatory activity assays and antinociceptive. Pretreatment of animals with Mef or LDH-Mef effectively inhibited edema reduced by the paw tissue myeloperoxidase (MPO) activity and total leucocytes and neutrophil counts of the peritoneal cavity as compared to the carrageenan group. In nociception models, Mef and LDH-Mef pretreatment reduced mechanical hypernociception in 1-4 h after carrageenan and also the number of writings induced by acetic acid.

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MOLECULAR MODELS OF CARBON DIOXIDE INTERCALATION IN MONTMORILLONITE

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*Naturally occurring clay minerals provide a distinctive material for carbon capture and carbon dioxide sequestration. Clay minerals, such as the swelling smectites, possess an aluminosilicate structure that is controlled by low-charge layers that readily expand to accommodate water molecules and, potentially, CO2. Recent experimental studies have demonstrated the efficacy of intercalating CO2 in the interlayer of layered clays, but little is known about the molecular mechanisms of the process and the extent of carbon capture as a function of clay charge, structure, and water content. A series of classical and DFT molecular dynamics simulations have been completed to assess the molecular interactions associated with incorporation of CO2 and H2O in the interlayer of montmorillonite clay and to help validate the models with experimental observation. Simulations were completed at pressure and temperature relevant to geological carbon storage. A set of interatomic potentials for flexible CO2 was developed and combined with Clayff potentials to help evaluate the intercalation mechanism and examine the effect of molecular flexibility on the diffusion rate of CO2 in water and in the clay interlayer. The classical simulations show that the degree of swelling caused by intercalation of CO2 strongly depends on the initial water content in the interlayer space and that CO2 intercalation stimulates inner-sphere adsorption of the positively charged interlayer ions on the internal clay surfaces, which modifies the wetting properties of the surfaces. DFT-based molecular dynamics simulations were used to interpret the origin of the observed shift in the asymmetric stretch vibration of CO2. The origin of the shift is attributed to electric field effects on CO2 induced by the water molecules.
Argillaceous rocks are in many countries considered as potential host rock formations for a deep geological repository for radioactive waste. In Switzerland for example an approximately 180 million year old marine Opalinus Clay (OPA) sediment has been identified and selected as the first-priority host rock for the disposal of long-lived intermediate- and high-level radioactive waste. In such a geological repository, the OPA acts as a natural barrier. OPA is a marly claystone consisting mainly of 40–80% clay minerals (including illite, ilite-smectite mixed layers, kaolinite), 10–20% quartz and 5–40% calcite in near neutral conditions. Today most of the understanding of uptake processes in such systems is based on experiments performed on pure 2:1 type clay minerals such as montmorillonite and illite. A major challenge for extrapolating the findings from pure to real systems is that the sorption in natural argillaceous rocks is an inherently complex process. Therefore a wet chemistry and geochemical modelling approach has been developed to predict uptake of sorbates in such complex systems. The so-called "bottom up" approach is based on the hypothesis that the uptake of sorbates in natural systems can be quantitatively described based purely on the understanding of the sorption mechanisms on 2:1 type clay minerals. In this study this hypothesis was tested by performing extended X-ray absorption fine structure (EXAFS) spectroscopy on Ni(II) and Zn(II) treated OPA rock samples in 0.2 M NaClO₄, and in a realistic porewater chemistry. The sorption prediction on OPA was carried out using the quasi-mechanistic sorption model developed for ilite, and the results scaled over the ilite and illite/smectite mixed layer weight content in the sample.

EXAFS measurements were applied to verify the sorption mechanisms along the isotherm at the molecular level, e.g. at loadings between 2–60 mmol/kg at pH 8.2 (porewater) and pH 7.0 (0.2 M NaClO₄). In the isotherm region, where prediction and measurement coincide, EXAFS data indicate that sorption was the only uptake-controlling mechanism. In contrast, in the isotherm region where prediction and measurement deviated, e.g. at higher metal loadings, EXAFS showed that neoformation of newly phases occurred as an additional uptake process. A further scientific question which is associated with repositories in clay-rich sediments is the interaction of cement-based materials with the argillaceous rock. Both materials, i.e. OPA and cement used for the construction of the repository, are heterogeneous mineral assemblages with discrete nano- to micro-scale particles. Hardened cement paste (HCP) consists of mainly calcium (aluminium) silicate hydrates, portlandite, calcium carbonates, and some minor phases such as calcite and hydrotalcite, in hyper-alkaline environment (pH > 11). Micro-scale information on the chemical reactions and the secondary phases formed in the disturbed zone at the HCP/OPA interface with its large chemical gradients is almost completely lacking.

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Synchrotron-based micro-X-ray diffraction (microXRD) was employed to characterize the complex heterogeneous phase assemblages at the HCP/OPA interface. The investigated samples were obtained from a long-term Cement/OPA-Interaction experiment ("CI-project") conducted in the Mont Terri Rock Laboratory (St-Ursanne, Switzerland). The alteration zone was found to extend over a few hundred micrometers into the concrete material. A semi-quantitative analysis of the XRD data, using heights of characteristic XRD peaks in these powder patterns as an indication for selected mineral phases, showed that it is straightforwardly possible to distinguish between the OPA, the alteration zone and the cementenous regions. For example, brownmellite (C₄A₅, Ca, Al(OH)₄) is a typical cement phase, which is progressively depleted in the alteration zone towards the clay interface. In contrast, the clay minerals kaolinite and illite, which are important constituents of OPA, are present in the clay region of the alteration zone. Furthermore, in the alteration zone an enrichment of carbonate phases (calcite, dolomite and varerente) was observed.

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Both studies demonstrated the high potential of applying synchrotron-based techniques such as EXAFS and microXRD to address open questions related to the disposal of radioactive waste in deep geological repositories. The EXAFS information on the uptake behaviour of heavy metals by argillaceous rock will be crucial for improving mechanistic models on the long-term fate of radionuclides in the geosphere. The microXRD mineralogical information from the cement-clay interface will be essential for the verification of currently existing models used to predict the long-term evolution of the cement/clay interface in a repository for radioactive waste.
THE IMPORTANCE OF CLAYS AND SHALE PROPERTIES FOR SHALE RESERVOIR HYDRAULIC STIMULATION AND GROUNDWATER PROTECTION

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Clay and shale properties can have a significant influence on the productivity results of hydraulic fracture stimulation, and on the fate and transport of stimulation water and chemical additives injected into shale fractures. This presentation will provide an overview of the current state of science regarding clay reactions in fracture stimulation performance, and the influence of diagenetically mature shale on stimulation fluid migration and attenuation.

The potential reactivity of clay minerals in shale reservoirs needs to be considered in the design of fracture fluid stimulation fluid composition. The clay mineral fraction has a significant influence on brittleness, a key geomechanical property for successful shale reservoir stimulation. Reactions between clay minerals and the stimulation fluid can result in fines migration and geomechanical softening of rock at the fracture face. These reactions can lead to plugging of fracture porosity, proppant embedment, and reduced fracture aperture width.

Societal concern have been raised about the fate and transport of hydraulic stimulation fluid (water and chemical additives) after it has been injected into a target shale reservoir, and particularly, the risk of fluid and chemical transport from the reservoir to shallow groundwater resources. The laterally extensive and continuous gas-bearing shale formations, common in the stratigraphic section of many shale gas basins, may be an important influence on potential fluid and solute migration. For example, numerous gas-bearing shales occur in the Appalachian Foreland Basin between the Marcellus Shale reservoir and shallow groundwater formations. Importantly, the Marcellus and other shale units contain highly saline residual formation brine in addition to the gas, in micropores between the minerals and organic matter. Based on current understanding, this combination of shale composition features results in a capacity for the shale to strongly attenuate water and dissolved chemical migration through the fractures, due significant capillary forces and diffusive and osmotic reactions acting on water and dissolved constituents. The sorptive capacity of such shale formations appears to be far in excess of the hydraulic stimulation fluid volume injected into shale per unit volume of stimulated rock.
INTERLAYER STRUCTURE OF TRIHYDRATED (3W) MONTMORILLONITE

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With increasing water activity, smectites exhibit a stepwise expansion, hosting 0, 1, 2, or 3 planes of H2O molecules within their interlayer space. The crystal structure of 0W, 1W, and 2W states have been extensively described using a wealth of experimental and computational techniques. On the other hand, the few structure models available for the 3W states determined from X-ray diffraction (XRD) modeling or Monte-Carlo simulations are not totally consistent, and a robust model is still to be reported. The present work will thus report on the organization of water in trihydrated montmorillonite interlayers by combining both XRD and Monte-Carlo molecular modeling. SWy-1 Montmorillonite sample was selected for this study and saturated with four cations (Na+, Ca2+, Mg2+, and Ba2+) to unravel the relative contributions of interlayer cations and water molecules. X-ray diffraction patterns were then collected above 95%RH (relative humidity). The four samples reached stable trihydrated states. Grand canonical Monte-Carlo (GCMC) simulations were performed using a homemade program as explained by Ferrage et al. The electron density profiles obtained from GCMC simulations were used as structure models for XRD calculations. Combined GCMC and XRD simulations are in good agreement with diffraction data. Electron density profiles derived from GCMC simulations can be described with four Gaussian curves, two close from clay basal surfaces and two other closer to the interlayer mid-plane, the latter being much broader than the former. The position of the Gaussian curves depends on the layer-to-layer distance but is independent on the nature of the interlayer cation. In addition, GCMC simulations allowed evidencing the increasing number of H2O molecules coordinating divalent cations with increasing hydration enthalpy. Divalent cations with the lowest hydration enthalpy are octahedrally coordinated by H2O molecules, while cations with a higher hydration energy present cubic or even superior coordinations. Interlayer cations are distributed either as a single (Mg, Ca) or as a double (Ba, Na) Gaussian profiles.
Clays are widespread natural resources convenient for various technical and geotechnical applications. Among which bentonites are intended to be used as barriers for radioactive and toxic waste deposits, highly influenced by the smectite properties. Smeectites are swellable low charge 2:1 layer silicates with high cation exchange capacity. Behavior modeling of bulk materials require the understanding of the influence of the physical and chemical properties of smectite as well as those of the accessory minerals as others clay minerals, feldspar or zeolites. The aim of this study is a quantitative approach of bentonite compositions and correlation of bulk material properties to component properties. To allow a thorough mineralogical characterization, fractionation of the bulk materials according to their particle size distribution, sandy fraction > 63 µm, three sily clay fractions 20-63 µm, 6.3-20 µm and 2-6.3 µm and three clayey fractions 0.6-2 µm, 0.2-0.6 µm and < 0.2 µm, was performed. This baseline study focuses on the characterization of the association of smectite minerals with accessory minerals in function of particle size distribution.

The bentonite "Calcegel" from the Bavarian region (Germany), "Volclay" from the Wyoming state (USA), "SWB3" from the Almeria region (Spain), and the "Ben P" provided by Süd-Chemie AG, Germany, were investigated containing smectites with different chemical compositions and layer charge distributions. The bentonites were fully dispersed according to Tributh-Lagaly (1986) treatment procedure coupled with Na-homoionisation treatments. Details are given in Wolters et al. (2009). The > 63 μm fraction was separated by wet-sewing. The fraction < 2 μm was extracted from the remaining clay in suspension by successive sedimentations according to the Stockes’ law. Then the silty fractions were separated by sedimentation and the clayey fractions by centrifugation. Then suspensions were dried with gentle drying at 60°C.

The baseline study of the bulk materials and their fractions focused on the characterization in function of the particle size distribution required the crosschecking of different methods. The mineralogical composition of the bentonites was determined by coupling the quantitative analysis performed using the Rietveld software "Autoquant" from X-ray diffraction (XRD) with elementary analysis by X-ray fluorescence (XRF) and simultaneous thermal analysis (STA). The layer charge (q) and cation exchange capacity (CEC) was determined by the alkylammonium method and the Cu-triethylenetetramine method, respectively. A detailed description of these methods is given in Wolters et al. (2009) and Steudel et al. (2013). The geometric properties of the smectite in function of its particle size distribution were investigated by gas and water adsorption/desorption isothersms as well as by atomic force microscopy (AFM).

The mineralogical characterization revealed different association for each bentonites. Comparisons of bulk material composition with the weighed proportion sum of phase composition for each fraction were close. Material fractionation allowed to identify phases that are diluted in mass of the bulk materials. For example, chlorite and certainly a mixed layer chlorite/smectite have been identified in the smily fractions up to the coarser clay fraction 0.6-2 µm of the bentonite "Calcegel". A zeolite has been identified in the sandy and smily fractions of the the bentonite "SWB3". The chemical reactivity of the bentonite being attributed highly to the colloidal fraction we have focused in mineralogical and geometrical properties of the smectite. Some high differences in gas adsorption properties caused our attention, with a A<sub>400</sub> of 133 m²·g⁻¹ for the bentonite "Calcegel" while bentonite "Volclay" developed only 33 m²·g⁻¹ of the < 0.2
μm fraction. Different dimension of the unit particle size was found by AFM measurement although equivalent sphere diameter was equal. Elongated particles were observed for smectite the bentonite "Ben P". These first results indicate that bentonites differ not only in smectite content and structure but also in surface properties and reactivity of bentonites will be influenced by accessory minerals in non-colloidal fractions.

In further work, particle size properties will be also investigated by environmental scanning electron microscopy (ESEM) for the coarser fractions and by laser-induced breakdown detection (LIBD) and flow field-flow fractionation coupled to ICP-mass spectrometric detection (FFFF-ICPMS) for the clayey fractions. A detailed description of these methods is given in Plaschke et al. (2001). Then the objective will be to correlate the mineralogical and geometrical properties of each fraction to their chemical reactivity. Influence of structural properties of smectite on their chemical behavior will be investigated in peculiar to trace metal interaction. Characterization of the nature and distribution of substitutions of the octahedral sheet will be decisive.
K-Ar and Ar-Ar isotope geochronology techniques commonly work on an assumption that no measurable external radiogenic $^{40}$Ar (“excess argon”) was locked in a mineral during its crystallization. The argon concentration and the $^{40}$Ar/$^{36}$Ar ratio in surface waters remains in equilibrium with the atmosphere; only isolated groundwaters can show the elevated $^{40}$Ar/$^{36}$Ar ratio. A high rate of Ar diffusion in water makes the $^{40}$Ar released from detrital minerals decomposing in sedimentary basins equilibrate with the atmospheric Ar dissolved in surface waters immediately instead of being incorporated into the neoformed minerals. Therefore, the only broadly accepted reason for the occurrence of the “excess argon” in sedimentary and diagenetic minerals is a contamination by older, detrital phases.

The solid-state mineral transformation seems the only feasible mechanism that may transport $^{40}$Ar from a detrital phase to a neoformed mineral in sedimentary basins. An example of such a transformation is the acid reaction with clays. Due to the incongruent character of the reaction, protonated and hydrated silica with a three-dimensional, cross-linked structure is formed as an acid treatment residuum of layer silicates. The new-formed silica develops a micro- and mesoporous structure resulting in a large specific surface area and micropore volume.

Our results indicate that a simple reaction of micaceous sedimentary and diagenetic clay minerals (illite, glauconite) with acid under pressure and temperature close to those at the Earth surface produces microporous silica that retains a great fraction of the initial argon, releasing potassium to the solution. In all tested cases the evolution of K-Ar isotope ages followed the very same pattern: the apparent K-Ar isotope age increased enormously after acid treatment and dropped significantly after silica removal (with hot Na$_2$CO$_3$), but never decreased lower than the initial K-Ar isotope age of the untreated sample. The amorphous silica content increased with the acid reaction time. Along with the increase of amorphous silica content in the product of the acid-clay reaction, the apparent K-Ar age strongly increases. This is, to our knowledge, the first experimental evidence that simple reactions can produce excess argon in natural-like solids formed under pressure and temperature close to those of the Earth surface.

Using molecular dynamics calculations, the mica-acid reaction by-product was shown to bend and wrap, producing three-dimensional, protonated and hydrated silica. As a consequence of dramatically different hydration energies of Ar and K, K is instantaneously released and hydrated outside the residual structure while Ar atoms remain inside due to almost the same hydration enthalpy and potential energy of argon adsorption on the silica surface. Our finding proves that the excess argon can be introduced into minerals under sedimentary and diagenetic conditions via solid-state reactions, which limits the application of the current paradigm of $^{40}$Ar behavior in sedimentary basins.
Clay minerals show remarkable possibilities for the design of new hybrid materials, by functionalizing their internal or external surfaces. This paper will describe applications of chemically modified clay minerals. Examples will be given for sepiolite on the applications in catalysis of gold nanoparticles deposited on sepiolite. Most of the presentation will however focus on controlling the functionalization of kaolinite and describing potential applications.

Kaolinite, the most abundant 1:1 clay mineral, has been so far scarcely used for the preparation of grafted organic-inorganic hybrid materials. Unlike other clay materials, it does not possess a high density of outer surface sites capable of being functionalized. The majority of the reactive sites of kaolinites are located on interlayer spaces which are not easily expandable. This makes the intercalation and the grafting of organic compounds on the internal surfaces of kaolinite challenging. Several works have shown that it is however possible to obtain Al-O-C covalent bonds on the kaolinite interlayer surfaces. Our team has synthesized successfully in recent years various derivatives of kaolinite by grafting alcohols, organosilanes and especially ionic liquids in the interlayer spaces. Stability tests have shown that these materials exhibit excellent resistance to hydrolysis.

A series of studies were recently conducted, showing that the grafting of ionic liquids in the interlayer spaces of kaolinite provide nanohybrid organo-mineral materials with anion exchange properties that can be used for electroanalysis of anions in aqueous solution. It was shown also that by controlling the d-spacing using grafted ionic liquids of various sizes, a selective size detection of anions could be achieved. An attempt for the use of these modified electrodes with anion exchange properties to perform quantitative analyses of anions was successful, with a very low detection limit of iodide being obtained. Interesting results have also been obtained for the detection of cations. Using a carbon paste electrode modified by a thiol functionalized kaolinite, a low detection limit of Pb(II) and a good selectivity toward other metallic cations were achieved. These results show that kaolinite can be successfully used in the modification of electrodes for qualitative and quantitative analysis.
Clays and soils have high sorption and retention capacities. Owing to their surface charge these minerals are able to reversibly adsorb cations, a property termed cation exchange capacity (CEC). The CEC is used to characterize soils and clays for decades. Many pitfalls were identified when CEC methods have been used to characterize these natural materials, particularly when soluble minerals such as Ca-carbonates or Ca-sulfates were present (e.g. Dohrmann & Kaufhold, 2009).

In recent years many studies focus on bentonites as candidate materials for the encapsulation of radioactive waste. In the ABM project (Alternative Buffer Material test) thirty blocks of nine different bentonites and two different clay stones were packed on each other with an iron-heater element in the centre. The buffer materials initially had very different exchangeable cation compositions. The first ‘ABM package’ was heated for approximately 1 year and the bentonites have been exposed to the maximum temperature of 130 °C (altogether 28 months in the crystalline rock).

The aim of the present study was first: to describe modification of the cation exchange population before and after the experiment, and second to understand the influence of the groundwater on cation exchange at different scales. Obviously ECs were exchanged to a larger extent than expected. No horizontal variation of any EC was detected between 1 and 7 cm distance from contact. On the other hand large total differences of the exchangeable cation population (EC composition) were measured for the blocks in comparison with the starting composition (n=21 blocks).

Bentonite CECs decreased on average by 5.5 meq/100 g after the experiment (Dohrmann et al., 2013). The neighbouring blocks had a minor influence on the cation redistribution during the ABM experiment. The observed differences cannot be explained assuming simply that a bentonite reacts only with neighbouring blocks, which would mean that the system was more or less closed. The differences are much larger and the only conclusion from this observation is that the whole package seems to be influenced by the groundwater which was added from a water tank at the experiment site, enabling at least partial equilibration between the different blocks.

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The smectite (S) to illite (i) conversion is of a special note in geochemistry. The S-i reaction is considered to be one of the most important mineral reactions during sediment diagenesis of mudstones and shales, as the degree of the smectite to illite reaction, termed "smectite illitization," is linked to maturation, migration, and trapping of hydrocarbons, development of pore pressures, growth faults, rock cementation and porosity reduction, and pore water chemistry. The smectite to illite reaction proceeds through mixed-layer illite-smectite (i-S) intermediates in which the percentage of illite layers increases with increasing temperature, time, K concentration, water/rock ratio, and pH. Recent studies have shown a significant effect of microbes in promoting the smectite to illite reaction (Kim et al. 2004). The microbially promoted smectite-illite reaction can take place at room temperature and one atmosphere within two weeks. This reaction typically requires conditions of 300–350 °C, 100 MPa, and 4–5 months in the absence of microbial activity. Further studies (Zhang et al. 2007b) have demonstrated a strong catalytic effect on the smectite to illite reaction of organic matter intercalated in the interlayer of the smectite structure. Even at diagenetically relevant temperatures, the smectite to illite reaction can be catalyzed by thermophilic bacteria (Zhang et al. 2007a). More recent studies have shown microbially mediated smectite-illite conversion by thermophilic bacteria (Jaisi et al., 2011), sulfate-reducing bacteria (Liu et al., 2012), and methanogen (Zhang et al., 2012).

The recognition of the microbial role in promoting the S-i reaction is important for multiple reasons. First, this microbially mediated S-i reaction provides an example of the catalytic effect of microbes in mediating certain geological processes; this recognition is in some sense comparable to the discovery of the microbial role in promoting dolomite precipitation (Vasconcelos et al. 1995). Second, the microbially catalyzed S-i reaction provides a physical basis and mechanism for refining the smectite illitization model, with possible implications for petroleum exploration (Pevear 1999). Third, when coupled with microbial measurements, this newly recognized model offers an explanation of why the S-i reaction occurs in certain modern sediments under low temperature and pressure (Kim et al. 2004). The microbially catalyzed S-i reaction has even been proposed to have occurred in ancient marine sediments, in which the reduction of structural Fe(III) dissolved smectite and formed biogenic minerals such as quartz, pyrite, and carbonates (Vorhies and Gaines 2009). Fourth, dramatic changes associated with the S-i reaction would significantly affect the physical and chemical properties of soils and sediments; thus, it is important to understand the rate and extent of this reaction when designing strategies for maximizing nutrient retention and minimizing contaminant mobility. Fifth, the illitization of smectite, a major component of bentonite used in radioactive waste disposal, releases water and leads to changes in hydraulic conductivity. This change would have a major effect on the stability of bentonites used for high-level radioactive waste disposal and could potentially result in the failure of waste canisters.

Such a microbially induced smectite to illite reaction has been either implicated indirectly or demonstrated directly in natural environments. Biogenic mineral assemblages such as authigenic quartz, calcite, pyrite, and illite have been used to infer past microbially mediated smectite-illite reaction in Cambrian marine sediments (Vorhies and Gaines 2009) and can be used as biosignatures (Dong et al., 2009, Dong 2012).
Minerals of a kaolinite group have a similar chemical composition and at the same time a wide variety of structures due to a large number of factors that influence on their synthesis, weathering and redeposition. Most of the kaolinite and halloysite structural features can be described based on XRD and IR-spectroscopy analyses. However, distinction of highly defective kaolinite and 7Å-halloysite is usually difficult. Vacancy displacements, layer rotation and its distortion within a unit structure lead to formation of many different defects both in the layer structure and their stacking. Detailed investigations of the kaolinite minerals structure (especially kaolinite's and halloysite's) can help to divide unsatisfactory formations of redeposited weathering crusts and to estimate their provenance area.

The aim of this research was to find out the influence of the kaolinite structural features on the differences in their formation conditions. Sixteen samples of clay fraction (<2 mm) were collected from four Portuguese deposits (Alvaraes, Barqueiros, Vila Fria and Vila Cha) for the investigation. The first three are redeposited and the last one is a residual weathered crust.

The characterization of clay composition and structure was carried out by XRD analysis, scanning electron microscopy (SEM), IR-spectroscopy, XRF-spectroscopy and laser particle size analysis.

Studied clay fractions consist of differently ordered kaolinite and 7Å-halloysite with a small admixture (<5 %) of illite, gibbsite, goethite and quartz. The samples can be subdivided into three groups: 1) relatively well-ordered kaolinites, 2) highly defective kaolinites and 7Å-halloysites; 3) mixture of well-ordered kaolinites and 7Å-halloysites (highly defective kaolinites). The subdivision was based on the similarity and distinction of the XRD patterns and micromorphology. Also the particles of 7Å-halloysite have nearly spideroid morphology and form relatively big aggregates. The particles of highly defective kaolinites have classic hexagonal morphology. The samples, which include well-ordered kaolinite and 7Å-Halloysite, have particles with different sizes, which was also confirmed by a laser particle size analyzes.

IR spectroscopy provides a lot of useful information for kaolinite investigations. It can detect even a rather small amount of halloysite. Also, it helped to detect that the samples have differently defective structure of the 1:1 layer. Dislocation of 1:1 layers causes changes in the OH-stretching region of spectra. Those conclusions were correlated with the XRD-analysis results and there were found a correlation between the distribution of intensity bands of the OH stretching and the peaks intensity in the 34-40° 2θ-CaKα range.

Therefore, samples can be divided into three groups with different defects of: 1) stacking faults of ordered layers; 2) stacking faults of defective layers; 3) ordered stacking of defective layers. Herewith it was observed that the increasing of defects in the samples is correlated with the increasing of FeO:Al2O3 amount. It is known that an increasing of iron content in the solution during the kaolinite synthesis leads to increasing its defects. It is also well known that the presence of iron in large quantities usually indicates on aridization. So in our case, it can be concluded that iron came at the time of kaolinite material's formation. On the other hand, it's clear that structural features of clay minerals depend on composition of parent rocks. According to geologic settings parent rocks of studied kaolin deposits can be granites, gneissose granites or shists. Historical for studied kaolin deposits probably for well-ordered kaolinites parent rocks are granits, for defective kaolinites—gneissose granites and for 7Å-halloysites—shists. Thus in the sequence of kaolin clay...
northwest Portuguese province the horizon formed in dryland conditions was pointed out, and it can be concluded that the forming material was redeposited from different types of weathered rocks, which are mentioned above.

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BEARING OF THERMAL STRESS ON MECHANICAL STABILITY AND IT’S IMPLICATION IN ASSESSING THE POSSIBILITY OF RADIOACTIVE WASTE DISPOSAL IN ARGILLITE OF VINDHYAN SUPERGROUP, INDIA

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Energy is the basic need of progressive civilization and a fast growing world. The pollution prone limited reserves of fossil fuels are still practiced as principal sources of energy. Hence, alternative are needed to enhance production of clean energy to meet future energy demands with minimized accumulation of carbon dioxide and other environment deteriorating gases. In such a current scenario, nuclear fuels seem to be one of the better options to fulfill the future energy need, with the least air pollution. However, the contaminations of sensitive radioactive waste released from nuclear power plants are critically complicated and problematic due to its long-lasting impact on biosphere, hydroosphere and atmosphere.

The disposal of radioactive waste in deep geological formations is considered to be one of the options to ensure expansion of the nuclear power programme. The involvement of long-term multiple polluting effects of waste, the development of geological repository requires proper insurance of the safety levels for long-time domain. Thus, number of rock-types has been evaluated globally to ensure their suitability for isolation of such sensitive waste. However, the safety concerns of disposal host structures are still debatable and under doubt. Besides many rock strata the argillite is also considered as one of the option due to its higher surface area, higher porosity and low permeability, and healing properties of fractures and cracks that can serve to improve stability of repository for the purpose. Hence, the numbers of nations i.e. like Italy, France, Japan, etc., are working on argillites in search of its suitability for disposal of radioactive waste. The multi-layered thick argillite beds of Paleo-Proterozoic and Mesoproterozoic age associated with limestone, siltsstones and sandstones seems to meets some of the primary requisite of host for permanent safe disposal of radioactive waste.

The disposed radioactive waste commonly emits charge particles such as helium and neutron in form of alpha, beta and gamma rays to the surrounding environment of excavated cavities. These ultimately enhance the temperature conditions of host rocks, which may causes change in their stability condition due change in their micro-constituents and textural fabrics controlled behavior which offers reevaluation of the factor of safety again and again. The progressive increase in temperature condition of host rocks transforms its stability which may breach the sealing capacity of surround rock layers and formation of cracks and fractures of repository enveloping layers. Hence, investigations regarding the effect of thermal stress on the mechanical stability of argillite are appears to be very relevant for the purposes.

Therefore, the present works is an attempt to investigate the effects of thermal stress on mechanical stability of argillite from Vindhyan Supergroup in view of checking its suitability for radioactive waste disposal. The Markundi argillite of Lower Vindhyan Supergroup was investigated from Son valley, Central India.

The argillite horizons of the area show pronounce laterally persistent and range in thickness approximately 66-70 meter. The argillite beds are associated with black shale with intervening limestone beds and sandstone beds. The proportion of black shale is highest (~78%) in the lower part of the Markundi argillite and decreases towards the top as it grades into the overlying Rohtas Limestone. The argillite exhibits wavy and crinkly laminated clayey and carbonaceous shales facies. Carbonaceous films of clayey shale facies are very thin, continuous to discontinuous wavy crinkly lamine of thickness ~0.01mm to 0.15mm, whereas the carbonaceous layer of the carbonaceous shale facies are found thick (up to 0.1mm) and made up of mostly continuous wavy crinkly laminae.

For the purpose the cubical samples of dimension ScmScmScm were deformed on servo-controlled Material Testing System (MTS) under incremental compressive and indirect tensile stress (Brazilian Test) environments after the treatment of samples at variable temperatures ranging from 25°C to 100°C. The experimentally conceptualize situations related...
to impact of thermal loading expected to experienced by waste disposal host structures analogously reveals that the samples deformed at normal temperature and pressure exhibits feeble effect of structural anisotropy caused by feasibility plane. The samples deformed perpendicular to the feasibility plane imparts the value of compressive strength to be 11.30 MPa, yield strength to be 11.10 MPa, tensile strength to be 1.17 MPa, shear strength to be 3.68 MPa, modulus of elasticity to be 1.86 GPa and Poisson’s ratio to be 0.221. However, the samples deformed parallel to feasibility plane exhibits slightly lower values of compressive strength (10.88 MPa), yield strength (10.76 MPa), tensile strength (1.34 MPa), shear strength (3.85MPa), modulus of elasticity (1.803 GPa) and Poisson’s ratio 0.234. The ratio between compressive strength, yield strength, shears strength, modulus of elasticity and Poisson’s ratio deformed perpendicular and parallel to feasibility planes imparts 0.967, 0.975, 1.162, 1.050, 0.979, and 1.030 respectively. The results related to the ratios of above described parameters indicate the low anisotropic effects. Hence, the feasibility planes contribute slight control on mechanical properties of argillite. In general the pattern of reduction in compressive strength reveals gradual loss of strength and decrease in values of modulus of elasticity. The reduction in strength is found continuous in decreasing trend up to value of 107°C. The samples subjected to heat treatment up to 107°C exhibit maximum strength even more than the strength values at normal condition (room temperature and pressure). In case of heat treated samples the pattern of yield strength imparts exactly the similar trend as observed in compressive strength variation. The maximum values of strengths (compressive strength, 12.46 MPa; yield strength, 12.18 MPa; tensile strength, 1.136 MPa; shear strength, 4.62 MPa), modulus of elasticity, 1.45 GPa and Poisson’s ratio 0.210 indicates the small changes in modulus of elasticity and Poisson’s ratio in comparison to strengths of argillite with respect to change in temperature condition.

The outcome of investigation suggests that the argillite of the area has habit to decrease in mechanical stability up to certain level of temperature values which shows further strengthening response at the temperature condition of threshold level 107°C. The study finally concludes that the radiation generated temperature if exceeds more than 107°C then the argillite beds became self supporting for enhance mechanical stability. However, the continuous decrease in modulus of elasticity and Poisson ratio shows the increase in brittleness of the strata which will require special care to protect the violent failure and development of discontinuities in the surrounding strata. In view of the above findings it appears that the argillite of the Vindhyan Supergroup has some potentiality in support of their suitability for the disposal purpose.

However, lot of works on various aspects will be required to conclude some specific and confident suggestions and recommendations.
THE MINERALOGICAL AND ENGINEERING CHARACTERISTICS OF CRETACEOUS AND TERTIARY SHALES IN THE LOWER BENUE TROUGH, NIGERIA

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The mineralogical and engineering characteristics of Cretaceous and Tertiary shales in the lower Benue Trough were determined with a view to establishing how they affect civil engineering construction, with emphasis on road pavements in the area. Shale samples from five geologic formations (Awgu, Enugu, Imo, Nkporo and Abakaliki shales) were subjected to the following laboratory tests: clay mineral content, organic matter content, Cation Exchange Capacity, Plasticity, California Bearing Ratio and slaking/abrasion according to methods specified by the British Standard and American Society for Testing and Materials. The shales were classified based on Plasticity index, liquid limit, Cation Exchange Capacity and slaking/abrasion. The class of shales ranged from non-plastic to extremely plastic, low to high reactivity and very low to high durability. The moisture content and plasticity values are related to the degree of weathering. The higher the weathering grade, the higher the moisture content and plasticity values. The organic matter content of the shales is generally low (0.2 to 11.2%). Cross plots reveal that the Slake Durability Index is inversely related to the organic matter content. The clay mineral composition from X-Ray Diffraction consists of illite-montmorillonite mixed layers, illite, and kaolinite. The illite-montmorillonite mixed layer clays are most prominent in road sections with most severe pavement failures. In contrast, sections with kaolinite as the dominant clay mineral experienced less severe and limited pavement failure. The contrasting engineering behaviour of these clay minerals is due to their structures. Although the California Bearing Ratio values (5-11%) show that the shales are of low to medium quality subgrade material according to specifications of the Federal Ministry of Works, the liquid limit and Plasticity Index values revealed the shales as highly substandard pavement materials which can only be used after successful stabilization. This explains the widespread severe pavement failures in road sections underlain by the shales.
This study explores the crystal chemical features from bulk to the uppermost surface layers of two trioctahedral Fe-rich mica-1M (space group C2/m) polytypes, i.e. a tetra-ferriphlogopite from an alkali-carbonatic complex near Tapira (Belo Horizonte, Minas Gerais, Brazil) and a Fe<sup>3+</sup>-bearing phlogopite containing a smaller amount of Fe<sup>3+</sup> in tetrahedral sites from the Kovdor carbonatite-bearing alkaline-ultrabasic complex (Kola Peninsula, Russia). The definition of the chemical and structural relationships between the bulk and the surface of the two Fe-rich mica-1M polytypes required a multi-analytical approach involving electron microprobe analysis (EMPMA), single crystal X-ray diffraction (SC XRD), and X-ray photoelectron spectroscopy (XPS).

Chemical formulae are \([\text{xi}](\text{K}0.99) \ [\text{vi}](\text{Fe}^{2+}0.05 \text{Mg}2.75 \text{Mn}0.01 \text{Ti}0.05) \ [\text{iv}](\text{Fe}^{3+}0.17) \ [\text{v}](\text{Mg9}0.82 \text{Si3.18}) \text{O}10.37 \text{(F}0.24 \text{OH1.39)} \) and \([\text{xi}](\text{K}0.94 \text{Na0}0.06) \ [\text{vi}](\text{Fe}^{2+}0.08 \text{Mg}2.76 \text{Ti}0.01) \ [\text{iv}](\text{Fe}^{3+}0.05) \ [\text{v}](\text{Fe}^{2+}0.15) \ [\text{v}](\text{Fe}^{2+}0.82 \text{Si3.18}) \text{O}10.37 \text{(F}0.24 \text{OH1.39)} \) for tetra-ferriphlogopite and Fe-bearing phlogopite, respectively. These two minerals show an evident difference in tetrahedral composition, where Fe for Si substitution is at 20.5% in tetra-ferriphlogopite and at 4% in Fe-bearing phlogopite. A significantly higher Fe<sup>3+</sup>/(Fe<sup>2+</sup>+Fe<sup>3+</sup>) ratio is observed in the octahedral sites of tetra-ferriphlogopite where the ratio is 0.65, compared to Fe-bearing phlogopite, which is characterized by a Fe<sup>3+</sup>/(Fe<sup>2+</sup>+Fe<sup>3+</sup>) ratio of 0.23. Fe<sup>3+</sup> substitution is related to a significantly less distorted tetrahedral site in tetraferri-phlogopite compared to Fe-rich phlogopite, as demonstrated by different values in flattening angle \(\alpha\). This crystal chemical feature can also be justified by the greater size of Fe<sup>3+</sup> with respect to Al<sup>3+</sup>, which is the main Si substituent in Fe-rich phlogopite. The tetrahedral rotation angle \(\psi\) changes remarkably from tetra-ferriphlogopite \((\tau = 10.5^\circ)\) to the Fe-bearing phlogopite \((\tau = 8.5^\circ)\), thus indicating a significantly greater tetrahedral ring distortion in the tetra-ferriphlogopite compared to the Fe-bearing phlogopite. This behavior can be ascribed to the interconnection between \(\alpha\) and tetrahedral flattening angle \(\epsilon\), and to the variation of this latter parameter due to Fe for Si tetrahedral substitution. The average \(\tau\) angle is lower in tetra-ferriphlogopite \((109.6^\circ)\) than in Fe-bearing phlogopite \((110.73^\circ)\), and closer to the theoretical value \((109.47^\circ)\), indicating a regular tetrahedral site with tetrahedral cations exactly at its center. Tetrahedral rotation angle \(\psi\) significantly impacts on the coordination of interlayer cation, reducing its coordination number with increasing \(\epsilon\).

Several methods are discussed in literature for the experimental determination of layer charge, and these methods always give an average value for the different micro-crystals used in the analysis. Mean layer charge may not be the absolute effective layer charge at the mineral surface because the surface refers not to randomly distributed substitutions, but to domains showing different chemistry which can be locally charge-neutralized. Furthermore, distortion parameters (i.e., \(\alpha\)), which affect tetrahedral topology and can also influence the formation of surface complexes, may locally differ from the determined mean value as obtained from single crystal diffraction. Crystal chemical modifications at the mineral surface of the two Fe-bearing trioctahedral micas were investigated via X-ray Photoelectron Spectroscopy (XPS) by comparing data related to the surface to data originating from the bulk by single-crystal XRD and electron microprobe analysis. The investigation at mineral surface identified differences in Mg binding energy among the two samples considered. NMR studies on Al-rich synthetic phlogopite \([1-3]\) demonstrated that OH and F ions form homogenous domains and that fluorine is usually located in Mg-rich octahedral and Si-rich tetrahedral clusters of Mg phlogopite structure. Considering XPS-derived binding energy (BE) values of tetra-ferriphlogopite and Fe-bearing phlogopite, respectively, these two minerals show an evident difference in tetrahedral composition, where Fe for Si substitution is at 20.5% in tetra-ferriphlogopite and at 4% in Fe-bearing phlogopite. A significantly higher Fe<sup>3+</sup>/(Fe<sup>2+</sup>+Fe<sup>3+</sup>) ratio is observed in the octahedral sites of tetra-ferriphlogopite where the ratio is 0.65, compared to Fe-bearing phlogopite, which is characterized by a Fe<sup>3+</sup>/(Fe<sup>2+</sup>+Fe<sup>3+</sup>) ratio of 0.23. Fe<sup>3+</sup> substitution is related to a significantly less distorted tetrahedral site in tetraferri-phlogopite compared to Fe-rich phlogopite, as demonstrated by different values in flattening angle \(\alpha\). This crystal chemical feature can also be justified by the greater size of Fe<sup>3+</sup> with respect to Al<sup>3+</sup>, which is the main Si substituent in Fe-rich phlogopite. The tetrahedral rotation angle \(\psi\) changes remarkably from tetra-ferriphlogopite \((\tau = 10.5^\circ)\) to the Fe-bearing phlogopite \((\tau = 8.5^\circ)\), thus indicating a significantly greater tetrahedral ring distortion in the tetra-ferriphlogopite compared to the Fe-bearing phlogopite. This behavior can be ascribed to the interconnection between \(\alpha\) and tetrahedral flattening angle \(\epsilon\), and to the variation of this latter parameter due to Fe for Si tetrahedral substitution. The average \(\tau\) angle is lower in tetra-ferriphlogopite \((109.6^\circ)\) than in Fe-bearing phlogopite \((110.73^\circ)\), and closer to the theoretical value \((109.47^\circ)\), indicating a regular tetrahedral site with tetrahedral cations exactly at its center. Tetrahedral rotation angle \(\psi\) significantly impacts on the coordination of interlayer cation, reducing its coordination number with increasing \(\epsilon\).
Mg seems to be preferentially associated with fluorine, instead of OH groups. In fact, if oxygen is substituted by fluorine, the binding energy of Mg was observed to shift to higher values (Mg(OH)$_2$, $\text{BE} = 1303.1$ eV; MgF$_2$, $\text{BE} = 1306.5$ eV). Tetrahedral ring distortion affects not only the topology of the cleavage plane, but also the coordination of the interlayer cation at the surface of the two trioctahedral micas becomes eight. The coordination of the other cations in the bulk remain the same.

The evidence of a reduction of the interlayer-cation coordination was also shown in dioctahedral micas such as muscovite, where Na substitutes K and its coordination at the mineral surface is reduced from eight to six. The interlayer cation K is eight-fold coordinated both in the bulk and at the surface, and the number of K cations decreases at the surface. For muscovite, this evidence, together with a significant Na increase at the surface with respect to the reduction of the number of K, is consistent with the presence of Na-dominant clusters close to the cleavage plane.
The objective of the present study was to elucidate the influence of layer structure and interlayer cation and process parameters on partial dehydroxylation and subsequent spontaneous rehydroxylation of Ca-rich and Na-exchanged montmorillonites under ambient conditions.

Simultaneous thermal analysis (STA) device (Netzsch, 449C Jupiter) was used for dehydroxylation at 540 and 700 °C and analysis of the rehydroxylated samples after storing at 53% relative humidity (r.h.). Both dehydroxylation and rehydroxylation duration were varied. Evolved water during dehydroxylation and during STA of rehydroxylated samples was recorded with a quadrupole mass spectrometer (Netzsch, Aeolos) linked to the STA device. Three montmorillonites (< 2µm) that differ in layer charge, cation exchange capacity and ratio of trans-vacant (tv) to cis-vacant (cv) 2:1 layers were used.

We showed that even pure cv montmorillonites lost about 81% of their hydroxyl groups when kept at 540 °C for 48 h. Montmorillonites with 34 to 45% of tv layers lost about 80 to 90% of their hydroxyl groups when kept at 540 °C for 12 h. Heating at 700 °C even for short periods produced nearly anhydrous montmorillonites from all starting materials. All dehydroxylated samples spontaneously rehydroxylated under ambient conditions (53% r.h.) and a high amount of cv layers in the starting material resulted in a higher extent of rehydroxylation after partial dehydroxylation but not after full dehydroxylation. While the degree of dehydroxylation of Na+-exchanged samples was lower than for Ca2+-rich samples, Na+ at interlayer positions increased mass loss during dehydroxylation at prolonged heating at 540 °C. In contrast Ca2+ on interlayer positions caused a higher degree of dehydroxylation at 700 °C. The degree of rehydroxylation was higher for Na+-exchanged samples but rehydration was only 0.2 to 3.1 H2O per Na+ compared to 1.3 to 8.4 H2O per Ca2+.
The project runs alongside experimental investigations and studies into early Earth peptide bond formation with electronic structure (DFT) and molecular dynamics simulations. This study addresses the Peptide World theory by demonstrating the ability of layered double hydroxides to select, shield and drive the formation of early macromolecules.

While understanding of the chemical processes surrounding our daily life are understood in ever greater detail, it is surprising how little we know about the origin of it. Life emerged 3.85 Ga from a harsh geochemical environment. Currently there are several debated theories on the origin of life, though these mainly separate into the Peptide-first and RNA-first hypotheses.

In this work we focus on the study of abiotic peptide bond formation. In aqueous solution the oligomerisation of amino acids would be an unfavorable process due to two main factors:
- Low concentrations of amino acids reducing the probability of pairs forming;
- High thermodynamic barriers, arising from water elimination.

Therefore, we are interested in investigating the ability of inorganic layered materials to promote the reaction by concentrating and dehydrating amino acids prior to oligomerisation.

Layered double hydroxides (LDHs) are brucite-based (magnesium hydroxide) materials, where a positive charge comes from substitution of Mg$^{2+}$ for Al$^{3+}$ and is compensated with weakly bound anions in the interlayer. In the reducing and alkaline environment of early Earth hydrothermal systems, amino acids would be negatively charged and, therefore, could be easily intercalated into the interlayer domain of the positively charged LDHs. This would allow concentration of amino acids and stablisation of the peptide products. These conditions are necessary for successful polymerisation.

A comparative DFT study of the energies and geometrical arrangements of L- and D-aspartic acids intercalated into LDHs has been performed. Charge-density of LDHs and the pH of the system were varied. Results confirm the experimental observations, and show different arrangement of the molecules, depending on the pH of the system, and charge-density of the LDH. An example of the arrangement of the aspartic acid molecules at different pH is shown in Fig. 1. The reaction mechanism of the peptide bond formation and the effect of the environment upon it is being currently investigated by DFT.

In order to observe larger scale arrangements and dynamics of the amino acids in the LDH interlayers we perform molecular dynamic simulations. Preliminary results highlighted that readily available force fields can be challenging to correctly optimise hybrid charged layered systems. Therefore, additional work is described to improve the currently available force fields for mineral systems.

The results obtained confirm the experimental observations and bring new insights onto the understanding of the mechanism of the peptide bond formation in the early Earth environment.
GLYCEROL CARBONATE-BENTONITE COMPLEXES FOR ENHANCED CONTAINMENT OF HYPERSALINE LEACHATES

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Saline (>0.1 M) liquors from industrial and mining activities represent a substantial environmental hazard, especially for groundwater resources. Increasing production volumes of these saline and hypersaline (>1M) leachates, together with the failure of traditional lining systems such as Compacted Clay Liners (CCLs) or Geosynthetic Clay Liners (GCLs), necessitate the development of alternative improvement methods over the use of conventional liners. One possibility is to modify the clay component of GCLs to make them more resistant to osmotic contraction under hypersaline conditions.

We have explored the possibility of employing glycerol carbonate (GC) as an inexpensive additive for robust new bentonite-based hydraulic barriers capable of retaining and attenuating the migration of hypersaline leachates. The cyclic glycerol carbonate is a viscous liquid with good miscibility with water, and can be produced using ‘green chemical’ methods (Turney et al., 2013) from glycerol and urea with a polymeric zinc monoglycerolate (ZMG) as a catalyst. Selection of GC as a potential additive to bentonite originated upon its favourable chemical properties, such as non-toxicity, high polarity, a higher dielectric constant than water, and high boiling point. Propylene carbonate (PC), a similar cyclic organic carbonate has been studied by Onikata et al. (1999) for the same purpose as here, but the higher dielectric of GC offers the possibility of a stronger interaction between the interlayer cation of the bentonite and the added carbonate, hence potentially a better liner performance in hypersaline liquids.

Swell Index tests of GC-bentonite and PC-bentonite were conducted according ASTM D5890 except that de-ionized water was replaced with calcium chloride solutions at ionic strength of 0, 0.125, 0.313, 0.625, 1.25, 2.5 and 6.25 M. While swelling of the modified-bentonites in deionised water was similar to that of Na-bentonite, the swelling index of both GC-bentonite and PC-bentonite complexes were significantly greater in CaCl2 compared to Na-bentonite. When comparing the two types of modified bentonite, GC-bentonite showed as much as two-times (2x) greater swelling at higher ionic strength (I≥2.5 M), than that of PC-bentonite.

To investigate the water retention characteristics of the GC-bentonite modified Fluid Loss tests (ASTM S890.02) were carried out in NaCl and CaCl2 solutions at various ionic strengths (Figure 1). Swell Index tests of GC-bentonite and PC-bentonite were conducted according ASTM D5890 except that de-ionized water was replaced with calcium chloride solutions at ionic strength of 0, 0.125, 0.313, 0.625, 1.25, 2.5 and 6.25 M. While swelling of the modified-bentonites in deionised water was similar to that of Na-bentonite, the swelling index of both GC-bentonite and PC-bentonite complexes were significantly greater in CaCl2 compared to Na-bentonite. When comparing the two types of modified bentonite, GC-bentonite showed as much as two-times (2x) greater swelling at higher ionic strength (I≥2.5 M), than that of PC-bentonite.

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in NaCl). Whereas GC-bentonite was more capable of retaining water under extreme conditions, comparison of the modified-bentonites products at lower ionic strengths exhibited similar behaviour. Our results also indicated that there was a hyperbolic relationship between the amounts of GC used for bentonite modification and the fluid losses. Consequently, the addition of GC at a rate greater than 1:1 (~100% in mass) with Na-bentonite is not recommended.
OBSERVING THE INTERACTIONS OF IONS WITH MUSCOVITE-WATER INTERFACES USING X-RAYS*

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The interaction of ions with charged mineral-water interfaces is a critical feature for understanding the transport of contaminants in the environment. A robust understanding of the actual ion distribution at these interfaces is often obscured by the presence of the liquid phase. I present recent work where we use X-ray reflectivity and resonant scattering to observe the structures and interactions of ions through direct in-situ measurements. Specifically, I will review our recent work on the distribution of adsorbed ions between distinct adsorption states (e.g., inner- and outer-sphere species, defined by the number of water layers separating the ion from the surface), including differences in the observed trends in ion distributions between mono-, di- and trivalent cations. I will also describe our recent work to observe and understand the thermodynamic controls over ion adsorption in this system which reveals the critical role of ion and muscovite surface solvation in understanding adsorbed cation properties at these interfaces.

*This work was done in collaboration with Sang Soo Lee, Neil Sturchio, Kathryn Nagy, and others. The work was supported by the DOE/BES Geosciences Research Program.
Natural organic matter (NOM) is often associated with clay minerals in soils and suspended colloids in natural waters, and the interaction of NOM with clay minerals is thought to be important in many geochemical processes including metal ion sorption and transport. As part of a project to investigate metal and water dynamics in NOM-clay composites and the mechanisms for NOM-clay binding, we have synthesized a series of NOM-hectorite composites and characterized them by powder X-ray diffraction (XRD); transmission electron microscopy (TEM); scanning electron microscopy and energy dispersive analysis (SEM-EDX), and He ion scanning microscopy (HeiM). The results show that the NOM coats the hectorite forming solid aggregates; that NOM is incorporated into the interlayer galleries of Na-hectorite but not Ca-hectorite, that the NOM is more intimately mixed with the Na-hectorite than the Ca-hectorite, and that the NOM in the composites is sufficiently ordered so that it yields detectable XRD intensity.

Base Na- and Ca-hectorite samples were synthesized by exchanging and filtering the <2 μm fraction of San Bernadino hectorite (available from the Clay Minerals Society) multiple times in NaCl and CaCl₂ solutions. NOM-hectorite composites were synthesized using these two samples and the as-received Suwannee River NOM (SRNOM) and the humic acid (HA) and fulvic acid (FA) fractions of this sample (all available from the international Humic Substance Society). The samples with the organic matter were made by suspending the clay and NOM in solutions of the desired salts, titrating to ~ pH 12 with NaOH or Ca(OH)₂, solution to dissolve the organic matter, titrating to ~ pH 2 with HCl to aggregate the sample, and finally freeze drying the sample. XRD data was obtained with a Rigaku D/Max Rapid II instrument, SEM data with an FEI Helios Nanolab instrument, and HeiM images with a Zeiss Orion Plus instrument. TEM images were obtained for the base Na-hectorite sample dispersed in deionized water using an ethanol and polymer infiltration method to prevent particle aggregation using an FEI Tecnai Spirit T-12 instrument.

The XRD data for the composites equilibrated at 43% R.H. shows that the basal spacings of the three Ca-hectorite samples are ~14.5Å, indicative of the 2-water layer structure expected at this R.H. For the Na-hectorite composites, however, the basal peak has multiple components. The maxima are at ~15.6Å, indicative of a 2-water layer structure, but the sample with HA has a shoulder at ~35.3Å, and the sample with SRNOM has a shoulder at ~26.6Å. We interpret the basal spacings larger than 15Å to be from the interlayer galleries that contain NOM. Incorporation of NOM into the interlayers of Na-hectorite but not Ca-hectorite is expected because the individual T-O-T layers of Na-hectorite delaminate in water, but those of Ca-hectorite do not. TEM images of the base Na-hectorite show substantial dispersion in deionized water.

The XRD patterns of the NOM-exchanged samples of Ca- and Na-hectorite also contain intensity in the 3.5 to 5.0Å range that is not present for the base samples. The strongest intensity in this region is for the Ca-hectorite with HA and SRNOM. We interpret this intensity to represent FA, HA, and SRNOM that is sufficiently structurally ordered by the presence of the clay and can yield detectable diffraction intensity. Humic substances have complex and diverse structures that contain aromatic and aliphatic hydrocarbon components as well as oxygen in carboxylic, phenolic, and other functional groups. Interaction with metal cations is thought to occur predominantly through the carboxylic and phenolic sites, depending on the pH. Graphite has a basal spacing of 3.55Å. If the humic molecules in our samples were oriented with their aromatic structural elements approximately parallel, we expect to see a minimum basal spacing of 3.55Å. If the humic molecules in our samples were oriented with their aromatic structural elements approximately parallel, we expect to see a minimum basal spacing of 3.55Å. 

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near this value. The larger spacings observed could arise if the molecules were held further apart by interaction with the cations and/or the clay basal surfaces. Computational molecular modeling will be needed to understand the structure and its origin in more detail.

HeiM and SEM images of the base Na-hectorite, Na-hectorite-SRNOM, and Ca-hectorite-SRNOM samples show significant differences in morphology. The base Na-hectorite shows aggregated clay particles. Both samples with SRNOM appear to consist principally of composites composed of both clay and NOM. EDX shows that for the Na-hectorite-SRNOM sample, most spots that were analyzed show both the elements of the clay (Si, Mg, F, Na, O) and C attributable to the NOM. A few spots show only C and O from the NOM, demonstrating formation of μm scale volumes of NOM coating. The Ca-hectorite-SRNOM sample has many more locations that show signal for only C and O from the NOM, sometimes with weak signal for the metals from the clay. Other spots yielded signal for both the clay and NOM, and a few yielded signals principally for the clay with little C intensity. We interpret these results to show that the NOM is much more intimately mixed with the Na-hectorite than the Ca-hectorite. This result is consistent with previous experimental results and also with molecular dynamics computational modeling that shows stronger NOM cross-linking with Ca in solution than with Na.

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Hydrotalcite clays with isomorphic substitution are increasingly finding applications as promoters in synthesis. Here we report a new application of these tunable clays for substituting polar aprotic (PA) solvents in nucleophilic aromatic substitution reactions (SnAr). Finding alternatives to PA solvents, such as Dimethylformamide (DMF), N-Methyl-2-pyrroldone (NMP), and Dimethylacetamide (DMAc), is critical to industry, given the mounting evidence of their toxicity and the potential for regulatory action. By using hydrotalcites as additives in SnAr reactions in toluene we find that we obliterate the need for the PA solvents and improve yield and selectivity. Furthermore, the selectivity can be tuned by using hydrotalcites with different isomorphic substitutions. We have also functionalized the hydrotalcites with an ionic liquid, and show that this can further increase the yield of the reaction. We thus propose that hydrotalcites act as heterogeneous catalysts for SnAr reactions.
The reduction and reoxidation of hydroquinone has been investigated as a function of pH at both a bare and modified Pt electrode. The modification is with the laminar silicate, SWy-1 montmorillonite clay. The goal of these studies is to ascertain the impact, if any that, of the clay matrix on the ability of microbially exuded quinones to act as redox mediators in delivery of charge to iron substrates. The presence of the clay has the ability to either accelerate or decelerate the reduction of quinone via electrode blockage, via charge exclusion, via enhanced acidity due to increased hydrolysis of compensating cations, and/or via alterations of hydrogen bonding of the quinone at the clay edges.

Results will be presented showing that the net rate of oxidation/reduction is accelerated in the presence of the clay at low pH. The results also shed some light upon the stability of various semiquinone intermediates and indicate that the potential for reduction changes due to stabilization of those intermediates with the clay surface.
ALTERATIONS IN 2,6-DISULFONATE ANTHRAQUINONE AQUEOUS ELECTROCHEMISTRY ASSOCIATED WITH MONTMORILLONITE CLAY

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9,10-Anthraquinone-2,6-disulfonate (AQDS) has been used as an electron mediator in microbial fuel cells and has been theoretically modeled for the rate of electron transfer to iron containing minerals. Here we report results on the enhanced stabilization of a (presumably) cation bridged quinone dimer formed by the mediator in the presence of iron rich nontronite clay. As found in the parallel study for hydroquinone the electrochemistry of the mediator is substantially altered by the presence of the clay in unbuffered solutions. In the case of simple hydroquinone reported in the companion study potentials are shifted, however, unlike the case of the simple hydroquinone in the multicycle ring interacts strongly with the clay to produce dimer intermediates that produce a hitherto unknown charge transfer band.

An experimental $E_p$-pH (Pourbaix) diagram for the molecule has been obtained for the first time and it will be used to illustrate why this molecule is capable of such dimer formation and why clay might alter the conditions under which the mechanism for dimer formation is preferred (related to proton transfer reaction). Very preliminary results for the difference in behavior between an rich iron clay and a less rich iron clay (nontronite to montmorillonite) are presented. These results may suggest that the presence of iron in the clay is crucial to the observed effect.

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A ‘CLUSTER’ COMPUTATIONAL MODELING METHOD TO EXPLORE THE EFFECTS OF METER IMPACTS ON CLAY MINERAL SPECTROSCOPY

Lonia Friedlander*, Gilles Frapper1, Timothy Glotch1, and Artem Oganov3
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Visible-near infrared (VNIR) detections of phyllosilicates on the Martian surface show that Mars may once have been extensively chemically altered and that water currently exists on there in mineral crystal structures. In contrast, thermal infrared (TIR) searches for phyllosilicates have been ambiguous [4, 5]. Clay deposits on Mars are thought to be early- to mid-Noachian in age, and are found in the heavily-bombarded southern highlands. Thus, it is probable that impacts played an important role in the evolution of clays on the Martian surface. Understanding the effects of impacts on clay mineral spectroscopy is fundamentally important for fully understanding Martian mineralogy.

In planetary science remote sensing, clays are often identified by the detection of VNIR bands at ~1.4 μm (O-H stretching overtone) and ~1.9 μm (4-H-O-H bending) [1–3]. Experimental results [8–10] show that these bands are retained even after impacts up to 39.1 GPa (Fig. 1A). In contrast, TIR emissivity spectra from the same shocked samples show progressive degradation of characteristic Si-O bending (~400–550 cm⁻¹) and stretching (~1000 cm⁻¹) bands beginning at 20.0 GPa (Fig. 1B). This indicates that phyllosilicates with severely altered silicate networks may still retain the ‘characteristic’ bands used for remote sensing identifications.

We present a computational method for approximating clay mineral vibrational spectra. This will help explore impact-driven structural change in clay minerals by computing the spectra of impact-altered clays, which can then be compared to laboratory spectra. Thus, we will determine whether (and how) impact-driven structural change associates with characteristic spectroscopic features. These findings will clarify the structures of the clay minerals indentified on the Martian surface, which will help explain their role in volatile retention, and in both the contemporary and historic Martian water cycles.

We used hybrid molecular orbital/density functional theory (MO/DFT) calculations on clay mineral ‘molecular clusters’ to model the IR and Raman vibrational frequencies of three clay minerals. We built our molecular cluster models using the ChemBio3D Ultra suite of programs. We tested several cluster models (size, composition), functionals, transition-metal pseudo-potentials, and basis sets. Where necessary, we scaled our computed frequency values by a priori factors to account for anharmonicy, basis set limitations, and inexact electron correlation determinations. All MO/DFT calculations were performed using the Gaussian09 package on Linux clusters run by the Applied Quantum Chemistry group at the University of Poitiers.

The clusters approach provides a reasonable approximation for clay mineral spectra (Figure 2). There are three advantages to this approach: 1) it is significantly faster than periodic approaches (hours vs. days) [13]; 2) it is easy to manipulate for the simulation of structural change. The simplified ‘clusters’ also clarify structural components, improving detail in the simulation of structural change. The simplified ‘clusters’ also clarify structural components, improving detail in the understanding of impact-driven structural change. The simplified ‘clusters’ also clarify structural components, improving detail in the understanding of impact-driven structural change.
assignment of atomic vibrations to spectral features. 3) It can be run in concert with more computationally heavy, periodic approaches.

Most drawbacks to the clusters approach are related to accuracy. The first is that charge balance requires "saturation" (i.e. the addition of sufficient H-atoms to balance formerly network Si-O bonds). This produces artifacts in the computed vibrational spectrum that must be taken into account. The second is the loss of some of the very low-frequency (long wavelength) "lattice mode" vibrations (~500 cm⁻¹), which cannot be obtained by the cluster approximation (Figure 2). In comparison with previous computational studies of clay mineral vibrational spectra [e.g. 14], this approach generates significantly redshifted high-frequency bands (Fig. 2, labeled arrow). Previous computations by periodic methods found slightly (< 30 cm⁻¹) blueshifted theoretical bands at high frequencies [14].

Despite these drawbacks, this technique shows potential as a valuable new tool for understanding impact-generated structural and spectroscopic change in clay minerals. Our future work will focus on using this technique as a starting point for the computation of structurally altered clay mineral spectra.

Figure 2. Vibrational spectra of kaolinite from laboratory ATR results and the kaolinite cluster approximation. We have labeled several key observations.
According to this research, clays rich in kaolinite, palygorskite and saponite-rich clays could be used for CO₂ sealing. Magnesium bentonite did not show physical adsorption of CO₂, but an increment of amorphous phase due to the acid retention of CO₂ mechanisms were determined, and the influence of the pressure, temperature and relative humidity, as well. Sepiolite and palygorskite are able of sequestering CO₂ through both physical and mineral mechanisms. The physical trapping is higher for palygorskite than for sepiolite. During the reaction, the minerals were attacked by CO₂ both under dry and wet conditions, leading to partial destruction of their structure together with a rock reduction volume and mechanical resistance. Therefore this attack may lead to the partial destruction of cap-rocks containing these minerals as major components, and to allow a loss of CO₂. In the case of palygorskite, however, because during reaction Mg-carbonate can precipitate, and some CO₂ is chemically bound (“trapped”), the CO₂ release is largely inhibited. Magnesium bentonite did not show physical adsorption of CO₂ but an increment of amorphous phase due to the acid attack was detected. Nevertheless the smectite exchange cations, leads to the precipitation of carbonates (dolomite), leading to a higher CO₂ retention. The smectite of the common clay was partially destroyed, and in the elapsed time, the illite too. But it was noted a certain physical retention and chemical reactivity. Finally the experiments carried out with kaolin, which contains nearly 30% of kaolinite, with illite and quartz; indicated that this material did not present physical trapping of CO₂ and any chemical reaction. According to this research, clays rich in kaolinite, palygorskite and saponite-rich clays could be used for CO₂ sealing reservoir. Figure 1 shows a hypothetic sandstone reservoir for CO₂, capped with the tested clay materials and the probably reactions to be occurred. Nevertheless a mathematical model should be developed to describe in a more general way the sequence and kinetics of reactions between CO₂ and clay rocks, to validate the experimental measurements for long-term reactive effects.
AUSTRALIAN CLAY SCIENTISTS WITH BROAD SHOULDERS

Will P. Gates*
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Australian scientists have had a long association with the study of clays and clay minerals. I cannot claim any intellectual connection to this genealogy, but while working with the Commonwealth Scientific and Industrial Research Organisation (CSIRO), several eminent clay scientists at (or associated with) the Division of Land and Water inspired me. They included Keith Norrish, Philip (Phil) G. Slade, Reginald (Reg) M. Taylor, William (Bill) W. Emmerson and James P. Quirk. Keith and Phil were still active scientists while I was there and Reg and Bill often came to work (Bill) or chat (Reg) regularly. It was very interesting sitting at a table with these gentlemen, especially when Jim visited from Western Australia, which he did once every year or so.

Keith Norrish and Jim Quirk, along with George Walker, all of CSIRO, were prime movers in creating the Australian Clay Minerals Society, which was officially established in 1962 with the 1st ACMs conference (Figure 1), held at the University of Melbourne. Many clay scientists of note were present at that conference, and two note-worthys happened to skip the photo opportunity—I. (Ted) R. Radoslovich and A.V. Blackmore. Many of them went on to careers that inspired many others, including those highlighted in Figure 1.

I'd like to briefly mention two individuals with whom I had the pleasure to work with: Keith Norrish and Phil Slade. Keith has had a long and illustrious career with the CSIRO and was awarded the CMS Marylin & Sturges W. Bailey Distinguished Member Award in 2001, a few years after his 'official' retirement. He was a key and early figure in measuring and understanding crystalline and osmotic swelling of clays, in developing methods to quantify the chemical make-up of clays and in designing the mechanisms of weathering in clay minerals. Keith was a ‘can do’ fellow—nothing was impossible. He also was a tinkerer and could never leave the settings on a diffractometer or spectrometer alone—much to the dismay of some of us who used the instruments afterwards. One late afternoon while talking about Fe K-edge X-ray absorption spectroscopy to determine Fe(ii) and Fe(iii) ratios, he said ‘let’s run some scans’ and proceeded to modify the goniometer and scintillation counter on an old Philips diffractometer. Before midnight we were able to see nicely the shift in energy expected between a ferric Fe bearing nontronite and a ferrous Fe bearing saponite. We also probably violated a few dozen OH&S and ARPNSA (The radiation authority in Australia) codes in the process, and it took a couple days to get the instrument back working like a diffractometer again.

I worked closely with Phil during my time at CSIRO and we published a number of papers on our research. Phil was an experimentalist of the highest standards and remains the most talented and gifted research scientist I’ve worked with. In addition to an innate ability to think in the reciprocal space, Phil understood and used the concepts of packing density, bond-valence and crystal symmetry to describe complex organo-clay superstructures. His experimental data for the location of interlayer cations in clays should be used in all molecular dynamics simulations. Phil also extended some of Keith’s and Jim’s work on crystalline and osmotic swelling of clays in salt solutions with seminal works published in the early 1990’s. Phil’s research in this area underpins much of my current work with industry. He suffered fools for no-one, and at times was prickly to work with—we had many heated discussions—but if you had evidence to back your arguments, he’d be the first to shift his concepts and inevitably come up with experiments to move the idea forward.

Phil sat on a lot of excellent research data that unfortunately rarely saw the light of day. He had a card filing cabinet filled with transmission X-ray diffraction negatives—mostly of organo-vermiculite intercalates. When a paper came out describing an organo-clay from researchers elsewhere, Phil could often find a digitafactograph he had made many years previously of that same material intercalated into vermiculite.

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Arguably the biggest legacies Keith and Phil have left the clay science community in Australia are their notebooks. Keith’s are filled with details on the chemistry of many hundreds of clay and clay mineral samples, written in his scrawling long-hand.
I conducted many analyses of some of the same materials and in all instances, Keith’s analyses, on home-made instrumentation and using a slide-rule, were as accurate as any of mine. Phil’s excellent and detailed notebooks were filled with not just experimental descriptions and results, but also recorded his thoughts on the work and proposed further work. He did keep his notebooks under lock and key as they were, in his words, “the property of the Queen”. Both Keith’s notebooks and Phil’s X-ray photographs are stored in the Library at CSIRO Land and Water, Waite Campus, Adelaide. I hope Phil’s notebooks are kept somewhere safe as well.

Understanding of the behaviour of geosynthetic clay liners (GCLs) when in contact with mining waste leachates, processing liquors or feed/return waters is growing as the results of recent research becomes available. Industrial and mining processes produce huge volumes of liquid and semi-solid wastes that generally have extreme values of pH and ionic strength. High ionic strength and extreme pH do not always result in loss of GCL barrier performance. The complex interactions of high levels of dissolved ions, often near thermodynamic saturation and changes to leachate pH upon contact with bentonite may result in pore-filling reactions. Metal ore heap-leach processing piles can impose both aggressively acidic leachates and excessive stresses on a GCL used as a hydraulic barrier. This paper highlights recent research associated with the use of GCLs as hydraulic barriers for aggressive leachates, such as strong acids, strong bases and strongly saline leachates often found in mining and industrial activities.

Hyper-saline brines from, for example, reverse osmosis plants associated with mining activities in Australia must be retained under very low confining stresses. In general Na+-bentonite GCLs are not expected to perform well to hyper saline (>1M) leachates because of the high ionic strengths which generally result in an increase in pore size and connectivity of pores within the bentonite. Often the saturated hydraulic conductivity (k) of GCLs can be more than an order of magnitude higher in >1M leachates, even when the GCL is pre-hydrated with high quality water. These reactions are exacerbated by the presence of divalent and trivalent cations in the leachate because of their preferential retention by the bentonite and subsequent effect on clay fabric and porosity.

Bentonites are largely unstable under acidic conditions and the reaction of strong acids with bentonite increases its porosity, thus it is not surprising that recent research has shown acidic mine leachates to have a negative effect on the hydraulic performance of GCLs (e.g. Shackleford et al., 2010). Interaction between bentonite and acidic solutions result in lower liquid limit, swell index and fluid loss values of bentonites, and an increase in k of GCLs. Pre-hydration with high quality water and increased effective stress may enable GCLs to attain satisfactorily low k to the same acidic solutions. At 200 kPa effective stresses and acid concentrations of 0.125 M, the resulting k was <1x10^-11 m/s, indicating manageable performance of GCLs under heap-leach conditions, at least in the short term.

If the leachates coming into contact with GCLs are near saturation with respect to certain ions (e.g., Si, Al), the development of a possible pH gradient between the leachate and pre-hydrated bentonite pore water may result in precipitation of new mineral phases. Such reactions have been shown to result in pore-clogging reactions which could potentially delay breakthrough of contaminants (Benson et al., 2010, Gates and Bouazza, 2010).

However, because of the lack of research evidence at this time, in general, we urge caution in the use of GCLs as barriers to strongly acidic or hyper saline leachates. The thinness of GCL barriers means their capacity to undergo extended long-term reactions is limited. We recommend that GCLs should always be used in combination with geomembranes to form composite liners and with engineered sub-base material.
ATOMISTIC MODELING OF ILLITE WITHIN SHALE: THE STORY SO FAR

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Recent developments in horizontal drilling techniques have rekindled interest in shale plays across the globe. These nascent energy stores are potential sources of massive amounts of natural gas and methane; the current estimate of the Marcellus shale play alone is 500 TCF, the equivalent of over twenty years’ worth of natural gas consumption in the entire United States. Such an abundant supply of a gas that when burnt, has a lower carbon footprint than other fossil fuels, makes methane an obvious transition energy source to lead us away from an almost entire dependence on fossil fuels, towards a more sustainable, mixed-energy and less carbon-dominant future. As well as being sources of large quantities of gas, exhausted shale beds could potentially store large quantities of captured and compressed CO₂ for long-term carbon sequestration. As attractive as this sounds, there is much controversy surrounding methane extraction and CO₂ storage, which means research is pressing at all length-scales. Shale is a composite material, with four main components, silica, carbonates, clay minerals and organic matter, which present both experimentalists and modelers alike with major challenges. These range from the measurement of the porosity and permeability of shale, to how the various components of the shale matrix interact with CH₄, CO₂ and water, thus affecting their extraction and/or storage.

Our area of research concerns the clay mineral/H₂O, CO₂ and CH₄ interactions at the smallest scale of investigation—the atomistic—using quantum mechanics in the form of density functional theory. The dominant clay minerals within mature shale are kaolinite, smectites and illite; robust, atomistic models of the first two are readily available, but such models of illite were not, which meant we had to build them. This presentation unfolds from a description of a simplistic version of the intermingling of organic matter and clay particles during the formation of shale, to the building of several varieties of 1M and 2M₁ illite models, based on crystal structure data and experimental results, and finally to exploring surface/H₂O, CO₂ and CH₄ interactions.
Ferrihydrite is probably the most widespread and environmentally important natural inorganic nanoparticle, composed of defective nanocrystals of hydrous iron(III) oxide. For many years, the accepted description of the structure of ferrihydrite has been a multi-phase model developed by Drits and co-workers (Drits et al., 1993). Recently, Michel and coworkers published a single-phase model for the structure of ferrihydrite (Michel et al., 2007, 2010). Remarkably, the Drits and Michel models each achieve arbitrarily good agreement with different forms of x-ray scattering data obtained from powder samples: the reciprocal-space diffraction patterns and real-space pair distribution function (PDF), respectively. Understanding this apparent paradox, and developing realistic structural models for ferrihydrite, remain a pressing need.

We implemented a new code to explore different types of occupational and structural disorder in whole-nanoparticle models of 6-line ferrihydrite. The approach used the reverse Monte Carlo method to evolve the nanoparticle structure so as to improve goodness of fit simultaneously to the experimental structure factor and PDF. This approach reproducibly generates nanoparticle models that are a better match to the total scattering data than either the Drits or Michel models. The improved agreement is correlated with the development of types of structural disorder that are difficult to reproduce by a single-unit-cell approach, and include the incorporation of explicit distributions of iron vacancies, subnanoscale internal porosity, and considerable structural disorder.
We use stable hydrogen and oxygen isotope ratios of residual kaolins from deposits and new prospects on the Proterozoic Fennoscandian shield to explore the age and conditions of kaolinisation. In southern Scandinavia, kaolin has been mined from the Ivä deposit in Skåne, southern Sweden, and the Rønne deposit on Bornholm Island, Denmark. Both deposits developed on ~1.46 Ga granitic rocks and were covered by Early to Late Cretaceous sedimentary rocks. Kaolinite separates yielded isotope compositions ($\delta^{18}O_{v}$-SMOW = 18.7 to 19.9‰; $\delta^{2}H_{v}$-SMOW = -83 to -82‰) that are similar to those of major kaolin deposits in Central Europe and indicate weathering under warm Mean Annual Temperatures (MATs) of >15˚C.

Deep residual kaolins covered by 10 to 30 m-thick Pleistocene tills also developed on the Palaeoproterozoic Svecofennian rocks in Finland. We investigated drill hole samples from the Virtasalmi deposit in Southern Finland, and Vittajärvi and Siurunmaa prospects in Northern Finland. These previously also have been regarded as products of humid tropical weathering of Palaeoproterozoic to Mesozoic age. New oxygen and hydrogen isotope ratios on kaolinite ($\delta^{18}O_{v}$-SMOW = 13.8 to 16.1‰; $\delta^{2}H_{v}$-SMOW = -126 to -105‰) indicate, however, weathering by cool groundwater under MATs of 13-15˚C.

These temperatures are below those that prevailed in Finland in the Cretaceous, yet substantially above Plio-Pleistocene MATs. Comparisons with palaeotemperatures in N Europe and around the Arctic Ocean indicate that the Finnish kaolins developed on the shield surface in the Palaeogene or, alternatively, Miocene when the Fennoscandian shield was already at high latitudes. Deep weathering selectively developed in highly fractured and altered shield rocks and took place after stripping of Palaeozoic cover rocks in response to latest Cretaceous and Palaeogene uplift.

The cool kaolins in Finland indicate that previous routine attributions of kaolinitic weathering products in the geological record to humid tropical environments should be closely scrutinised.
Influence of Smectite Mineralogy on Measured Redox Properties: A Combined Electrochemical and Spectroscopic Study

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Fe-bearing clay minerals serve as important redox buffers in both natural and engineered systems, where they readily undergo electron transfer reactions with a wide range of environmental constituents, including bacteria, nutrients, metals, and organic contaminants. Despite much effort, attempts to model the extent and kinetics of such reactions have proven to be challenging due to the inability to describe clay mineral redox properties in terms of reduction potential (E_H) values. Difficulties in obtaining such values are due largely to the lack of reactivity between clay minerals and electrode surfaces.

Recently, we demonstrated that this challenge could be overcome using soluble electron transfer mediating compounds to facilitate rapid electron transfer reactions between clay minerals and electrodes. This approach allowed us to relate the oxidation state of structural Fe to applied E_H values. Here, we apply this approach to measure the redox properties of four natural Fe-bearing smectites with varying structural Fe-contents, layer charges, elemental compositions, and redox histories to determine how clay mineral redox properties deviate as a function of these variables. X-ray absorption and Mössbauer spectroscopies complimented these measurements and were used to determine how structural molecular-scale variations influenced macroscopic redox properties.

All four smectites studied exhibited unique and complex redox properties, which could be related to both their macroscopic and molecular-scale attributed. Effective standard reduction potential values (E_H0) varied considerably among the smectites, with more negative values linked to both larger bulk layer charge values and hyperfine parameters collected from Mössbauer spectra. Additionally, each of the four smectites were redox-active over a wide E_H range, and covered an array of redox regimes, ranging from methanogenesis to aerobic respiration. These ranges varied for each smectite, and were linked to structural Fe contents. Redox cycling of the smectites revealed changes in the coordination environment of structural Fe for all four smectites, which had varying effects on redox properties. Collectively, these results serve as a first step towards modelling and predicting the redox properties of natural and engineered clay minerals. This work also indicates that clay minerals are capable of acting as redox buffers under a wider range of E_H conditions than previously thought.
This talk will focus on Oil-Dri Corporation of America, its raw materials, and the major requirements of four of our markets. Oil-Dri Corporation is predominantly a vertically integrated clay minerals mining, processing, and marketing company. Our company mission statement is “Creating Value from Sorbent Minerals.” What is a sorbent? It is basically clay (or closely related mineral) particles with a lot of holes in them. The idea is to sorb material (either adsorb or absorb) and then retain it, i.e., suck and cling. Our company is publicly traded, with the controlling interest being held by the Jaffee family. Our start was in floor absorbents (i.e. the name Oil-Dri) which shortly thereafter expanded to industrial absorbents. In this application, a material is mined, sized, heat treated to an LVM (low volatile material) state, and packaged. The primary purpose of the initial application was to remove oily liquids from floors. The material must retain its shape during use and suck up a liquid, leaving little or no “smear” on the floor; and retain the liquid in a sanitary landfill. This requires a large pore volume with small pore diameters so the material will suck and cling. A second application is pet box absorbents. In this application, a clay product requirement is again sorptivity. It may absorb a liquid (e.g., cat urine) and adsorb odors (i.e., suck and cling). The better it does this, the better the product. Processing is normally raw material selection, drying, sizing, and packaging. Cat litters today come in a variety of shapes and sizes. There may be large granules, small granules, unscented products, scented products, or various scoopable products. One of our claims to fame is a flushable product. The product must form a hard clump on urine contact yet promptly disintegrate on flushing. Talk about a formulation challenge! A third application is pesticide carriers. Here a material commonly must absorb a liquid (the pesticide), hold the liquid during packaging and transport, and release the liquid on application. We need it to suck and cling, but not cling too tight. Raw material is selected, dried, sized, and may or may not be heat treated. Sizes come in a wide variety, from large granules to a powder. A fourth application is edible oil purification. All the oils we eat (e.g., soybean oil) require purification once extracted from the seed. At one stage in the purification process, the oil is contacted with a clay mineral, normally under heat and a vacuum. The clay mineral is then removed by filtration. The purpose is to reduce color, metals, and various other undesired materials. In this case we want the product to suck, but not too tight because one wants the oil back, and cling really tightly. Sucking, clinging, and selling holes are requirements. But the products must suck and cling just so.
Zn SORPTION MODIFIES DYNAMICALLY THE LAYER AND INTERLAYER STRUCTURE OF VERNADITE

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In surficial environments, the fate of many trace metals is influenced by their interactions with the phyllomanganate vernadite, a nano-sized and turbostratic variety of birnessite. To advance our understanding of the surface reactivity of vernadite, synthetic vernadite (β-MnO2) was equilibrated at pH 5 or 7, reacted with dissolved Zn to produce Zn-sorbed β-MnO2 with Zn/Mn atomic ratios from 0.003 to 0.156, and characterized structurally. The octahedral layers in the Zn-free vernadite contain on average ~0.15 vacancies, ~0.13-0.06 Mn3+ and ~0.72-0.79 Mn4+. The layer charge deficit is compensated in the interlayer by Mn3+ bonded over Mn vacancy sites and Na+ located in the interlayer mid-plane. The average lateral dimension of coherent scattering domains (CSDs) deduced from X-ray diffraction (XRD) modeling is ~5 nm, consistent with that observed by transmission electron microscopy for individual crystals, indicating that the amounts of edge sites can be estimated by XRD. The average vertical dimension of CSDs is ~1 nm, equivalent to 1.5 layers and less than the observed 3 to 4 layers in the particles. Zinc sorption at pH 5 and 7 on pre-equilibrated vernadite induced crystal dissolution reducing the lateral CSD size ~15-20%. Zinc K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy and xRD show that Zn occurs in the interlayer above vacancies as a triple-corner-sharing surface complex, which is fully tetrahedral at low Zn/Mn ratios and increasingly octahedral at higher ratios. As Zn/Mn increases, the site density of layer Mn4+ decreases from 0.13 ± 0.01 to 0.03 ± 0.01 at pH 5 and from 0.06 ± 0.01 to 0.01 ± 0.01 at pH 7, and that of layer vacancies correspondingly increases from ~0.15 to 0.24 and 0.21 at pH 5 and 7, respectively. These changes likely occur because of the preference of Zn2+ for regular coordination structures owing to its completely filled third electron shell (3d10 configuration). Thus, sorption of Zn into the interlayer causes the departure of layer Mn4+, subsequent formation of new reactive layer vacancies, and an increase in surface area through a reduction in particle size, all of which dynamically enhance the sorbent reactivity. These results shed new light on the true complexity of the reactive vernadite surface, and pose greater challenges for surface-complexation modeling of its sorption isotherms.
ILLITE AND ITS POLYTYPES: WHAT WE KNOW AND DON’T KNOW

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illite has intrigued clay scientists at least since the founding of the Clay Minerals Society in 1963. Why? Initially because of its abundance in sedimentary rocks but now because of the complexity of its origins, complexity of its structure, complexity of its mixed layering and that it can be age dated. Therefore it is difficult to define the mineral illite.

What we know about the mineral illite and its polytypes can be summarized as

• a dioctahedral monoclinic 2:1 phyllosilicate with mainly fixed K or NH4 interlayer and some expandable interlayers (based on the research of Ralph E. Grim, S.W. Bailey, Jan Środoń and others).
• its polytypes consisting of $1M_d$ (with a range of structural and chemical disorders), $1M_{cis-vacant}$, $1M_{trans-vacant}$, $2M_1$ (based on the research of S.W. Bailey, Robert C. Reynolds Jr., Victor Drits and others).
• forming authigenically from surface temperatures to metamorphic temperatures in very many different rocks such as sandstones, shales, slates, bentonites, as well as in very many different settings such as during burial, hydrothermal settings, faults, weathering, microbial activity and glauconites and many more.
• dynamically changing as a function of Temperature, time, and K concentration (based among others on the research of John Hower and David R. Pevear).

Some open questions for discussion include:

• What are the mechanisms of illitization and what role do the different polytypes play during illitization? One mechanism and its polytypes, such as burial diagenesis in shales, is different to illitization in sandstones. Why?
• Is there a fundamental illite particle common to all illites as first suggested by Paul Nadeau?
• What role does the microenvironment play in the formation of illite?
• What processes control the order and disorder in illites?
Geopolymer cements are alkali activated meta-clays with similar strengths to Portland Cement, high fire resistance and low CO$_2$ footprint. Typical geopolymer cements are produced from meta kaolinite (heated to 550°C). In this study we investigated the potential of using illite/smectite rich Eocene Friedland clay, from NE Germany to seal boreholes. Friedland Clay contains 75 wt.-% clay minerals, with R0 i(0.3)/S as the most abundant clay mineral together with illite, muscovite, kaolinite and some minor chlorite. Buchwald et al. (2009) claimed that they were able to produce a geopolymer from Friedland clay using 5M NaOH solution, which unfortunately we were not able to reproduce.

The goal of the project is to develop a sealing cement that hardens under wet conditions at or below room temperature. Typical geopolymers harden at higher temperatures and therefore cannot be used for such applications. We have performed in-situ heating experiments using temperature X-ray diffraction and simultaneous thermal analysis to establish the behaviour of dehydroxylation and structural breakdown of the reactive clay mineral phases. Additionally, nuclear magnetic resonance spectroscopy of heated samples was used to detect and quantify temperature dependent changes in 5-fold coordinated aluminium, important for geopolymer cement reactions. It is commonly assumed that the reactivity of the meta clay is dependent on the amount of 5-fold coordinated aluminium.

With the help of additives to enhance the reactivity we have been able to develop a low permeable geopolymer cement that hardens without shrinking under room temperature and wet conditions in the laboratory.
Clays and clay minerals comprise a large fraction of soils and crustal rocks, and an understanding of their hydration and swelling behavior is important to assess long-term underground storage options for nuclear waste, binding of groundwater contaminants, availability of biologically relevant nutrients, and borehole stability in drilling activities. A better understanding of how the structural and thermodynamic properties of clays vary when exposed to changing humidity levels, temperatures, and pressures is needed to design more accurate macroscale models.

We used large-scale classical molecular dynamics simulations to determine the swelling behavior of both montmorillonite and beidellite at room temperature (25 °C) and a higher temperature of 150 °C representative of reservoir conditions. Four different interlayer cations were considered, including two monovalent cations, Na+ and Cs+, and two divalent cations Mg2+ and Ca2+. Model systems included random charge substitution sites to avoid biasing results. Water contents ranged from that of a dry clay to that beyond a two-layer hydrate. Additionally, water adsorption isotherms from grand canonical Monte Carlo simulations relate clay water content to relative humidity.

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EVALUATING THE SWELLING & EXFOLIATION OF TREATED CLAY MINERALS THROUGH COMPUTER SIMULATION

H. Christopher Greenwell1, James Suter2, Richard L. Anderson1, and Peter V. Coveney3

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Clay minerals are an example par excellence of the concept of structure-reactivity relationships in chemistry. The atomic scale electronic structure of the constituent elements in turn imparts a net negative charge on the nanometer sized 2-dimensional layers. The charge balancing cations therefore required have enthalpies of hydration, which result in the scale electronic structure of the constituent elements in turn imparts a net negative charge on the nanometer sized clay minerals.

In a technology context this manifests itself directly in two important areas:

i. In oil and gas drilling operations, drilling fluids perform essential tasks such as lubricating the drill bit, providing hydrostatic pressure and removing drill cuttings. One important function of the drilling fluid is to stop compacted clay minerals, commonly encountered in drilling operations, from taking up water from the drilling fluids and consequently swelling. Such a scenario can have an adverse impact on drilling operations and may lead to significantly increased oil well construction costs. With increasingly stringent environmental guidelines determining which swelling inhibitors are available for use in the oilfield as drilling fluid additives, there is a need to fully understand the mechanisms of clay hydration in order to design new swelling inhibitors, which conform to evolving regulations.1,2

ii. In the preparation of lightweight, yet resilient, clay reinforced polymer nanocomposite materials, the maximum strength effect and barrier properties to prevent gas ingress are found for clay layers that are fully dispersed in the polymer matrix. However, the full dispersion of clay particles in polymers of different types requires exfoliation to be carried out in a range of solvents. This leads to compatibilization of the clay mineral through surfactant type molecules. Here, as above, the ability to understand the processes leading to exfoliation are key.3,4

Computer simulations have been shown to offer excellent insight at atomic and molecular resolution into the interlayer structure and dynamics of clay minerals.5 Here we highlight the results from some recent studies undertaken using molecular dynamics computer simulations to screen various clays, solvents and swelling inhibitor structures against a hydration/solvation energy parameter.

Using large-scale molecular dynamics simulation, combined with experimental results, we have devised a set of “rule-based” design criteria for clay swelling inhibitors. To achieve this, we have formulated a hydration energy parameter (Eq. 1.), which assesses the changes in energy during the step-wise progression from mono- to bi- to trilayers of water in the clay galleries. This parameter can be used to rationalise and predict the swelling profiles for clays containing both cationic and neutral clay swelling inhibitors.

In further work, we tested the robustness of this approach to address the relative exfoliation properties of a range of clay minerals, with and without the presence of a range of surfactant type molecules, and in ethanol solvent as well as water.

\[ \Delta U(\text{monolayer}) = U(N) - U(N+1) \]

\[ \Delta U(\text{bilayer}) = \frac{U(N) - U(N+1)}{N} - \frac{U(N) - U(N+2)}{N} \]

\[ \Delta U(\text{trilayer}) = \frac{U(N) - U(N+1)}{N} - \frac{U(N) - U(N+2)}{N} - \frac{U(N) - U(N+3)}{N} \]

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In further work, we tested the robustness of this approach to address the relative exfoliation properties of a range of clay minerals, with and without the presence of a range of surfactant type molecules, and in ethanol solvent as well as water.
The results from our clay swelling inhibitor studies show that: (i) Cationic inhibitors should be able to replace sodium ions in the interlayer; (ii) Cationic inhibitors should possess a hydrophobic backbone; (iii) Cationic inhibitors should have primary di-amine or mono-quaternary amine functionality; (iv) Cationic inhibitors should have little alcohol functionality; (v) The hydrophobic backbone of the cationic inhibitor should be long enough to form a dense monolayer in the interlayer; (vi) For neutral inhibitors, the inhibitor should be a water-soluble organic molecule of low molecular weight with well-defined domains of relatively high hydrophobicity and small domains of hydrophobicity. Our “rule-based” criteria will facilitate the rational design of improved—and more environmentally acceptable—clay swelling inhibitors for oilfield drilling operations. The latest results from our research on the solvation of organo-clay with ethanol will also be presented.

Figure 1. Snapshot from simulations showing coordination of organo-ammonium at the clay silicate sheet surface. Colours: N = blue, H = white, O = red, C = grey, Si = orange, Al = green.
LAYERED DOUBLE HYDROXIDES AS NANOREACTORS FOR PREBIOTIC CHEMISTRY

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One of the most enigmatic steps in Earth’s ancient transition from a lifeless planet to a living world was the process or processes by which prebiotic organic molecules were selected, concentrated, and organized into the essential macromolecules of life. More than half a century of theory and experimental investigation points to the critical role of mineral surfaces in the formation of proteins. Since the formation of peptide bonds requires dehydration, the reaction is thermodynamically unfavorable in aqueous solution. However, clay mineral suspensions in alternating drying-wetting cycles have been found to promote the oligomerisation of amino acids. The possible roles of mineral surfaces in protecting, selecting, concentrating, templating and catalyzing reactions of prebiotic organic molecules are recurrent themes in discussions of the origins of life. Here, we propose that layered double hydroxides (LDHs), which could have been present in the Early Earth in alkaline pH hydrothermal vents, played a major role in prebiotic chemistry. LDH systems consist of layers of inorganic sheets, whose structure is analogous to brucite, Mg(OH)2. They carry a net positive charge because of the substitution of divalent cations by trivalent ions. Electro-neutrality is achieved by the presence of anions along with water molecules intercalated between the two sheets, i.e. in the interlayer domain. Due to the presence of high charge-density on the layers, these materials may concentrate amino acids in the interlayer domain to a greater extent than do the surfaces on three-dimensional minerals. The presence of a nano-scale “gallery” may also act as a sheltering environment, thus enhancing the stability of the intercalated amino acid.

To correlate the structure of the interlayer domain with its reactivity, well-crystallized materials with only aspartate molecules in the interlayer gallery was a prerequisite. The synthesis of this material can only be obtained by exchange reactions. Solid-state analysis performed on these samples indicated the successful intercalation of the target molecules, and no trace of other anions was detected. Interestingly, by varying the layer charge density of the LDH or the water content of the interlayer gallery, the aspartate is accommodated in different orientations. Since the driving force of the formation of peptides is dehydration, the LDH materials were heated to 250 °C and changes in the structure were monitored by in-situ infrared, in-situ Raman and in-situ X-ray diffraction. Combining these techniques is particularly interesting in elucidating the structure and the chemistry of the interlayer domain. Similar experiments were performed on the aspartate salt, serving as a reference sample. It has been shown that the interlayer domain of the LDH enhances the thermal stability of the amino-acid since its degradation takes place at 100 °C higher than the pristine aspartate salt. At around 250 °C, chemical reactions take place both in the aspartate salt and in the aspartate-LDH. Interestingly, the nature of the products formed was found to be completely different. Upon heating, the salt formed exclusively polysucinimide species, while the presence of amide bonds was detected in the interlayer domain of the LDH. Though these experiments were not carried out under geochemical conditions representative of the Hadean, the data demonstrate that lamellar species such as LDH are an ideal environment to protect and promote the condensation of amino-acids to form peptides. In addition, as emphasized by Greenwell et al., these materials provide a high coding environment and have the theoretical capability of self-replication with a high degree of fidelity.
FEDERAL LEGISLATIVE AND REGULATORY UPDATE
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This paper will look at a variety of federal legislative and regulatory issues impacting the clay industry thus far in 2013, and looking forward to the remainder of the 113th session of Congress.
ABSTRACTS

S.W. BAILEY: MODEST AND RESERVED, TEACHER AND RESEARCHER

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Sturges W. (“Bull”) Bailey, deceased since November, 1994, at the age of 75, was one of the founding fathers of The Clay Minerals Society. His early involvement with the Society included (but was not limited to) being the Technical Program Chair for Society meetings in 1964 and co-chair in 1966, 1969, 1977, and 1983-4. He was Editor of Clays and Clay Minerals from 1964-70, on Council from 1964-84, on or chaired the CMS-Nomenclature Committee from 1968-1993, CMS President from 1971-2, Distinguished Member from 1975, and he presented the George W. Brindley Memorial Lecture in 1988. The Distinguished Member Award is now called the Marilyn and Sturges W. Bailey Distinguished Member Award, an award initiated by Bull before he died and funded by his children, Linda and David.

In 1949, Bailey headed to the Cavendish Laboratory at the University of Cambridge, England, with a Fulbright to study officially with Sir Lawrence Bragg for his doctorate, but W. H. Taylor was Bailey’s actual thesis advisor and met with him about once per week. The actual day-to-day learning of crystallography was from J. V. Smith, his office mate. Bailey’s early work was on the feldspar structures (with Taylor and Smith), but he later turned to phyllosilicates at Wisconsin after S. A. Tyler involved him in a study on clays from the Lake Superior iron ores, and he was encouraged to continue with clay mineral studies by M.L. Jackson, G.W. Brindley, and Bill Bradley. In 1957, Smith and Yoder published the derivation of the mica polytypes. Bailey used a similar approach for the serpentines, and later, he integrated the mica stacking derivations into his modified approach. Although Bailey published well over 100 papers on phyllosilicates, any current review paper on the subject of phyllosilicate structures must reach back to his fundamental studies of polytypism of the serpentine-kaolin, chlorite, and mica groups as the first step in describing these minerals. As more precise structures are determined of phases he may have studied, the derivation of the stacking of the clay-mineral structures will always be the start of any review. His development of how components of layer-type structures combine to form component units is the essence of how to predict limitations to composition and geometric stability of phyllosilicates.

Bailey always said that he considered teaching to be one of the most important parts of his work, and he seemed particularly pleased when complimented on his teaching. Bailey seemed to have infinite patience, and he was always fair and inclusive. He let the subject matter lead in lectures: never very flashy with little humor. However, for some reason, he did not seem to need the flash and humor; instead each lecture was perfectly organized, absolutely clear and precise, and inclusive. He let the subject matter lead in lectures: never very flashy with little humor. However, for some reason, he did not seem to need the flash and humor; instead each lecture was perfectly organized, absolutely clear and precise, and he laid the foundation for complex topics. He used visual aids where possible, but I do not remember that he used such aids often. Bailey never taught an introductory class, and it is perhaps doubtful that he would have done as well in introductory classes, where students seem to want entertainment over substance. Nonetheless, he had the qualities that make an exceptional teacher, which are also the same as the qualities of an outstanding person: insight and respect. In 1990, Bailey received the Neil Miner Award for teaching excellence of the National Association of Geology Teachers.
NEW X-RAY ENVIRONMENTAL INSTRUMENTATION FOR STUDYING SOLIDS IN SOLID-LIQUID-GAS SYSTEMS UNDER CONFINING PRESSURES AT ELEVATED TEMPERATURES

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There is a surprising lack of information on both the geochemistry (including mineralogy, mineral kinetics) and the interaction of minerals under deep-ocean floor and at deep-sediment (to 10,000 meters depth) conditions. To better study mineral reactions in these two environments in real time, a high-pressure environmental chamber (HPEC) was constructed using in situ X-ray diffraction for studies (from near vacuum) to 1000 bars and (from -20 °C) to 200 °C. In the HPEC, a liquid, e.g., a brine, plus sample in suspension is pressurized by gas, e.g., CH₄ or CO₂, or liquid, e.g., supercritical CO₂. The unique aspect of this chamber is that the sample + liquid (~ 2 mL) forms a dynamic system, and particles can move freely in the liquid while being illuminated by the X-ray beam. The dynamic aspect of the HPEC allows the study of clay minerals in fluids, even if flocculation occurs. In addition, it allows long-duration studies on the effect of micro-organisms on these mineral reactions, a large-bore (~ 25 mL), Morey-style “incubation” chamber was devised for off-line experiments that could be regularly examined via injection at appropriate P/T conditions into the HPEC.

The potential significance of these devices goes beyond the ocean or deep sedimentary environment because materials and reactions can be studied while using nearly any liquid as an immersion agent.

Possible research programs utilizing the HPEC include, but are not limited to, studies of: a) formation of authigenic minerals, such as dolomite, b) the stability and nature of clay minerals, including biological enhancement of the illitization reaction, and how biological material (DNA, proteins) may interact with clays as a function of salinity, temperature, and pressure, c) deep-ocean alteration processes, d) sea water interactions with minerals as a function of salinity, temperature, and pressure, e) alteration processes of continental-derived materials, f) methane- and CO₂ hydrate formation and possible methane or CO₂hydrate–smectite formation as a function of salinity, pressure, temperature and methane or CO₂ content, g) the effects of pressure, temperature, salinity, and biota on sediment-related reactions, and h) mineral-brine reactions associated with CO₂ sequestration in deep sedimentary basins.

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ANoxic CONDITIONS WITHIN THE SMOKY HILL CHALK MEMBER OF THE NIOBRARA FORMATION AND ITS EFFECT ON ORGANIC AND INORGANIC C-N ASSEMBLAGES

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World fossil fuel supplies continue to be constrained by the ever-increasing need for energy. Traditionally conventional hydrocarbon deposits, such as oil and gas, which are produced by simple pumping, have supplied world energy. Geoscientists are now searching to satisfy global demand for unconventional hydrocarbon deposits, which are often produced from shales using secondary or even tertiary stimulation methods. Understanding the provenance and depositional history of the organic material in these unconventional shale deposits can greatly benefit exploration and recovery. Oceanic Anoxic Events (OAEs) may influence the quality and type of organic/inorganic sediments preserved in shales. OAEs are interpreted as rapid, global depositions and concentrations of organic-rich marine facies. The Smoky Hill Chalk Member of the Niobrara Formation was deposited in the Western Interior Seaway during the Cretaceous (Coniacian–Santonian) and has been hypothesized as an OAE event. X-ray diffraction (XRD) and stable carbon (C) and nitrogen (N) isotopes were used to determine the concentrations of C and N in the inorganic/organic phases. Carbon pools identified include carbonates and organic matter (OM) with sub-pools of C-OM located as particulates and in interlayer sites of the expandable part of mixed layered clay minerals (i.e., smectite). Nitrogen pools identified include N-OM particulate and N-OM in interlayer sites of smectite. Fixed N in the interlayers sites of illite was not detected. The mineralogical and isotopic data support the hypothesis of an oxic to anoxic transition with time. An increase in the total percent carbon and nitrogen available within the organic assemblages was found, along with an increase in laminations and abundance of pyrite. Understanding the accumulations of organic material and the progression of anoxia can assist scientists to pursue similar formations in the exploitation of unconventional hydrocarbon deposits.
Saponite has been widely used in a number of industrial fields because of its higher surface acidity and thermal stability when compared with other clay minerals. Due to its limited natural resource, synthesis of saponite has attracted much attention during the last two decades. The main aim of this study is to investigate occupancy of Al ions and its effect on the structure of synthetic saponites.

In this study, two series of saponites with fixed (Si+Al)/Mg and Si/Mg ratios, respectively, were successfully synthesized by using hydrothermal method. The crystallinity, morphology and occupancy of Al ions in the synthetic saponites were investigated by using a combination of different characterization techniques (XRD, XRF, $^{27}$Al and $^{29}$Si MAS NMR, SEM and TEM).

XRD patterns indicated that well-ordered saponites were obtained when the initial Si/Al ratio located at 5.43—7.89 in both two series, in which well crystallized large clay layers could be extensively observed. However, those poorly crystallized saponites showed small particle aggregates under SEM, which contained small crystallized saponite particles with random orientation as indicated by TEM images. Intercalation experiments with surfactant, hexadecyltrimethylammonium bromide, further demonstrated that all synthetic saponites have well layered structure.

$^{27}$Al and $^{29}$Si MAS NMR spectra demonstrated that substituting Al ions occupied both tetrahedral and octahedral sites. Well crystallized synthetic saponites had a higher Al(V)/Al(VI) ratio than poorly crystallized samples. Al occupancy in octahedral sites showed a negative effect on the crystallinity of the synthetic saponites. Meanwhile, a one-to-one (1 $\text{Al}^{3+}$ → 1 $\text{Mg}^{2+}$) substitution actually occurred in the octahedral sheets. The resulting positive charges compensated part of the negative charges resulted from the isomorphous substitutions of Si$^{4+}$ by Al$^{3+}$ in the tetrahedral sheets, leading to a decrease of saponite’s CEC. In $^{29}$Si MAS NMR spectra of the synthetic saponites, a signal at ca. -86 ppm decreased whereas that of Q$^2$ Si(IIA) and Q$^2$ Si(1IA) increased. Silane grafting experiments strongly supported that the signal at ca. -86 ppm should be attributed to Q$^2$ Si at the edges of saponite layers.
Clay minerals possess structural and chemical analogies to major minerals in cement. We explain how approaches for force field parameterization for clay minerals that have revealed detailed knowledge of interlayer properties can be applied to cement minerals. The result is similarly quantitative insight into crystal structures, cleavage energies, mechanical properties, and the role of organic modifiers in cement minerals, including many similarities with clay minerals.

As a key example, we explore nanoscale interfaces of tricalcium silicate (C₃S), the major constituent of cement clinker. An extensive set of possible cleavage planes of the non-hydrated mineral shows cleavage energies in a range of 1300 to 1600 mJ/m² consistent with the observation of faceted crystallites with an aspect ratio near one. Using pure and hydroxylated surface models that represent the first step in the hydration reaction, we examined the adsorption mechanism of several organic amines and alcohols at different temperatures. Strong attraction between -20 and -50 kcal/mol is found as a result of complexation of superficial calcium ions, electrostatic interactions, and hydrogen bonds on the ionic surface. Agglomeration of cleaved C₃S surfaces in the absence of organic molecules was found to recover less than half the original cleavage energy (~450 mJ/m²) associated with reduced Coulomb interactions between reconstructed surfaces. Additional adsorption of organic compounds below monolayer coverage reduced the attraction between even surfaces to less than 5% of the original cleavage energy (~50 mJ/m²) related to their action as spacers between cleaved surfaces and mitigation of local electric fields. Computed agglomeration energies for a series of adsorbed organic compounds correlate with the reduction in surface forces in the form of measured grinding efficiencies in a ball mill.

The reduction in surface agglomeration through organic molecules in C₃S is very similar to the effect of organic surfactants on layered silicates. However, the much higher cation density and layer charge per unit area in calcium silicates and the comparatively isotropic, non-layer-like structure leads to much stronger cohesion and less hydration in comparison to micas, vermiculites, and a particularly huge difference to smectites.
CHARACTERIZATION OF NATURAL ZEOLITE MOLECULAR SIEVES USING ZERO-LENGTH COLUMN CHROMATOGRAPHY TECHNIQUE

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Zero-length column (ZLC) technique has been widely used to measure intracrystalline diffusivity and mass transfer kinetics in porous materials. This method can be used in studying the effect of particle size on intracrystalline diffusion for composite natural zeolite membranes. High carrier flow rate (50-250 ml/min) and a dilute mixture of N₂ in He (5% N₂ in He) was passed through a very thin zeolite layer to ensure intracrystalline diffusion controlled regime and minimization of heat and external mass transfer effects. The flow was adjusted using a Bronkhorst mini CORI-FLOW mass flow meter. A three-way valve was used to switch between the carrier and the sweep gas. The micro column was placed inside a Hewlett-Packard HP 5890 Series II GC and the GC was used to vary the testing temperature. High-resolution data (20 Hertz) was obtained using a sensitive quadrupole mass spectrometer (PEElFER VACuLM OmnİStar™-GSD 320). The decrease in the concentration profile in the fluid phase was recorded by the mass spectrometer. A schematic diagram of the testing apparatus is shown in Figure 1.

A wide range of natural zeolite particle sizes was prepared and tested at cryogenic conditions. This can lead to understand the significance of monolithic natural zeolite over a wide range of particle sizes made from dense geomorphic molecular sieve. Natural zeolite mordenite was chosen as the first candidate because it allows us a range of particle sizes without binders that cannot be achieved with conventional zeolites and will also support composite membrane development to create faster diffusion membranes. Eight sets of mordenite particle sizes were prepared and tested by ZLC technique at different temperatures from -40 °C to 30 °C.

A small amount of zeolite (5-40 mg) was placed between two 20 micron pore size porous metal frits. Frits were used as a support and also to distribute the flow through the zeolite bed. The column consists of 1/8” stainless steel union Swagelok fitting with one inlet from the switching valve and two outlets, one to the detector capillary and the other as the vent (Figure 1). The zeolites were activated at 573-623 K before each cycle of runs. The hypothesis is that if the particles behave as perfectly dense monolithic aggregates a continuous downward trend of diffusion time constant (vs. particle size is expected.

Figure 2 shows the effect of mordenite particle size on the diffusion time constant (at -20 °C). A small amount of zeolite (5-40 mg) was placed between two 20 micron pore size porous metal frits. Frits were used as a support and also to distribute the flow through the zeolite bed. The column consists of 1/8” stainless steel union Swagelok fitting with one inlet from the switching valve and two outlets, one to the detector capillary and the other as the vent (Figure 1). The zeolites were activated at 573-623 K before each cycle of runs. The hypothesis is that if the particles behave as perfectly dense monolithic aggregates a continuous downward trend of diffusion time constant (vs. particle size is expected.

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resistance controlled system. A downward trend is observed for particles between 22 μm to 55 μm. This may suggest there are no significant defects in the crushed samples. A possible conclusion could be that particles between 22 μm to 55 μm act as dense clusters of single crystals of zeolite since the individual zeolite grains that make up the monolith are orders of magnitude smaller than the particles tested in this study. Particles within this range (22 μm to 55 μm) act as a macropore resistance controlled system and by breaking the particles to smaller sizes the effective dense cluster size is reduced and therefore, diffusion time constant (τ) is decreased. However, particles larger than 55 μm consist of agglomerated clusters of similar size (55 μm). Therefore, changing the particle size in this range (> 55 μm) has minor influence on the diffusion time constant (micropore resistance controlled system). This hypothesis can be a possible explanation for this behaviour and should be verified with more experiments and other techniques.
Due to increasing commodity prices and desired independence therefrom, possible ways of gaining lithium in Germany were examined. Beside the recycling of lithium batteries and the processing of deep groundwaters the re-exploration of the tin and tungsten mines in the Erzgebirge, Germany began. Veins of lithium-iron micas were excavated. A grained concentrate from the deposit of Zinnwald, Germany was studied. The raw material is identified as Zinnwaldite with contaminations of Polylithionite and quartz. Different methods were used to characterize the composition and structure of this mica (see Tab. 1 for the composition).

The temperature dependence and the influence of different salts on the alteration of the mica are investigated. For the dissolution experiments a pressure apparatus was developed (see Fig. 1). Hence the realization of four separate trails at one time is possible. Experiments with different CO₂ pressures can be conducted and hydrothermal conditions up to 473 K and 40 MPa can be applied. The modules of this apparatus are based on well-established HPLC-equipment.

First results of the experiments showed a correlation between interlayer ion leaching and lithium extraction from the octahedral layer. Furthermore a contraction of the unit cell after hydrothermal leaching with sodium-solution and an expansion after heating to 1073 K on air could be found. These results give an insight into structural relations. Due to the high fluorine content the characteristics of the mineral differ from other micas. Thus a detailed investigation on the structural chemistry is applied and the evaluation of possible dissolution mechanisms is done.
THE TEMPERATURE-DEPENDENCE OF SOLUTE DIFFUSION IN SMECTITES: COMPARING EXPERIMENTS AND MOLECULAR DYNAMICS SIMULATIONS

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Engineered bentonite clay barriers are widely used in isolation of contaminated sites and are considered for use in geological storage of high-level nuclear waste. In recent years it has been shown that Molecular simulation techniques, such as Molecular dynamics (MD) simulations, can in combination with experimental data be used to constrain many theoretical models of these clay barriers. The overall advantage of Molecular simulations techniques is that they can provide detailed insight about coordination and dynamics of water and solutes on the atomic level. In the context of contaminant transport, one particular parameter of interest is the temperature-dependence of diffusion, expressed as the activation energy of diffusion ($E_a$). This is because although it is calculated from macro-scale diffusion coefficients [through the Arrhenius relation $D = \mu \exp(-E_a/RT)$, where $R$ is the ideal gas constant and $T$ is absolute temperature], it reflects—if tortuosity and other features that determine the geometric factor of the porous medium be invariant with $T$, as generally assumed at high compactions—the potential energy landscape explored by the diffusing species at the pore-scale.

In a previous study (Holmboe & Bourg, 2013), we performed a sensitivity analysis and developed a robust methodology in how to model diffusion of Na$^+$ in hydrated montmorillonite over a wide range of temperatures and hydration states. In this study, we compare pore-scale $E_a$ values of Na$^+$, Cs$^+$, Ca$^{2+}$, and Cl$^-$ at different hydration states (i.e. water contents), with the corresponding experimental macro-scale $E_a$ values reported in several studies by Prof. Kozaki and co-workers.
[Hokkaido University, Japan], obtained from diffusion experiments at different conditions such as clay compactions and ionic strengths, see for instance (Kozaki, Fujishima, Saito, Sato, & Ohashi, 2005). Thus, from the temperature-dependence of interlayer diffusion obtained from MD simulations, along with the information of the relative distribution of smectite hydration states as a function of compaction (Holmboe, Jonsson, & Wold, 2012), it is our hope to predict the pore-scale $E_a$ in the individual hydration states with sufficient accuracy to aid in the interpretation of experimental data on the macro-scale $E_a$ (cm-scale) from compacted montmorillonite reported in the literature.

The particular smectite used in this study was a generic Kunipia-F type montmorillonite [Japan], having the unit cell. In brief, our methodology uses the versatile MD code LAMMPS, the rigid SPC/E water model and the CLAYFF force field (Cygan, Liang, & Kalinichev, 2004), which is known to satisfyingly predict structural and thermodynamical properties of smectite interlayer water and exchangeable cations.
In the diffusion experiments with Cs+ and Co2+, the radiation-induced effects were in general more noticeable for Co2+ than for Cs+, which generally showed no significant differences between irradiated and unirradiated clay samples.

Nevertheless, the effects appeared to depend on the Montmorillonite concentration in the irradiated dispersions, indicating effects, evident as an increase in Montmorillonite colloid stability, regardless of the structural Fe(ii)/Fe(iii) ratio. From the colloid stability study, the aggregation kinetics and sedimentation experiments revealed significant radiation effects, evident as an increase in Montmorillonite colloid stability, regardless of the structural Fe(ii)/Fe(iii) ratio. Nevertheless, the effects appeared to depend on the Montmorillonite concentration in the irradiated dispersions, indicating that the change in surface characteristics was induced by the aqueous radiolysis products.

From the diffusion experiments with Cs+ and Co2+, the radiation-induced effects were in general more noticeable for Co2+ than for Cs+, which generally showed no significant differences between irradiated and unirradiated clay samples. For Co2+, the sorption to irradiated MX80 Bentonite was significantly lower than to the unirradiated clay samples regardless of the experimental conditions.

Upon reaction with the oxidizing and reducing species formed by water radiolysis, the structural Fe(ii)/Fe(iii) ratio of Montmorillonite and the overall redox conditions in the Bentonite barrier may change. In this study, we have investigated the influence of γ-radiation on i) Montmorillonite colloid stability (Holmboe, Wold, Jonsson, & Garcia-Garcia, 2009), ii) the radionuclide retention in compacted and saturated Montmorillonite and MX80 Bentonite (Holmboe, Norrfors, Jonsson, & Wold, 2011), and iii) the reactivity of Montmorillonite towards hydrogen peroxide, H2O2 (Holmboe, Jonsson, & Wold, 2012).

From γ-irradiation under anoxic conditions of the Montmorillonite suspensions, the structural Fe(ii)/Fe(iii) ratio of Montmorillonite increased from ≤ 3 to 25-30%, using γ-doses comparable to repository conditions. Furthermore, a strong correlation between the structural Fe(ii)/Fe(iii) ratio and the H2O2 decomposition rate in Montmorillonite dispersions was found. This implies that the structural Fe in Montmorillonite could be a sink for one of the major oxidants formed upon water radiolysis in the Bentonite barrier, namely H2O2.
An important event in the evolution of life was the rise of atmospheric oxygen during the Proterozoic. Preceding the rise in O$_2$ was a decline in atmospheric methane concentrations, likely due to decline of methanogenic Archaea. Based on Ni concentrations in banded iron-formations (BIF), Konhauser et al. (2009) hypothesized that mantle cooling during the Archaean reduced the amount of Ni present in igneous rocks and in oceans, causing a Ni shortage for methanogens. Methanogens use Ni for cofactor F430, a catalyst during methanogenesis. To confirm Konhauser’s hypothesis, a proxy for methanogen productivity is necessary, in order to determine whether a decline in methanogen populations correlated with the observed decrease in Ni in rocks from the Archaean.

Ni isotope ratios recorded in BIF (oceanic sediments consisting of layered iron oxides and cherts) may provide evidence of a decline in methane production. Cameron et al. (2009) have shown that methanogens preferentially assimilate light Ni isotopes. Thus Ni isotopes in BIF have potential use as biomarkers for methanogenesis. During BIF deposition ferrihydrite was the dominant Fe oxide precipitating. Thus we investigated experimentally the relationship between Ni isotopes in solution and Ni associated with ferrihydrite.

We conducted two series of experiments: adsorption of aqueous Ni onto surfaces of synthetic ferrihydrite and the coprecipitation of aqueous Ni with ferrihydrite. Preliminary results indicate that light isotopes are preferentially associated with ferrihydrite in both adsorption and coprecipitation experiments, with an average fractionation of 0.4‰ in terms of $\delta^{60/58}$Ni. Future experiments will investigate whether the observed isotope fractionations reflect kinetics or equilibrium, thus determining whether or not BIF provide a straightforward record of Ni isotopes of the water mass.
Zearalenone is a phenolic resorcylic acid lactone produced mainly by Fusarium graminearum, and F. culmorum. The molds can grow on corn, wheat, barley, oat, sorghum, hay, and other crops. The contamination of food and feedstuff by zearalenone is a worldwide problem for humans and livestock. Strategies are needed to prevent the health risks and economic losses from zearalenone contamination. Inspired by reported high adsorption capacity (up to 20% by weight) of many smectites for aflatoxins, another mycotoxin produced by Aspergillus flavus and Aspergillus parasiticus, researchers have made efforts to seek clay minerals to detoxify/decontaminate zearalenone by adsorption. The object of this study was to find the deterministic mineralogical properties of smectites in zearalenone adsorption. More specifically, we wanted to test if there was a “size and polarity matching” rule for the adsorption of zearalenone on smectite as has been observed on the adsorption of aflatoxin.

We used three approaches to modify the interlayer surface polarity of smectites on the nanometer scale: 1) selecting smectites with different layer charge densities, 2) reducing the layer charge density of smectite with the Hofmann-Klemen effect, 3) replacing exchange cations with different hydration energy and valences and 4) increasing the solubility of zearalenone with ethanol. Experimental results indicated that layer charge reduction on two smectites (code as SOK and 1MS) with the Hofmann-Klemen effect showed larger improvement on the adsorption of zearalenone among four test smectites. Replacing exchange cations with Ba and Ca on charge reduced SOK suggested that Ba saturation produced the greatest adsorption capacity of 0.056 mol/kg (or 1.78 % by weight), which was about 10% of its adsorption capacity for aflatoxin B1. We also tried to enhance the accessibility of the interlayer space by increasing ethanol concentration in the solvent, yet increasing the ethanol concentration resulted in decreased adsorption capacity.

Overall, the preliminary results indicated that the nature or modified smectites were less efficient in adsorbing zearalenone than in adsorbing aflatoxin. This is more likely related to its higher hydrophobicity than aflatoxin despite of their similar size and elemental composition. Yet, the results also suggested that it was possible to enhance the adsorption by modifying the interlayer surface polarity of smectite. The optimal mineralogy properties for zearalenone adsorption are under further verification and will be reported.
Environmental endocrine phthalates (PAEs) is a hydrophobic trace organic pollutant commonly existed in aquatic environment. Dimethyl phthalate (DMP) is one of the relatively stable compounds in natural environment, and its hydrolysis half-life is estimated to be about 20 years. Photocatalytic oxidation is a commonly used, advanced oxidation technology, which can effectively degrade organic pollutants. The commercial TiO₂ nanoparticles have many disadvantages for photocatalytic degrading hydrophobic trace organic pollutants. Hydrotalcite have excellent properties and are an appropriate disperser and carrier for TiO₂ nanoparticles. This paper presents a new organic hydrotalcite/TiO₂ composite in an improved preparation method to efficiently remove DMP in an aqueous solution. The hydrotalcite/TiO₂ weight ratio = 4:3, 4:2, 4:3, 4:4, 2:4 was labeled as HT41, HT42, HT43, HT44, and HT42, respectively. The optimal hydrophobic hydrotalcite/nano-TiO₂ ratio was screened by the photocatalytic experiments of DMP, and the photocatalytic mechanism was discussed. This study aims at providing technology and theory for purifying drinking water contaminated by organic pollutant with low concentration.

The result of XRD indicated that sodium dodecyl sulfate (SDS) anions are successfully intercalated into the interlayer of hydrotalcite. The orientation angle between the SDS anions and c-axis is calculated to be 30°. As the ratio of TiO₂ to organic hydrotalcite increases in the composites, randomly immobilized TiO₂ onto the surface of high-ordered sheets forms a mixed and disordered composite. High resolution Ti 2p and O 1s XPS showed that TiO₂ dispersed on the SDS-hydrotalcite still has octahedrally coordinated anatase structure. Also, TiO₂ and SDS-hydrotalcite are not simply a physical mix, but combined together by chemical bonds. SEM image (Fig. 1) provides direct evidence that the reconstructed SDS-hydrotalcite are consisted of interconnecting nano-flakes with an average thickness of approximately 20 nm, which would provide abundant adsorption sites for adsorbate. The results (Fig. 2) of adsorption and photodegradation experiment showed that SDS-hydrotalcite/TiO₂ composites can effectively adsorb DMP in aqueous solution, which will promote the catalysts photocatalytic degrade the adsorbates in situ. Both adsorption and photocatalytic degradation contribute to removal of DMP with SDS-hydrotalcite/TiO₂ composites under UV light. The photocatalytic ability of SDS-hydrotalcite/TiO₂ composites is much higher than that of bare TiO₂. The optimum mass ratio of hydrotalcite: TiO₂ is 1:1. HR-XPS patterns of fresh and used SDS-hydrotalcite/TiO₂ composites indicated that the photogenerated electrons incline to transfer onto the surface of Mg in the hydrotalcite. Such an electron transfer leads to the depression of electron-hole recombination and the improvement of the photocatalytic activity of TiO₂.
New drill cores from the largest known impact structure in Europe, the relict of the late Devonian Siljan meteorite crater in central Sweden, provide new possibilities to reconstruct Early Paleozoic marine environments and ecosystems, and to document changes in sedimentary facies, sea level and paleoclimatic in Baltoscandia (Juhlin et al. 2012). Three cores, provided by the private Swedish company igrene AB, comprise more than 1500 m of Proterozoic basement and strata ranging from the late Tremadocian to Wenlock in age (Lehnert et al. 2012b). The crater relict is an important target of the project “Concentric Impact Structures in the Paleozoic” within the framework of the “Swedish Deep Drilling Program”. The two core sections recording K-bentonites, Mora 001 and Solberga 1, have been analyzed. The volcanic record, expressed by Ordovician and Silurian K-bentonites, may be compared to occurrences of ash layers in other parts of Baltoscandia which serve as time lines in a detailed stratigraphic framework including litho-, bio-, chemo- and sequence stratigraphic parameters. This report is focused on the mineralogy and geochemistry of these ash beds with the intent to explore possible correlations with previously described K-bentonites throughout Baltoscandia.

The adjacent figure shows the K-bentonite samples in the Mora 001 core from the lower shale and the lower shale-mudstone members in the siliciclastic succession (Telychian). The Solberga 1 core has a series of K-bentonites in the Dalby Ls (Sandbian) to Freberga Fm (Katian) interval as well as the Motala Fm (Rhiuddanian-Aeronian) to Kalholmn Fm (Aeronian-Telychian) interval. A portion of each sample was gently disaggregated and suspended in distilled water after particle separation by ultrasonic disaggregation. The <2μm was used to make orientated slides by the smear technique for powder X-ray diffraction (XRD) analysis. After drying and vapor saturation with ethylene glycol for 48 hours at 50°C, the slides were analyzed by powder X-ray diffraction using a Siemens D-500 automated powder diffractometer. Slides were scanned at 0.2° 2θ/minute using CuKα radiation and a graphite monochromator. Biotite from the S032-S035 samples was also analyzed by EDAX. In addition, these samples contain euhezidal zircon and apatite phenocrysts.

The Sandbian samples consist of mixed-layer illite/illite with 80% illite while the Llandovery and Wenlock samples vary from I/S to dominantly illite and chlorite, but some with substantial amounts of kaolinite, particularly in the Telychian sequence SO16-SO20. The Middle Ordovician section at Röstänga in Scania (Bergström et al. 1997) contains eighteen K-bentonite beds ranging from 1-67 cm in thickness, and all occur within the D. multilinii graptolite biozone. Several beds correlate equally well with the Kinnekulle bed and thus argue strongly for the composite nature of what is called the Kinnekulle K-bentonite. We suggest the same for the OS32-OS35 sequence. And similarly, the succession SO16-SO20 in the Lower Telychian Kalholmn Fm is both kaolinite-rich and has a much higher proportion of smectite in the I/S-phase compared with the Kinnekulle samples. This succession is consistent both stratigraphically and mineralogically with the position and composition of the Osmundsberg K-bentonite that is known throughout the Baltic (Huff et al. 1997), and thus we suggest that these samples represent a composite succession of the Osmundsberg K-bentonite.
CHARACTERISATION OF GLAUCONY FROM THE SHALLOW MARINE UPNOR FORMATION, LONDON BASIN

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Glaucony comprises up to 50% of the Upnor Formation, a grey to green sandstone, of variable thickness and composition, that was deposited in a shallow marine to estuarine environment, ~55.6-56.2Ma. The Upnor Formation has not been buried more than a few 100m at most; the glauconite has not therefore undergone diagenetic modification. The chemical and textural maturity of glauconite predominantly reflects the residence time of the granules at the seabed. The morphology and the K2O content are taken together are good indicators of the maturity. Using these criteria, the Upnor glauconite may be defined as evolved. The absence of any trends in major element chemical composition, swelling clay content or oxygen isotopic composition, either vertically or laterally, suggests that the glaucony has been extensively reworked. This is consistent with the high proportion of glaucony that is granule fragments rather than whole granules, and with its occurrence in high-energy depositional environments. However the REE data suggests more than one source for the sediment from which the glauconite formed. The highly fractured, delicate nature of some granules indicates that some maturation of the granules has occurred in situ, after reworking. Oxygen isotopic analysis of Upnor Formation sharks teeth and glaucony have yielded compositions that point to a low salinity water with a temperature of 21–23°C.
RALPH GRIM’S EARLY COLLEAGUES AT THE ILLINOIS STATE GEOLOGICAL SURVEY: WILLIAM F. BRADLEY, W. ARTHUR WHITE, AND HERBERT D. GLASS

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I think Ralph Grim had a vision of clay science from his earliest days. With Grim as petroglyphist, this vision was Bradley (1934) in mineralogy/crystallography, 2) White (1943) in clay-resources/technology, and 3) Glass (1948) in clay mineralogy/stratigraphy. When Grim’s Ph.D. committee at Yale rejected his study of clays, he took joint appointments at the U of Miss. and Miss. State Survey. Ralph said he learned he’d be fired in the newspaper, and in 1931, Chief M.A. Leighton hired Ralph and seven others in a major program expansion. I hope in the following to give some insight into these earlier workers.

Bill Bradley was hired in 1934, completed his Ph.D. in XRD in 1935, and rose to Chemist and Head of the X-Ray Division 1946-1961. In 1961, Bill moved to Professor of Chemical Engineering at the U of Texas-Austin, although he continued to visit the Survey and Geology Dept. First with homemade X-ray cameras and then the 1952 GE XRDs, Bill began what became our special sample collection. Bill liked students, and at meetings, he defended students that he felt were unfairly criticized by senior members. I recommend reading Bills’ ~70 publications list. H. Steinfink and R.A. Rowland said they thought Bill’s 1940 paper on the structure of palygorskite was an “unparalleled example of the derivation of such a difficult structure from this type of data” (Steinfink, H., and R.A. Rowland, 1974. Memorial of William Frank Bradley January 29, 1908—January 16, 1973. Amer. Mineralogist, V. 59, p. 404-408). They also stated that Time magazine thought Bill’s move to Austin was important enough to cite in its Education section. I remember especially learning from the discussions Bill and Herb Glass had in the XRD lab. One summer visit involved xraying dozens of slides of a Texas K/S sample. I sat at the third chair and listened to Bill and Herb discuss each variation in treatment. A driver ran a stop sign and killed Bill in 1973. I think often of how much more he might have contributed.

Art White was Grim’s student assistant in 1937-38, rejoined the IGS in 1943, and rose Geologist and Section Head, 1958-1972. Art’s most important role was hiring and guiding all the clay science students. Art gave us many responsibilities, and when we proved a new idea to him, he would help get it published and ensure that we received credit—rare then and now. Art retired in 1979, called my wife Bette for an OK, and arranged an offer for me to return to the IGS. Art’s rural upbringing helped him talk to landowners and industrial minerals companies. Years later, Art could recall exactly where we could find special clay samples. Art fit perfectly into Leighton’s and Grim’s idea that state funding and fundamental science came from addressing apparently mundane problems, e.g., brick manufacture and road building. As part of a 20-year study of brick expansion, Art kept a tropical humidity in his lab with a bubbling steam line. Art oversaw the IGS’s particle-size and engineering-testing labs, and this kept him in the forefront of testing methods. Art’s 1969 report on septic-field and foundation problems was an early report of this kind (Hackett, J.E. and M.R. McComas, Geology for Planning in McHenry County. IGS Circular 438, 29 p.). Art studied syneresis cracks and showed that many had been misinterpreted as mud cracks; some also caused rapid groundwater flow and leaks in waste disposal sites. Art showed how to avoid underclay squeezes in coal mines that sometimes caused roof collapses. In 1970, Art was a visiting Professor in Universidade Federal do Rio Grande do Sul, in Porto Alegre, Brazil. Art loved to travel to foreign meetings, often at his own expense. When he asked about an East German acquaintance on one trip, Art learned that the fellow was undone by his assistant and probably was sent to the Gulag. Art thought this showed how lucky we were to live and work here. I miss his incredible memory and help.

Herb Glass was hired by Grim in 1948, “retired” in 1986, came to work early the next day and most other days until 2003, when he and wife Edna moved to North Carolina. Herb grew up in Brooklyn and learned to love opera in 50-cent “nosebleed” seats. He was a baseball fan, and for many years, he was a local Little League umpire. Herb memorized the revised Little League rule book each year; players and coaches learned early that he did not tolerate rule breakers.
Herb earned a BS degree in geology from New York University, and after he rose to Captain in the Army field artillery in WWII, he earned a Ph.D. from Columbia. Herb also swam professionally in the Aquacades with such stars as Esther Williams and Buster Crabbe. Herb played and taught a local contract bridge course, and while changing XRD slides during lunch, he often reviewed the latest international bridge-tournament results. In 1958, Herb was transferred to the Stratigraphy Section to work on Quaternary stratigraphic problems using clay-mineral identification. His transfer resulted in a series of publications, and data and advice for at least 50 student theses. Herb used the same GE XRD for over 50 years, and to increase his output, he often prepared clay slides on Saturday and Sunday mornings. Herb’s over 100,000-sample database is being digitized and this database, along with his notes and drawings is a treasure. Herb received an Illinois DNR citation for over 55 years of service. Herb was a very capable but exasperating editor. He would read a manuscript out loud with emphasis on errors and clumsy wording. I tested student assistants to see if they could work with Herb. The “keepers” did well; the others were soon gone. Dewey Moore and I gave Herb drill samples from an Illinois Superfund site that was part of a $12 million suit against IEPA-USEPA. In a few days, Herb correctly identified the Quaternary and bedrock strata that had been misidentified. With his input, our report, according to IEPA, was instrumental in winning their case. I miss our always lively and wide-ranging discussions.
DIFFERENCES IN PORE-FILLING CLAY MINERAL COMPOSITIONS IN ILLINOIS RESERVOIRS AND THEIR IMPACT ON RECOVERY OF OIL

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SEM/EDX, thin section, and Quantitative XRD studies for enhanced oil recovery (EOR) in Illinois showed that reservoir strata of three different ages had distinctly different pore-filling clay mineral compositions. These studies further indicated that the variation in clay mineral content affected the efficacy of well completion and EOR treatments. Quantitative clay mineral analyses included 1) bulk powder XRD with an added internal standard, 2) a ~16µm smear slide of the clay mineral fraction, 3) 15% replicate samples, and 4) a ~2µm sedimented slide for D.M. Moore’s chlorite peak intensity and width measurements. The smear slides were x-rayed air dry, after ethylene glycol solvation, and after heating to 325°C and 550°C. Selected bulk samples were extracted by weight with dilute acetic acid. The carbonate percentages by weight loss plotted against the carbonate content from bulk XRD gave a correlation coefficient >0.9. Clay and nonclay minerals were reported on a bulk percentage basis, and separately, clay minerals were reported on a 100%-basis. We used the 020 peak common to clay minerals in the bulk XRD calculation to estimate bulk clay mineral content. The 4.25Å quartz peak was assigned a reference intensity ratio (RiR) of 1.0, then, the 020 from illite and i/S was assumed to be 1.0, and the weaker 020 peaks of chlorite and kaolinite were assumed to have an RiR of 0.5. We also evaluated an LOI method that showed promise to obtain accurate hydroxyl water contents. However, as shown from field evidence and other tasks in this project, the varieties of clay minerals were far more important to well completion and enhanced recovery than were the bulk clay mineral percentages. Finally, spectra from a PiMASP-TM (portable infrared mineral analyzer) showed that it was possible to rapidly assess the varieties and abundance of clay and carbonate minerals in cores and hand specimens.

Aux Vases Sandstone reservoirs. The Aux Vases Sandstone reservoirs of Mississippian age differ from most reservoir sandstones in that the Aux Vases is cemented by an unusual suite of diagenetic clay minerals. The potential of this sandstone as a petroleum reservoir was overlooked for decades, because water bound to the clay minerals gave false geophysical log measurements that indicated the pores were filled with water rather than oil. These clay mineral coatings also inhibited quartz overgrowth. Samples from nine Aux Vases Sandstone reservoirs contained illite (~50%), i/S (~30%), and chlorite (30%). The chlorites in these samples varied from high-Mg to intermediate Mg-Fe varieties. Attempts to separate lighter and heavier clay mineral fractions by sedimentation showed that illite, i/S, and chlorite were intimately intergrown. SEM/EDX analysis of clay mineral pore fillings showed textures typical of smectite.

Cypress Sandstone reservoirs. Six fields from the Mississippian Cypress Sandstone contained illite (~25%), i/S (~20%), Fe-rich chlorite (~15%), and kaolinite (~40%). The chlorites had XRD peaks typical of high-Fe chlorites with 004/003 XRD peak area intensity ratios from about 2.5-5.3. SEM analysis showed that kaolinite occurred as euhedral stacks and books, i/S (~20%) as fibrous illite, and chlorite as rossettes.

Pennsylvanian-age reservoirs. These reservoirs showed a third diagenetic clay mineral suite that was very similar to typical clay minerals in shales and other strata of this age. Illite had small amounts of smectite interlayering that gave a sharper peak after heating to 325°C. Kaolinite had XRD peaks that appeared typical of Pennsylvaniaian shales, and, also like shales, chlorite in these reservoirs had a 004/003 peak ratio of about three. These reservoirs showed a third diagenetic clay mineral suite that was very similar to typical clay minerals in shales and other strata of this age. Illite had small amounts of smectite interlayering that gave a sharper peak after heating to 325°C. Kaolinite had XRD peaks that appeared typical of Pennsylvaniaian shales, and, also like shales, chlorite in these reservoirs had a 004/003 peak ratio of about three.

Conclusions. Because the characteristics of the clay minerals in the Cypress reservoirs matched well with many reported examples, we assumed normal diagenesis gave rise to these suites. The unique chlorite in Aux Vases reservoirs suggested that it may have been derived from precursor smectite and that the chlorite was di-tri and intergrown with illite-i/S derived concurrently from smectite. The diagenetic clay mineral suite in the Pennsylvaniaian reservoirs was more like...
shales and similar non-reservoir strata of the same age. Most important, characterization of the clay mineral content and especially the chlorite varieties in these reservoirs is critical to optimal oil recovery.

**Reflectance infrared spectroscopy.** Preliminary analysis with the PIMA analyzer showed that it was possible to collect spectra from cores and hand samples as fast as 30 seconds each, and using custom standard spectra libraries, these spectra can be converted to percentages in a few seconds per spectrum. The cost savings of this method show great promise for the future.
The barrier soils used in low-level radioactive waste (LLW) disposal must provide long-term attenuation of radioactive compounds. LLW disposal facilities in the US are required to have a service life in excess of 1000 yr. Radionuclide transport is limited by the inherent sorptive capacity of the materials utilized as barriers within disposal systems. With the reliance on barrier soils to ideally prevent, but more realistically limit, contamination of the environment surrounding LLW disposal facilities, understanding sorption as a solute transport mechanism through these materials is fundamental for improving disposal systems. Although playing a primary role in containment theory, knowledge of sorption processes for barrier materials in the context of radionuclide transport is still under development. Of further concern is the potential for inaccurate estimates in quantifying sorption for natural barrier soils. The current approach for determining sorption behavior of radioactive compounds in barrier soils relies on experimental data from purified minerals that are not representative of the heterogeneous mineral assemblages found in natural soils or proposed for use in practice. Full understanding of the sorption processes affecting radionuclide transport will allow for more accurate modeling of future disposal systems.

In this study, non-synthetic barrier soils were used to conduct experiments in order to provide a more realistic evaluation of the sorption processes involving radioactive compounds. The proportionality of radionuclide sorption to the exchange capacity of soils, as a function of the type and magnitude of the minerals within the soil column, was investigated. Four liner soils with varying properties, along with glass beads serving as a sorption control surface, were used for batch sorption experimentation. Quantification of the cation exchange capacity (CEC) and amorphous and crystalline iron content was coupled with X-ray diffraction (XRD) to determine the bulk and clay mineralogy of the soils. Uranyl acetate dihydrate (UO₂(C₂H₃O₂)₂.2H₂O) served as the representative radionuclide in solution for initial experimentation, at concentrations derived from LLW leachate data obtained from the Department of Energy (DOE). Experimentation was conducted over a range of pH values encompassing those found within the DOE leachate.

Differences between the mineralogic content of the four study soils, depicted in Figure 1, are shown to influence the sorption capacities of the soils. Iron (oxy)hydroxide and carbonate content are highlighted for their impact to the sorption capacity of soil systems over a range of pH values. Although cation exchange is frequently cited as a principle mechanism for the enhanced uptake of radionuclides by purified clays, natural heterogeneous soil mixtures show a reliance on the interplay of both the CEC and concurrent iron-content. Results from this study are compared to literature values for sorption on purified clay and iron-based minerals.
HECTORITE CLAY—A UNIQUE, MULTI PURPOSE RHEOLOGICAL ADDITIVE

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Hectorite clay occupies a unique place among the various clay minerals that are commercially mined in the world. Hectorite is rare in occurrence and the clay deposit mined near Hector in the Mojave desert in particular defines the mineral composition as it is unparalleled in purity and quality.

In this paper, we will review the chemistry and compare properties of some natural hectorite clays. In addition, we will discuss some typical applications of the unique Hector clay in coatings, drilling fluids, construction, water treatment and personal care consumer applications to show the diverse range of benefits it provides.
STRUCTURES OF CHLORITE/SERPENTINE MINERALS IN TOYOHA GEOTHERMAL SYSTEM, SOUTHWESTERN HOKKAIDO, JAPAN.

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Tokyoio geothermal system, southwestern Hokkaido, Japan yields polymetallic vein-type ore deposits of mainly Pb, Zn and Ag ores associated with Mn, In, Bi, Cu, Sn, W and Co. Chlorite/serpentine minerals are ubiquitous in the system with various occurrences which are roughly divided into two types by its origin: the product of propylitic alteration at an earlier stage of alteration such as chlorites in matrix, and that formed by the boiling of ascending fluid which took place at a later stage such as vein-filling and pore-filling chlorites (Inoue et al., 2012). In order to understand the relationship between their crystal structures and occurrences in the system, the chlorite/serpentine minerals have been investigated using selected-area electron diffraction (SAED), high-resolution transmission electron microscopy (HRTEM) and micro-specimen X-ray diffraction (XRD).

In the present samples, chlorite/serpentine minerals coexist with fittle and other phyllosilicates, which made difficult to analyze these minerals by the diffraction profile of conventional powder XRD patterns. To overcome this problem, minute mono-mineral specimens of a ~20 mm cube were picked up from petrographic thin section using the focused-ion-beam (FIB) technique, and the diffraction pattern was obtained from the cube using a convergent X-ray source with confocal optics and two dimensional X-ray recording using imaging plates. Accordingly, XRD patterns with sufficient photon counts could be obtained from such small specimens without synchrotron X-ray source (Fig. 1a). This new micro-specimen XRD technique was successfully applied to the present samples.

The results revealed that the pore-filling mineral is mostly chlorite, though it is a mixture of Ilib and IIb (Fig. 1b, c). On the other hand, vein-filling Fe-rich mineral is mostly serpentine (berthierine). Comparison with the diffraction profile calculated by Diffax (Treacy et al., 1991) indicated that the stacking structure of the serpentine is a mixture of two polytypic groups, A and C. The same specimens were also investigated by TEM, and both serpentine and randomly interstratified serpentine/chlorite minerals were observed (Fig. 2). HRTEM images indicated that both chlorite and serpentine layers are a mixture of different polytypic groups; chlorite layers consist of Ilib and IIb stacking, and serpentine layers groups A and C as suggested from XRD (Fig. 2). These stacking structures may be formed metastably by boiling of Fe-rich fluid. On the other hand, the product of propylitic alteration was revealed to consist of chlorite by XRD and HRTEM. Its stacking structure often exhibits a mixture of Ilib and IIb.

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INDUSTRIAL-SCALE PURIFICATION OF KAOLIN USING A CONDUCTION-COOLED SUPERCONDUCTING HIGH-GRADIENT MAGNETIC SEPARATOR

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Quantum Design, Inc. has developed a high throughput, conduction-cooled, superconducting high-gradient magnetic separator (SHGMS) which operates at 5 Tesla with a 10% uniformity over 406 mm. This long uniformity range, along with its 203 mm diameter bore and high magnetic field, result in a single system capable of processing $10-15 \times 10^6$ kg of clay per year. The magnet temperature is maintained using an Energy Smart 1.5W Gifford-McMahon refrigerator, which dramatically reduces operating costs compared to a liquid helium cooled magnet ($40 to cool down at $0.10/kWhr). The small footprint of this magnetic separator combined with the inexpensive operating costs allow for a modular design so that multiple systems can be used in parallel to fit the needs of each kaolin mining facility. The SHGMS is an efficient method to increase the brightness of kaolin at an industrial scale which is commercially important for a variety of industries such as ceramics, paint, cosmetics, paper, and more. Tests carried out to process kaolin from three different mines show a reduction in Fe$_2$O$_3$ by over 60%. For example, the as-received specifications for one sample containing 0.85wt% Fe$_2$O$_3$ and a fired brightness of 88% was reduced to 0.29wt% and 92.5%, respectively. This equated to a 65% drop in the Fe$_2$O$_3$ content. These dramatic results equate to a three-fold increase in the value of the clay.
MOLECULAR SPECTROSCOPY AND MODELING OF DIOXIN AND POLYAROMATIC HYDROCARBON INTERACTIONS WITH CLAY MINERALS

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In recent years the interaction of dioxins with clay minerals and related geosorbents has received increased attention. This paper will examine/review the interaction of several dioxin congeners with clay minerals and related geosorbents using sorption, molecular spectroscopy, molecular modeling, and bioassays. To explore structure-activity relationships, the behavior of three congeners will be presented for non-chlorinated dibenzo-p-dioxin (DD) and for DD substituted with chlorine substituents at the 1 and 2 positions. In prior work, we found that saponite exchanged with weakly hydrated monovalent cations (e.g., Cs+) had an unexpectedly high affinity for DD with maximal sorption values approaching 10,000 mg/kg. FTiR and Raman spectroscopy revealed that the vibrational modes of DD were influenced by the nature of the interlayer cation and molecular modeling provided additional insight. The presence of the chlorine substituents lowers the aqueous solubility of dioxin congeners. In addition, Cl-substitution also presents steric hindrance that interferes with the energetically favorable ‘tilted’ orientation of the molecule in the interlayer observed for DD. These relationships will be demonstrated based on structural, spectroscopic and molecular modeling approaches for the interaction of the three congeners (DD, 1ClDD and 2ClDD) with smectites. In addition, one of the central questions about dioxins bound to clay minerals pertains to their bioavailability. Prior work showing the immunotoxic effects in vivo of 2,3,7,8 tetrachlorodibenzo-p-dioxin sorbed to K-saponite will be reviewed. Comparison of TCDD-induced suppression of humoral immunity was nearly identical for TCDD delivered in corn oil to that of TCCDD sorbed to the K-saponite.

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In recent years the interaction of dioxins with clay minerals and related geosorbents has received increased attention. This paper will examine/review the interaction of several dioxin congeners with clay minerals and related geosorbents using sorption, molecular spectroscopy, molecular modeling, and bioassays. To explore structure-activity relationships, the behavior of three congeners will be presented for non-chlorinated dibenzo-p-dioxin (DD) and for DD substituted with chlorine substituents at the 1 and 2 positions. In prior work, we found that saponite exchanged with weakly hydrated monovalent cations (e.g., Cs+) had an unexpectedly high affinity for DD with maximal sorption values approaching 10,000 mg/kg. FTiR and Raman spectroscopy revealed that the vibrational modes of DD were influenced by the nature of the interlayer cation and molecular modeling provided additional insight. The presence of the chlorine substituents lowers the aqueous solubility of dioxin congeners. In addition, Cl-substitution also presents steric hindrance that interferes with the energetically favorable ‘tilted’ orientation of the molecule in the interlayer observed for DD. These relationships will be demonstrated based on structural, spectroscopic and molecular modeling approaches for the interaction of the three congeners (DD, 1ClDD and 2ClDD) with smectites. In addition, one of the central questions about dioxins bound to clay minerals pertains to their bioavailability. Prior work showing the immunotoxic effects in vivo of 2,3,7,8 tetrachlorodibenzo-p-dioxin sorbed to K-saponite will be reviewed. Comparison of TCDD-induced suppression of humoral immunity was nearly identical for TCDD delivered in corn oil to that of TCCDD sorbed to the K-saponite.
AN IMPROVED UNDERSTANDING OF IRON (HYDR)OXIDE FORMATION ON ENVIRONMENTALLY ABUNDANT MINERALS

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The heterogeneous nucleation and growth of Fe(III) (hydr)oxides on mineral surfaces are important processes in natural and engineered aquatic systems. Often Fe(III) (hydr)oxides precipitate on other rocks’ surfaces via heterogeneous nucleation, and change the reactivity of the pre-existing rocks, which may previously have low sorption capability for pollutants. To predict the fate of aqueous pollutants, a better understanding of heterogeneous Fe(III) (hydr)oxide nucleation and growth on mineral surfaces is needed.

In this study, we measured in situ heterogeneous Fe(III) (hydr)oxide nucleation and growth on quartz, muscovite, and sapphire (Al2O3) in 10^{-4} M Fe(III) solution (in 10 mM NaNO3 at pH = 3.7 ± 0.2) using grazing incidence small angle x-ray scattering (GISAXS). Quartz, muscovite, and sapphire are ubiquitous in the environment and they have been widely used in industrial applications. Interestingly, both the fastest heterogeneous nucleation and slowest growth occurred on sapphire. To elucidate the mechanisms, zeta potential and water contact angle measurements were conducted. Electrostatic forces between the charged Fe(III) (hydr)oxide prenucleation clusters and substrate surfaces—which affect local saturations near the substrate surfaces—controlled heterogeneous growth rates. Water contact angles (7.5° ± 0.7, 22.8° ± 1.7, and 44.8° ± 3.7 for quartz, muscovite, and sapphire, respectively) indicate a highest substrate-water interfacial energy for sapphire. Further, comparison of structural mismatches between the substrates and precipitates indicates a lowest precipitate-substrate interfacial energy for sapphire. The fastest nucleation on sapphire suggests that interfacial energies in the solution–substrate–precipitate system controlled heterogeneous nucleation rates.

The unique information provided here bolsters our understanding of nanoparticle-mineral interactions, mineral surface modification by iron oxide coating, and pollutant transport. The fundamental knowledge of different surface processes gained in this study can also be valuable for environmentally benign materials synthesis (e.g., heterogeneous catalyst synthesis, nanoparticle deposition, and semiconductor processing).
ILLITE FORMATION DURING GEOLOGIC CO2 SEQUESTRATION

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For sustainable geologic CO2 sequestration (GCS), a better understanding of the effects of brine cation compositions on mica dissolution, surface morphological change, and secondary mineral precipitation under saline hydrothermal conditions is needed. Batch dissolution experiments were conducted with biotite and phlogopite under conditions relevant to GCS sites (55–95°C and 102 atm CO2). To mimic different brine compositions, 1 M NaCl, 0.4 M MgCl2, or 0.4 M CaCl2 solutions were used, and for comparison deionized water was used. To characterize nanoscale morphological changes resulting from the dissolution of pre-existing minerals and the precipitation of new mineral phases, fluid chemistry results are incorporated with high resolution x-ray diffraction, atomic force microscopy, and scanning electron microscopy combined with energy dispersive X-ray spectroscopy.

Faster ion exchange reactions (Na+–K+, Mg2+–K+, and Ca2+–K+) occurred in these salt solutions than in water (H+–K+). Electron microscopy combined with energy dispersive x-ray spectroscopy.

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Faster ion exchange reactions (Na+–K+, Mg2+–K+, and Ca2+–K+) occurred in these salt solutions than in water (H+–K+). Electron microscopy combined with energy dispersive x-ray spectroscopy.

The ion exchange reactions affected bump, bulge, and crack formation on the biotite basal plane, as well as the release of its framework ions. The early stage release rate of biotite framework ions followed the same order: CaCl2 > MgCl2 > NaCl >> water, which agreed with the order of the hydrated cation size and the expansion caused by the different ion exchange reactions. In these salt solutions, numerous illite fibers precipitated after reaction for only 3 h at 95°C. Brine cation composition also affects the kinetics of illite precipitation as well as its resulting shape. This illite formation also occurred in phlogopite systems. Interestingly, when dissolution is slow, slow illite precipitation processes caused oriented aggregation of hexagonal illite nanoparticles forming the fibrous illite.

This observation suggests new possible mechanisms for fibrous illite formation. Precipitation of fibrous illite in sandstone pores has attracted much interest because the illite fibers can lower the permeability in porous media significantly and cause serious problems for hydrocarbon production. Our observations provide insight for future work to improve the understanding of the fundamental mechanisms controlling the morphology of illite precipitates. These results also provide new information for understanding scCO2–brine–mica interactions in saline aquifers with different brine cation compositions, which can be useful for GCS as well as other subsurface projects.
SUPERCRITICAL CO2–BRINE–CLAY MINERAL INTERACTIONS DURING GEOLOGIC CO2 SEQUESTRATION

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Geologic CO2 sequestration (GCS) is a promising means of mitigating anthropogenic CO2 emissions. To realize this promise, we must achieve a holistic understanding of potential reactions under GCS conditions that can impact operational safety and sustainability. Understanding the shape, size, location, and phase of secondary minerals during the early period of CO2 injection for geologic sequestration is crucial in order to more accurately predict how the permeability and wettability of formation rocks can become altered. This presentation will focus on the mechanisms and kinetics of key reactions at supercritical CO2–water (brine)–clay mineral interfaces, using micas (phlogopite, biotite, and muscovite) as model clay minerals. These minerals are abundant in both formation rock and caprock at potential CO2 sequestration sites.

To characterize nanoscale morphological changes resulting from the dissolution of pre-existing minerals and the precipitation of new mineral phases, fluid chemistry results are incorporated with high resolution x-ray diffraction, atomic force microscopy, and scanning electron microscopy combined with energy dispersive X-ray spectroscopy. The formation of nanoscale amorphous silica and precipitation of illite at mica surfaces was observed after reaction times as brief as a few hours. Formation and relocation of these nano- and micro-particles can result in pore clogging and consequently affect the permeability of the formation rock.

This study provides important fundamental information for designing a more accurate reactive transport model as well as for understanding pore clogging in the geo-media of caprocks under GCS conditions. Although this work focused on geologic CO2 sequestration, the results are applicable to other water-energy nexuses (e.g., nuclear waste disposal, desalination, managed aquifer recharge, and shale gas production).
Exposing palygorskite to steam may have little effect on rheological properties or surface areas of the clay. These results, particularly the reduced surface areas for water and EGME, may represent a reduced affinity for polar molecules in general. Heating palygorskite in air or in steam-treated materials were examined by X-ray powder diffraction (XRD), Bruker D8 Advance), thermogravimetric analysis (TGA, TA Instruments SDT 2960), X-ray photoelectron spectroscopy (PHI Ver- saProbe II), zeta potential (Malvern Zetasizer Nano ZS), and rheological measurements (ATS Rheologica Viscoanalyzer AB). XRD and TGA data show that the crystal structure, mineralogy, and dehydration behavior of steamed palygorskites were unchanged after steam treatment. X-ray photoelectron spectroscopy revealed no changes in binding energy peak positions of the surface Si, Mg, and O ions (XPS provides no information on the chemical state of H atoms). Rheological measurements showed that suspensions of steam-treated palygorskite in deionized H2O (5% w/w) are unstable and have very low viscosity (<0.1 Pa s between shear rates of 10 s⁻¹ and 500 s⁻¹). Their viscosity curves do fit any flow behavior models at low shear rates, and the suspensions are Newtonian in nature at high shear rates (Fig.1). The viscosity curves also reveal a significant reduction in yield stresses after steam treatment, indicating collapse of the clay particle network in water. Zeta potentials were reduced after steam treatment, with untreated palygorskites having values of -50.9 mV (PFl-1) and -47.2 mV (Minugel) and steam-treated samples having values of -28.3 mV (PFl-1) and -23.0 mV (Minugel). The reduction of surface charges may be sufficient to reduce the electrostatic repulsion between the clay particles, thereby allowing van der Waal attractive forces to dominate. Hence, steam-treated palygorskite flocculates and settles quickly in water. The decreased zeta potentials are likely associated with decreased Lewis basicity, which can render the clay particles less hydrophilic or even moderately hydrophobic. Both N₂ (BET) and ethylene glycol monoethly ether (ECME) adsorption surface areas of palygorskites were reduced by 40-50% after steam treatment. The reduced affinity for water and ECME may represent a reduced affinity for polar molecules in general. Heating palygorskite in air or in liquid water at 225°C had little effect on rheological properties or surface areas of the clay. These results, particularly the XPS spectra, coupled with the observed large changes in rheological properties, suggest that steam may have altered the hydrogen ion environment and/or concentration on palygorskite’s surface. Exposing palygorskite to steam may have significant implications for its industrial applications, adversely impacting some applications and enhancing others.
MINERALOGY AND CHEMISTRY OF NICKEL-CHROME-BEARING NONTRONITE AND MONTMORILLONITE IN GARNIERITE OCCURRENCES ASSOCIATED WITH LATERITIZED OPHIOLITE-RELATED ULTRAMAFIC ROCKS IN THE SOUTHERN PART OF THE MURATDAGI AREA (USAK, WESTERN ANATOLIA), TURKEY

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The mineralogical and chemical characteristics of Ni-Cr-Fe-rich smectites associated with lateritized ophiolite-related ultramafic rocks in southern part of the Muratdagi area constitute a significant source of nickel production for industry, which until now, has been unrecognized. Widespread lateritic zones within ultramafic units of the Muratdagi area developed in the uppermost levels of ophiolite peridotites. These lateritic zones, with high Ni, Cr and Co concentrations, have been strongly affected by hydrothermal events in the area. Laterites and their host rocks were examined using polarized-light microscopy, X-ray diffractometry, scanning electron microscopy and energy dispersive analyses (SEM-EDX), differential thermal analysis–thermogravimetry (DTA-TG), infrared spectroscopy (FTIR), and chemical methods. Petrographic studies revealed that the ultramafic units comprise mainly dunite, harzburgite, serpentinitized harzburgite and serpentinite. The green, garnierite-bearing altered parts of the ultramafic rocks are rich in smectite (associated with illite), kaolinite, serpentine, alunite, Fe-(oxyhydr)oxide phases, opal-CT, olivine, pyroxene, amphibole, feldspar, quartz, calcite and dolomite. Micromorphologically, smectite exhibits a flaky form, locally edging illite fibers. Kaolinite generally occurs as irregular platy forms. Cubic alunite, hexagonal gypsum, anhedral gibbsite, and fibers and fiber bundles of sulfur developed along fractures and dissolution voids. The surfaces of the altered units are locally covered by subrounded Fe-rich particles. Development of saprolitization suggests weathering, and the presence of a silica cap, Fe (oxyhydr)oxide phases associated with gypsum and alunite and, locally, with sulfur “dolomite” along fault systems are indicative of hydrothermal alteration processes. The ratio of Fe₂O₃+Cr₂O₅+Ni+Co/MgO increases significantly with increasing degree of alteration. Thus, the alteration process(es) resulted in formation of nontronite, Fe-rich and –poor montmorillonite, serpentine, and locally Fe-rich kaolinite with average structural formulae of

(Si₆.₈₈₉Al₀.₅₈₁Fe₀.₅₃₆)(Fe₃.₆₇₈Mg₀.₄₆₁Mn₀.₀₄₆Ti₀.₀₀₂Cr₀.₂₂₂Ni₀.₀₇₇)(Ca₀.₀₆₂Na₀.₀₁₅K₀.₀₂₂P₀.₀₁₀); (Si₇.₈₅₃Al₀.₄₉₂Fe₀.₁₆₀)(Al₀.₇₅₀Fe₂.₁₇₅Mg₁.₀₀₆Mn₀.₀₄₂Ti₀.₀₀₅Cr₀.₃₇₁Ni₀.₂₅₁)(Ca₀.₀₄₈Na₀.₀₁₉K₀.₀₃₈P₀.₀₀₂); (Si₇.₇₃Al₀.₂₇₁)(Al₂.₂₆₅Fe₀.₅₈₂Mg₁.₃₇₆Ti₀.₀₄₁Mn₀.₀₁₃Cr₀.₀₀₄Ni₀.₀₇₁)(Ca₀.₁₂₁Na₀.₀₄₆K₀.₂₈₁P₀.₀₁₆);

respectively. Ni and Cr substitute for octahedral Fe in the structure of montmorillonite, serpentine and kaolinite. Thus, Ni and Cr are concentrated significantly in altered units, and are correlated positively with Fe₂O₃ content, controlled mainly by the formation of nontronite and Fe-rich smectite, and partially by serpentine and Fe-bearing kaolinite rather than Fe-(oxyhydr)oxide phases. Thus, Ni-Cr-bearing nontronite and montmorillonite precipitated from alkaline water rich in Al, Fe and Mg under the control of both weathering and hydrothermal alteration process(es). The Fe, Al and Mg (associated Ni and Cr) required for smectite formation were supplied in solution(s) involved in the alteration of Co-Ni-Cr-bearing olivine, pyroxene, amphibole and serpentine minerals in the ultramafic host rocks.

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MINERALOGY AND CHEMISTRY OF NICKEL-CHROME-BEARING NONTRONITE AND MONTMORILLONITE IN GARNIERITE OCCURRENCES ASSOCIATED WITH LATERITIZED OPHIOLITE-RELATED ULTRAMAFIC ROCKS IN THE SOUTHERN PART OF THE MURATDAGI AREA (USAK, WESTERN ANATOLIA), TURKEY

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respectively. Ni and Cr substitute for octahedral Fe in the structure of nontronite, montmorillonite, and kaolinite. Thus, Ni and Cr are concentrated significantly in altered units, and are correlated positively with Fe₂O₃ content, controlled mainly by the formation of nontronite and Fe-rich smectite, and partially by serpentine and Fe-bearing kaolinite rather than Fe-(oxyhydr)oxide phases. Thus, Ni-Cr-bearing nontronite and montmorillonite precipitated from alkaline water rich in Al, Fe and Mg under the control of both weathering and hydrothermal alteration process(es). Fe, Al and Mg (associated Ni and Cr) required for smectite formation were supplied in solution(s) involved in the alteration of Co-Ni-Cr-bearing olivine, pyroxene, amphibole and serpentine minerals in the ultramafic host rocks.

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This paper deals with the mineralogy, geochemistry and isotopic characteristics of the Guzelyurt alunite-bearing kaolinite and discusses its origin. The Guzelyurt kaolinite in Aksaray is hosted by the Late Miocene Gordeles ignimbrite, which comprises dacitic and andesitic tuffs and is overlain by basaltic lava. The Guzelyurt kaolinite deposit formed via hydrothermal alteration along NE-SW-trending faults, and is more than 300 m long and up to 100 m wide. The altered units and related host rocks were examined using polarized-light microscopy, X-ray diffraction (XRD), scanning electron microscopy and energy dispersive analyses (SEM-EDX), differential thermal analysis–gravimetry (DTA-TG), infrared spectroscopy (FTIR), and chemical and stable isotopic analyses. Mineralogical zonation is reflected by a prevalence of kaolinite and alunite, and locally halloysite-7 Å, at the center of the deposit, a relative increase in smectite and illite outward, and a silica cap (opal-ct, quartz) and Fe-(oxyhydr)oxide phases associated with sulfur and cinnamon upward; these zones demonstrate that multiple hydrothermal-alteration processes resulted in kaolization and alunitization. Under the microscope, feldspars show kaolinization, and amphibole, pyroxene and mica exhibit iron (oxyhydr)oxide. The Guzelyurt kaolinite deposit is identified by its sharp 7.20 and 3.57 Å reflections, whereas alunite is identified by 4.97 and 2.98 Å basal reflections. Kaolinite generally exhibits stacked and locally book-like crystal morphologies. Halloysite rods coexist with alunite and are subparallel to fracture surfaces. Smeectite flakes formed as “blankets” on devitrified volcanic precursors, edging illite fibers that reveal in situ precipitation driven by dissolution and precipitation mechanisms. Leaching of Si, Mg, Ba and Rb, and an increase of Al/Si ratios, Al and Fe with degree of alteration, resulted in precipitation of kaolinite, halloysite and montmorillonite characterized by the following structural formulae:

$\text{(Si}_{4.465}\text{Al}_{3.079}\text{Fe}_{0.092}\text{Mg}_{0.041}\text{Ti}_{0.051}\text{Mn}_{0.0009})(\text{Ca}_{0.026}\text{Na}_{0.086}\text{K}_{0.115}\text{P}_{0.014})$,

$\text{(Si}_{4.561}\text{Al}_{2.985}\text{Fe}_{0.120}\text{Mg}_{0.074}\text{Ti}_{0.034}\text{Mn}_{0.0009})(\text{Ca}_{0.045}\text{Na}_{0.006}\text{K}_{0.030}\text{P}_{0.004})$, and

$\text{(Si}_{7.674}\text{Al}_{0.33})(\text{Al}_{2.39}\text{Fe}_{0.876}\text{Mg}_{0.694}\text{Ti}_{0.048}\text{Mn}_{0.010})(\text{Ca}_{0.351}\text{Na}_{0.057}\text{K}_{0.089}\text{P}_{0.010})$, respectively.

The oxygen- and hydrogen-isotopic compositions of the kaolinite, smectite, kaolinite+smectite and smectite+illite, kaolinite+alunite fractions range from -4.33 to 7.64‰ and from -101.81 to -150.09‰, respectively, suggesting the mixing of magmatic and meteoric waters. The oxygen- and sulfur-isotopic compositions of alunite range from 5.5 to 10.3‰ and from 6.0 to 9.4‰, respectively, and reflect the involvement of both magmatic hydrothermal- and steam-derived sulfur. Therefore, the Guzelyurt alunite-bearing kaolinite deposit is presumed to have formed by sulfur-bearing hydrothermal alteration of volcanic glass, feldspar, horriblende and pyroene via a dissolution-precipitation mechanism which operated under acidic conditions within Neogene dacitic and andesitic tuffs.

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$\text{(Si}_{4.365}\text{Al}_{3.093}\text{Fe}_{0.096}\text{Mg}_{0.041}\text{Ti}_{0.051}\text{Mn}_{0.0009})(\text{Ca}_{0.026}\text{Na}_{0.086}\text{K}_{0.115}\text{P}_{0.014})$, and

$\text{(Si}_{4.561}\text{Al}_{2.985}\text{Fe}_{0.120}\text{Mg}_{0.074}\text{Ti}_{0.034}\text{Mn}_{0.0009})(\text{Ca}_{0.045}\text{Na}_{0.006}\text{K}_{0.030}\text{P}_{0.004})$, respectively.

The oxygen- and hydrogen-isotopic compositions of the kaolinite, smectite, kaolinite+smectite and smectite+illite, kaolinite+alunite fractions range from -4.33 to 7.64‰ and from -101.81 to -150.09‰, respectively, suggesting the mixing of magmatic and meteoric waters. The oxygen- and sulfur-isotopic compositions of alunite range from 5.5 to 10.3‰ and from 6.0 to 9.4‰, respectively, and reflect the involvement of both magmatic hydrothermal- and steam-derived sulfur. Therefore, the Guzelyurt alunite-bearing kaolinite deposit is presumed to have formed by sulfur-bearing hydrothermal alteration of volcanic glass, feldspar, horriblende and pyroene via a dissolution-precipitation mechanism which operated under acidic conditions within Neogene dacitic and andesitic tuffs.

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TACKLING THE NANOSCALE STRUCTURAL AND COMPOSITIONAL DIVERSITY OF CLAY-WATER INTERFACES IN MOLECULAR SIMULATIONS: RECENT PROGRESS, CHALLENGES, AND OPPORTUNITIES

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Thermodynamic, structural and transport properties of hydrated clays and clay-related materials are extremely important for many geochemical, environmental, and technological applications. Experimental nanoscale studies of such systems are not always feasible, and their results often require considerable interpretation in the efforts to extract quantitative surface-specific and confinement-specific information from the measurements. Computational molecular modeling techniques significantly complement such experimental efforts by providing invaluable atomic scale background understanding, and they are already routinely used in the clay studies. However, until very recently, the simulated molecular models of clays were typically simplified and limited in size to ~2–3 nm, thus limiting our capabilities to represent in molecular simulations the true scale of the structural and compositional complexity of clays, and possibly also limiting the predictive power of such models. On the other hand, rapid advancements in the parallel supercomputing applications and the development of specialized force fields for clay modeling allow now to quantitatively address many of those prior simplifications and limitations.

In my lecture I’ll give a brief overview of the progress achieved in this field in recent years, primarily focusing on the results obtained by our group and by others based on the successful development and implementation of the CLAYFF force field a decade ago (Cygan et al., 2004, 2009). The selected examples cover quite a broad range of materials, including clays, LDHs, and other layered and nanoporous minerals. The discussion allows to make some general conclusions concerning the capabilities of such molecular modeling approaches in clay science, to probe the potential limits of their applicability, and, finally, to formulate the emerging challenges for future research and the new opportunities it offers.
Most of the interesting properties of smectites, such as swelling and sorption, are determined by the layer charge which results from both the CEC and the variable charge. In the case of dioctahedral smectites the variable charge is determined by edge alumino groups which due to the amphoteric character of the Al may be either charged (low pH: positively charged, high pH: negatively charged) or neutral. The portion of the permanent charge is determined by the structural formula method or by the alkylammonium method—both methods are used to determine the layer charge density (permanent charge). However, the variable charge often is not considered. Therefore, the present study was conducted to test and compare different methods for the measurement of the variable charge of dioctahedral smectites (mainly montmorillonites) and to characterize the range of differences of the variable charge of smectites from different deposits. Finally the reason for the different amounts of variable charge of different smectites was investigated.

Based on a simple theoretical approach, i.e. assuming a 0.1 x 0.1 nm smectite particle and 4.5 edge alumino groups per unit cell, a variable charge of a pure smectite of 8 meq/100 g was calculated which is roughly 10 % of the CEC. Two different variable-pH-CEC-methods which were applied to a set of different bentonites yielded 2—14 % of the CEC between pH 4 and pH 6 and 10—30 % between pH 4 and 9. In addition, potentiometric titration was tested to determine the variable charge, i.e. the amount of alumino groups. With the potentiometric titration method larger values for the variable charge were determined (15—35%).

All three different methods were found to be suitable to distinguish smectites with a larger amount of variable charge from some with less variable charge. One reason for the differences of the variable charge of different bentonites may be the variable chemical composition of the smectites, particularly the Mg content. Also the roughness of the edge surface and the submicron particle size distribution may play a role.
The Morrow Plots were established at the Urbana campus of the University of Illinois in 1876 to answer agricultural questions. They are the oldest agronomic experiment fields in the United States with a recorded history of cropping practices (systematic monoculture, crop rotations, and fertilization, etc.). The exceptional series of samples available thus represent a unique opportunity to investigate both short- and long-term influence of cropping practices on the status of potassium, an essential plant nutriment. As clay minerals represent, together with K-feldspars and micas, a major reservoir of potassium potentially available for plants their mineralogy is likely to be impacted by potassium uptake resulting from plant growth.

In 2012, top soils were sampled from four plots representing continuous corn crops with and without fertilization (CC_F and CC_NF, respectively) and corn-oats-fodder crop rotation with and without fertilization (CR_F and CR_NF, respectively). The clay size fraction of the samples was sub-fractionated, and 2.0-0.2 µm, 0.2-0.05 µm, <0.05 µm sub-fractions were separated and X-rayed in their Ca-saturated form. X-ray diffraction (XRD) patterns were simulated using a trial-and-error approach both to determine structure models for discrete and mixed layer contributions, and to estimate quantitatively their relative contributions.

Discrete chlorite, kaolinite, and chlorite are present in all samples together with randomly interstratified illite-expandable (ill-exp), kaolinite-expandable (kaol-exp), and chlorite-expandable (chl-exp). Logically, the relative content of discrete minerals decreases with decreasing size fraction for all samples, chlorite being systematically absent in the finest fractions. In all samples, illite and ill-exp dominate the 2.0-0.2 µm fraction with 66-71%, the global proportion of these two contributions decreasing to 38-45% in the 0.2-0.05 µm fraction, and to 27-29% in the <0.05 µm fraction. Simultaneously, the relative proportion of kaol-exp increases from 9-17% in the 2.0-0.2 µm fraction, to 33-49% in the 0.2-0.05 µm fraction, and to 61-64% in the <0.05 µm fraction. The chlorite contribution decreases only slightly with decreasing size fraction from 10-16% in the 2.0-0.2 µm fraction to 7-9% in the <0.05 µm fraction. The proportion of chlorite layers in ill-exp systematically increases in the sequence CC_F<CC_NF<CR_F<CR_NF, whereas no systematic trend is observed for kaol-exp.

The behavior of illite and ill-exp contributions is most relevant with respect to the fate of K in these soils. Although these two contributions are globally similar for all fractions of the different samples, there is a major difference between CC and CR plots however. The 2.0-0.2 µm fraction of the latter samples is dominated by illite (38-43% compared to 28% of ill-exp), whereas ill-exp dominates in CC samples (45-49% compared to 21-23% of illite). The contrast between CC and CR samples is less pronounced for finer fractions. For a given sample, the relative contribution of illite systematically decreases with size fraction. In addition, the composition of ill-exp differs in the 2.0-0.05 µm fraction between the two sample sets with 27-28% and 48-52% of illite layers in ill-exp in CC and CR samples, respectively.

Illite thus appears most degraded, and possibly transformed to ill-exp, in continuous corn plots compared to crop rotation ones. This effect is enhanced when size fraction is decreased likely owing to the increased specific surface areas of the finest fraction which favors K uptake by plants. The increased corn yield induced by fertilization has favors the degradation of illite and the formation of ill-exp. (Formation of) kaol-exp appears favored in these soils and systematically dominate the finest size fractions of all samples.

Influence of Cropping Practices on Clay Mineralogy: Insights from the Morrow Plots Experimental Fields

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The metal sulfides have attracted great interest because of their excellent electrical and magnetic properties and wide range of applications. Metal sulfides, which exist in nature as minerals, are cheap, abundant, and promising semiconductor materials. Hence, the deposition of metal sulfide minerals is expected to lead to easy transportation for electrons; thus, it can enhance the overall reactivity of iron nanoparticles (FeNPs). Recently, we reported iron sulfide-coated FeNPs (Fe/FeS) exhibiting a higher reactivity than conventional forms of FeNPs. In the present work, we prepared four different metal sulfides-coated FeNPs (Fe/MeS), and the obtained Fe/MeS was used in the reductive dechlorination of trichloroethylene (TCE), a model compound for environmental remediation and toxicological studies in vitro.

Of all Fe/MeS, the reduction rates of TCE were significantly greater than bare FeNPs. The enhanced reactivity of Fe/MeS was attributed to an increase in surface conductivity because the metal sulfides are generally known as either semiconductors or metallic conductors due to the presence of delocalized electrons in the layers. Also, these metal sulfide coatings decreased the cytotoxicity of FeNPs toward the bacterial cells. In summary, the sulfide mineral coatings are justified as an innovative modification approach to improve both contaminant reactivity and biocompatibility of FeNPs.

Fig. 1 TEM images of (A) Fe, (B) Fe/CoS, (C) Fe/CdS, (D) Fe/ZnS, and (E) Fe/Cu2S NPs.

Fig. 2 Reduction of TCE by 2 g/L Fe and Fe/MeS NPs (C0, TCE = 0.11 mM). The lines represent the fit to pseudo-first-order kinetics.

Fig. 3 Bacterial cell viability after exposure to 200 mg/L of Fe and Fe/MeS NPs for 10 h.
Selected applications highlighting these tools will be presented.

• restriction of the calculation to tools for the calculation of partial structure factors enabling the recursive calculation of patterns from layered structures with different types of stacking faults
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• combined refinement of structural parameters employing multiple measurements, e.g. from various treatment stages of clays.

Tools for modeling the diffraction effects of stacking faults available in the BGMN interpreter language are:

- simple peak profile splitting and shifting/broadening of "sub-phase" peaks, suitable for empirical approximation of hkl-dependent line broadening, applied to special classes of peaks
- use of hkl files (lists of structure factors) for modeling of clay patterns without knowledge of crystallographic reasons for the disorder, especially for phase quantification
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PHASE ANALYSIS OF CLAYS

THE RIETVELD PROGRAM BGMN—A TOOL USEFUL IN STRUCTURE AND PHASE ANALYSIS OF CLAYS

Reinhard Kleeberg*1 and Kristian Ufer2

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In memory of Jörg Bergmann, our friend.

Rietveld software was originally developed for structure refinement from powder diffraction data, employing the classical models of diffraction from structures described by small elementary cells. Reflection intensities are calculated usually for well-defined lattice planes hkl, causing a single peak profile. Such approach has many restrictions, limiting the usability of Rietveld programs for analyzing the diffraction patterns of complex and disordered structures like clay minerals. Nevertheless, the Rietveld method has been introduced especially in phase analysis because of the advantage of standard-free quantification, independency from instruments, and, maybe, the broad availability of software.

The BGMN Rietveld software as developed by Jörg Bergmann bases on a stable numerical kernel for refinement and parameter reduction when inadequate models are chosen by users and a powerful programming language plus predefined functions for modeling of complex structures. These features can be used effectively for solving common tasks in clay science as phase analysis and structure refinement. As the software code is now freely available under GNU General Public License, we want to present the most important tools to the clay community, hoping to come up to a broader distribution and collaboration in further development.

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Haydn Murray is a highly respected researcher, teacher, and business leader who has shaped modern applied clay science as we know it today. He was first introduced to the field while studying under Ralph Grim in the 1950’s. At the time, applied clay science was a relatively young discipline that straddled clay mineralogy and engineering. He entered the field just as it was gaining momentum and acceptance as a critical and legitimate research discipline. It was an exciting time marked by opportunities for making significant and lasting contributions to an important body of scientific work. Hayden Murray recognized this opportunity and, for the past 60 years, he has devoted his passion and energy to leading the field from its infancy to a mature scientific discipline.

His career began with a faculty position at IU which he held until 1957 when he joined Georgia Kaolin Company as Director of Research. After building a preeminent research lab he was promoted to Executive Vice President, where he led the company to become the world’s largest producer of kaolin clay. In 1973, he returned to IU to chair the Department of Geological Sciences. During this period he continued to be an influential leader. He recognized that industry needed skilled professionals with rigorous scientific training so he created the only academic program in applied clay science in the U.S. While at IU he advised over 90 PhD and masters students and numerous post-doctoral students. Many of these students now hold important government and industry positions and can be found in research labs, board rooms and leadership roles across the globe. He also was one of the founding members of the Clay Minerals Society which was established to allow free and open exchange of scientific ideas between industry, academic and government scientists working with clays and clay minerals.

His accomplishments are many and he has garnered numerous accolades, awards and recognitions. Some of his most notable achievements are: elected to the National Academy of Engineering (2003), Honorary Doctor of Science Degree from Indiana University (2004), Department of Geology Alumni Achievement Award from the University of Illinois (2003), President of AIPEA (1993–1997), President of the Society for Mining, Metallurgy and Exploration (SME) (1988), Clay Minerals Society Distinguished Service Award (1980), Recipient of the Hardinge Award from SME (1976), Distinguished Member of AIME (1976) and President of the Clay Minerals Society (1965-66). However, what sets Haydn Murray apart from others, are not his awards and accomplishments but his visionary leadership and his influence on a generation of clay scientists and industry leaders.

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APPLIED CLAY SCIENCE—HAVE WE LOST OUR WAY?

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Science, a purely human endeavor, evolved from the observation of natural phenomena and an attempt to bring systematic understanding to the natural world. Early humans wanted to understand the patterns that governed their lives—the daily setting of the sun, the annual seasons, the monthly waxing and waning of the moon and the cyclical changes in ocean tides. This inquiry laid the foundation for modern science which today has two main branches: pure science and applied science. Pure science investigates nature through experimentation and observation and is driven by the need to know. Applied science uses pure science to solve practical problems. In this context science serves two distinct purposes: to understand nature and to apply this understanding to develop technology or inventions. Historically academic institutions tended to focus on pure science while industry focused on applied science.

Applied Clay Science did not emerge as a formally recognized stand-alone discipline until the 1950’s when Ralph Grim and his students engaged in research that applied fundamental knowledge of clay minerals to their industrial use. This pioneering work not only put the discipline on the map but it launched an exciting era of discovery and innovation that led to many new products and technologies for industries including ceramics, paper, oil and gas, geotechnical engineering, paint, plastics, catalysts, pet litter and environmental engineering. Although applied clay research was not invented by Ralph Grim he was the first to legitimize it as a body of academic research. He was able to do this because, as a university professor with a reputation for rigorous research, he had the respect of the academic community and, as a consultant for industry where he had a proven track record of discovery and innovation of marketable products; he had the respect of the business community. This close connection between basic and applied research was critical for bringing clay mineralogy out of the academic laboratory into the realm of applied research.

It was this same connection that led to the founding of the Clay Minerals Society (CMS) which was originally organized to facilitate collaboration between clay specialists engaged in pure research and clay scientists engaged in applied research. The CMS provided a fertile ground for the exchange of ideas to both inform academic research and advance applied research. The founders of the CMS recognized that, for clay science to reach its fullest potential, the two approaches needed to be done in parallel and with open exchange. The CMS membership was originally comprised of approximately equal proportions of industry, academic and government scientists. The pages of Clays and Clay Minerals were devoted to the publication of research papers in both pure and applied clay science. However, in the intervening decades the rosters of the CMS have changed. There are fewer industry scientists who are members and even fewer that attend the annual meetings. Today Clays and Clay Minerals focuses on pure research papers and Applied Clay Science, a competing publication, is now the go to source for applied clay research. What had been a diverse organization of industry and academic researchers has become a much more academically focused institution.

What has our scientific community lost in this transition? I believe that we have potentially lost an opportunity to help advance the field in new directions, create economic value and secure a future for clay science as a viable and vital discipline with real social outcomes. Industry needs knowledge (pure research) and universities need the intellectual and economic benefits of applied research. However, there is a barrier between the two and this barrier is not unique to the clay science community. Many scientific disciplines suffer from an academic and industry divide. The academic community often believes that industry scientists only care about making profits and that their research is biased and not rigorous. Industry scientists often characterize academic scientists as lacking practical knowledge and having little understanding of the real (business) world. Neither depiction is accurate, and only serves to stifle communication between the two groups. In reality, both groups are trying to solve the same problems albeit from different perspectives and within different sets of constraints.

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ABSTRACTS

We have an opportunity to close this divide but we must find new ways of working together. Many of the old models no longer serve us. This is because circumstances have changed since the founding of the CMS—intellectual property laws, more rigorously controlled budgets and a more competitive business environment to name a few. On the academic side there have been changes as well including new business models for licensing university research, shrinking resources (labs, students, funding) and more pressure to publish. Hidden in all of this is an opportunity to work together to advance the field of applied clay science and the CMS provides a natural platform for this endeavor.
Illite, dioctahedral aluminous potassium-micas with deficient interlayer cations, is a ubiquitous clay mineral but its crystal structure is diverse and mysterious. Muscovite mostly adopts $\delta$-$\text{I}_{20}$ mutual layer rotations, resulting in the polytypes of $2M\text{I}_c$ or $3T$. On the contrary, illite commonly adopts regular $1M$ stacking without layer rotations, beside $2M\text{I}_c$ and $3T$. Moreover, occurrence of illite-$2M\text{I}_c$ a subfamily B polytype, has been occasionally reported in spite of the large ditrigonal rotation angle. Such occurrence of various polytypes in illite may be related to the distribution of cations in the dioctahedral sheet. Drits and Zviagina (2009) suggested that the interlayer configuration is considerably different between cis-vacant (cv) and trans-vacant (tv) illite, and $1M$ stacking is favorable if the dioctahedral sheet is cv-vacant. Discrimination of cv- and tv-illite is possible using X-ray diffraction, thermal analysis, or IR spectroscopy. However, if the two polymorphs can be distinguished using microscopic methods, we can obtain more insights for the structural variety of illite. We started working together to identify cv-illite directly using HRTEM from 2004, but never observed distinct contrast which corresponds to cv-illite in several samples for which X-ray diffraction indicates that cv-illite is the major phase. Later, Kogure (2007) indicated that HRTEM contrast of dioctahedral 2:1 layers does not correspond to its natural state but topotactically dehydroxylated one formed by the intense beam radiation. As Drits et al. (1995) reported, cv-illite transforms to the structure with tv-like cation distribution by dehydroxylation. Hence, at present, HRTEM imaging of cv-dioctahedral 2:1 layer is almost impossible without some new idea for electron microscopy (Kogure and Drits, 2010).

Although it is not so direct as HRTEM imaging, electron diffraction is a way to discriminate cv- and tv-illite for individual particles. Kinematical intensity distribution in the $hkI$ patterns (for instance $I_{hkI}(I_{hkI})$) is considerably different between the two illite structures, although it can be altered by the crystal thickness, nature and amount of stacking disorder, etc. (Gaillot et al., 2011) We also considered the axial ratio ($a^*b^*/c$) in the $hkI$ patterns. Owing to the difference of the $\beta$ angle between the two illite structures, $a^*b^*/(b/c\sin(\beta))$ values for cv- and tv-illite are expected to differ by $-0.5^\circ$. In order to distinguish such subtle difference, we need to determine the diffraction position accurately and distortion caused by the imaging lens of TEM must be eliminated completely. For this purpose, a processing program for the diffraction patterns acquired using a CCD camera has been developed by which the axial ratio can be determined with $0.1\%$ accuracy. Using this diffraction analysis, the cv- and tv-illite particles could be distinguished in their mixed specimens.

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STRUCTURE OF PRISMATIC HALLOYSITE

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Halloysite, Al2Si2O5(OH)4·xH2O, is one of the most common and ubiquitous clay minerals on the terrestrial surface. However, it is also true that the real structure of halloysite has yet to be fully understood despite the amount of research devoted to this mineral. Actually, no three-dimensional periodicity has been reported for halloysite because of very limited information from conventional diffractometry, which leads to the possibility that halloysite contains intense structural disorder. Moreover, from the standpoint of electron microscopy, halloysite is too beam-sensitive to apply recent high-resolution structure imaging in order to analyze its atomic structure.

Halloysite from Olkhon Island, Lake Baikal, Russia has been investigated using x-ray diffraction (XRD), scanning electron microscopy (SEM), selected-area electron diffraction (SAED) and, in particular, high-resolution transmission electron microscopy (HRTEM) using a new computer-assisted minimal-dose system, to reveal its atomic structure and formation process. XRD analysis indicated a basal spacing of ca. 7.2 Å and two characteristic peaks on the tail of the 02, 11 band in the XRD pattern. Based on these results, it is proposed that tubular halloysite initially forms as a hydrated one with the pseudo-mirror plane of the kaolinite layers perpendicular to the tube axis, then dehydrates and frequent alternation of τ+ and τ−, is formed, to minimize morphological change of the tubes.
DEVELOPING AN EFFICIENT POLYMER-MINERAL SORBENT FOR FILTRATION OF DICLOFENAC IN THE PRESENCE OF DISSOLVED ORGANIC MATTER

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Diclofenac, a non-steroidal anti-inflammatory drug, is one of the most frequently detected pharmaceuticals in water bodies since its removal by most conventional wastewater treatment plants is low (20-40%). It has been found that diclofenac possess environmental risks such as bioaccumulation in fish and alternation of their organs.

Recently, we have developed an efficient sorbent for diclofenac removal based on the adsorption of a specially synthesized polymer, poly N-methyl 4-vinyl pyridine iodide co styrene (QPvPcS), to montmorillonite. Unlike many polymers, QPvPcS is not pH dependent enabling stable electrostatic interaction between the polycation and the negatively charged clay. Indeed, zeta potential of the clay (-20 mV) decreased (less negative) with an increase in polymer loading (0.2 g/g). Positive charge of the composites promotes electrostatic interaction between the composite and anionic diclofenac (pKa=4.15). To estimate the contribution of these interactions, diclofenac removal (1 mg/L) by a QPvPcs-clay composite and by polydiallyldimethylammonium-chloride (PD-)clay composites, at increasing ionic strengths (0-100 mM NaCl), was studied (Figure 1). Both composites exhibited complete diclofenac removal at low ionic strength. At higher ionic strengths its removal by PO-clay composite decreased substantially while its removal by the QPvPcs composite was only slightly compromised. In addition to the positive charge that exists in both polymers, QPvPcs also has aromatic groups. Hence, we suggest that the m–m interactions have a dominant contribution to diclofenac removal.

The adsorption kinetics of diclofenac to the composite was faster than to granular active carbon (GAC) reaching complete removal within 15 minutes and 3 hours, respectively. The efficiency of diclofenac filtration (1 mg/L) by GAC and QPvPcs filtration columns in the presence of humic acid (HA, 5 mg/L) was studied. Previously we have demonstrated the efficient removal of HA by polymer-clay composites. Diclofenac removal in the presence of HA was complete by the QPvPcs column and only 77-92% removal was obtained by the GAC column (up to 76 pore volumes) (Figure 2), indicating that the affinity of diclofenac to the composite is higher than to GAC. However, the capacity of GAC was higher than that of the composite as seen at higher pore volumes. Hence, we suggest that a mixed column (GAC and QPvPcs) will maximize diclofenac removal.

To conclude, a non pH dependent positively charged polymer-clay composite was designed. It exhibits characteristics of high affinity and fast kinetics towards the pollutant in comparison to GAC. Therefore, efficient removal of an anionic emerging micro pollutant was achieved as reflected in the filtration experiment. We suggest that clay composites may be applied as sol sorbents or mixed with GAC, in filtration columns for the removal of anionic organic pollutants.

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ORGANOPHILIC MODIFIERS AND PROPERTIES OF RUBBER NANOCOMPOSITES

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Organically modified layered silicates have been widely studied for the past decade as property enhancers for polymeric materials. Improvement in mechanical, thermal, flame resistance, barrier and other properties of thermoplastics has been achieved by addition of organically modified layered silicates to polymer matrices to prepare Polymer-Layered Silicate Nanocomposites (PLSN). The filler content is frequently as low as 2–6 wt. %. Due to property enhancement even at small clay loadings, the PLSN systems possess several advantages compared to conventionally filled polymers, such as lower weight; enhanced flame retardance and thermal stability, outstanding barrier properties without requiring a multi-layered design, etc.

Four organo-cations of octyl- and hexadecyl-ammonium type were carefully selected and the organo-clays were prepared from a sodium-saturated <2 µm fraction of Jelšový Potok bentonite (Slovakia). The samples contained two or four octylammonium chains in the organo-cations, namely diocetylammonium (2CO) and tetrachloroammonium (4CO). Two other cations had chains with 16 carbons each, hexadecylammonium (1C16) and dihexadecyldimethylammonium (2C16). The d₀₀₁ values depended on the size and structure of the organo-cation. The height of the interlayer space in the 2CO–4CO montmorillonite series increased from 0.96 to 1.68 nm. 2CO cation opened the interlayer space more than 1C16; 2C16 was more effective than 4CO. Mass losses between 150 and 800 °C in N₂ flow were 26–38 % for 2CO–4CO organo-clays and 40 % for that with 2C16. Infrared (IR) spectra were similar for 2CO–4CO organo-clays but different for the samples with 16 C and 32 C atoms due to altered ratios of CH₃ and CH₂ groups. Downward shift of the CH₂ stretching bands with increasing size of the alkylammonium cation suggested that alkyl chains adopted more ordered structure. Based on the stretching (ν) and bending (δ) vibrations in the middle IR (MiR) region, the first overtone (2νX) and combination (ν + δ)XH modes of XH groups (X = C, O, N) were identified. The effect of larger alkylammonium cations in the vibrational spectra of Si–O and OH bonds in montmorillonite layers was observed. The changes in the intensity of the (ν + δ)XH,O band near 5250 cm⁻¹ allowed for comparison of the amounts of water adsorbed on the organo-clay surface. The water content decreased with the size of the organic cation reflecting increasing hydrophobicity of the montmorillonite surface. The spectra in the NIR region showed the 2νCH₂, 2νCH₃, and 2νCH₂ bands in the 5900–5550 cm⁻¹ region. The NIR spectra were extremely useful in identification of NH₃⁺ and NH₄⁺ groups. These are difficult to recognize in the NIR spectra of organo-clays due to overlapping with other absorption bands. The intense bands corresponding to overtones and combination vibrations of NH₃⁺ and NH₄⁺ groups were found in the 6600–6050 cm⁻¹ and 5000–4600 cm⁻¹ regions, the (ν + δ)NH₃⁺ was unambiguously identified near 4750 cm⁻¹.
The suitability of the prepared materials to be used as fillers for polymer nanocomposites was assessed according to rheological measurements of dispersions in solvents taking solubility parameters as primary factors for comparison of particular solvent and polymer. Mechanical properties of the cured rubber containing nanoclay were compared with the reference compound without the filler. Marginal if any changes in mechanical properties were achieved for small organic cations; however, stress and strain at break of clay/rubber nanocomposites increased with rising number of octyl chains in the interlayer spaces of organo-clays. The most important mechanical parameters, i.e. elongation at break and tensile strength differed significantly depending on the surface modification of the filler. The most efficient modifications were with 4C8 and 2C16 (Fig. 1). Mechanical properties of composites were positively affected by clays modified with alkylammonium cations of higher molecular weight (4C8 and 2C16), while rubbers filled with clays modified with smaller cations of lower molecular weight exhibited strength and elongation even lower than the one containing organically unmodified bentonite.

Fig. 1. Elongation at break (left columns) and tensile strength at break (right columns) of rubber filled with modifiers with various content of carbons.
A substantial layer charge decrease, from 210 to 140 meq/100 g, occurred during the natural weathering of phlogopite from Kansas through vermiculite to saponite. A comparison of the Fe$^{2+}$ content and layer charge of the coarse fraction (72% phlogopite) and the fine fraction (71% saponite) indicated that iron oxidation cannot account for the layer charge decrease during the above transformation. Control studies on iron oxidation during vermiculitization of biotites and lepidomelane did not correlate with layer charge decrease. Layer charge decrease by tetrahedral Fe$^{3+}$ cation removal and silicon incorporation was postulated as the layer charge decrease mechanism during natural weathering of this unique phlogopite to saponite.

Exchange saturation with Li$^+$ and washing resulted in exfoliation of large flakes of phlogopitic vermiculite and freeing of saponite (18 Å peak upon glycerol solvation) layers which proved the transformation of mica to saponite through vermiculite. The density of artificially produced blisters [swollen (001) surfaces] and their relief increased with an increase in hydration of the cation and a decrease in the layer charge density. These studies showed the interrelationships among charge density, cationic hydration and osmotic swelling.

The above lessons learned in Jackson's laboratory led to my creative design and synthesis of novel clays and other analogous layered phases, which are expected to have an impact on environmental quality and clean drinking water worldwide through filtration as well as soil remediation. Several novel synthetic clays and other layered phases were developed and their cation exchange properties in terms of kinetics, equilibria and thermodynamics were investigated with publications in Science (1983 and 1989) and Nature (1982, 1992 and 2001) which received world-wide publicity in news media. Some insights and stories about M. L. Jackson, my mentor (1969-1975) and his contributions to clay science will be brought out during this presentation in this symposium entitled "Some intellectual genealogies: honoring those who came before us". I will also comment on my associations with two other stalwarts of clay science, Professors S. W. Bailey and G. W. Brindley.
THE STRUCTURAL AND CHEMICAL MODIFICATION OF NONTRONITE ASSOCIATED WITH MICROBIAL Fe(III) REDUCTION UNDER VARIOUS REDOX CONDITIONS: INDICATORS OF “ILLITIZATION”

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The modification of clay properties with respect to the “illitization” associated with the microbial Fe(III) reduction in nontronite (NAu-1) structure and the re-oxidation by O2 gas bubbling were investigated. Clay fraction less than 0.2 mm was inoculated with FeRB S. oneidensis MR1 in M1 medium with the structural Fe(III) of NAu-1 as the sole electron acceptor and Na-lactate as the electron donor in the anaerobic chamber up to 12 months. Two sets of microbial structural Fe(III) reduction experiments were prepared and one set of the bio-reduction experiments was re-oxidized for 24 hours by pure oxygen gas bubbling through the autoclaved needle. The reaction was stopped at each time point by freezing the samples with LN2. The reduced and re-oxidized nontronite was characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM) with analytical electron microscopy (AEM) at nano-scale, and the wet chemistry analysis including cation exchange capacity (CEC) and the extent of Fe(III) reduction. Furthermore, the structural as well as chemical modification was measured simultaneously using nondestructive Terahertz time domain spectroscopy (THz-TDS). THz-TDS depict the illitization progress by measuring the free electron density and electron conductivity as well as electrical-optical property of bioreduced nontronite at various redox states. Electron density and conductivity, and electrical-optical property measure the chemical and physical (structural modification) modification, respectively. The changes in proportion of K and Ca upon various redox states of Fe and its consequences on the clay structures will be discussed.
Bentonite deposits formed from acidic rocks with high Si:Al ratios and low Mg content require intense leaching to remove silica and a source of Mg to form montmorillonite. Many rhyolite-based bentonite deposits are hosted in marine strata and seawater is usually considered as the main source of Mg in smectite. However, existing stable H-O isotope data of smectites often indicate the involvement of meteoric fluids and thus contradict the geological and geochemical evidence.

Boron in clay minerals is an excellent tool to trace fluid origin, water-rock interactions and salinity but has not yet been systematically applied to understand bentonite formation. Boron is incorporated into smectite as tetrahedral, fixed boron, and as interlayer boron. We explore the systematic boron analysis in smectite and apply a simply method of size fractionation and washing of the 0.2 µm fraction. Bentonite was dispersed in de-ionized water, centrifuged and the supernatant solution evaporated to retrieve a smectite concentrate. Samples were subsequently mannitol-washed to remove adsorbed boron and dialyzed to remove water-soluble minerals prior to Prompt Gamma Activation Analysis (PGAA).

We use mineralogical well characterized calcium bentonites from a distinct freshwater environment in Bavaria (Southern Germany) as a base of comparison for marine and possible non-marine calcium and sodium bentonite from various deposits in the USA (Mowry A, Otay and Beaver), Spain (Troncos), Sardinia (Bussu A pit/S’Aliderru), Greece (Zoulas and Angeria), and Turkey (Pertek). Preliminary results of untreated and mannitol-washed samples reveal a clear reduction in the boron concentration after washing. Terrestrial bentonite from Bavaria, however, shows a boron reduction of only about 10 ppm while the Troncos bentonite shows a drastic reduction after mannitol-washing of about 100 ppm. Our first results demonstrate that our methodology reduces significantly the adsorbed boron, that boron concentrations in smectite from bentonite deposits can be successfully measured by PGAA and that smectites from different bentonite deposits show discernible differences in their boron concentration. The complete results and data-set of this on-going study will be presented during the CMS 2013.

Boron in smectite forms from calcium and sodium bentonite deposits
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Composite materials composed of clays with organic- or bio-molecules in the interlayer galleries are readily synthesized and have many important applications. They may also be important in near-surface geochemical environments and sedimentary rocks. Detailed characterization of the molecular scale structure and dynamics of the interlayer galleries is very difficult experimentally because of static and dynamic disorder but can be obtained by molecular dynamics (MD) simulation using classical force fields. This presentation describes an MD study of Na-montmorillonite (MMT)–poly(ethylene glycol) (PEG) composites with and without CO₂ also present in the interlayer. Clay-polymer composites have a range of potential industrial applications in nuclear waste disposal and gas storage and separation, and there is significant interest in understanding the structure and energetics of clay composites containing polymers that interact positively with CO₂. PEG is an environmentally benign polymer that shows high selectivity for CO₂. It is used to make CO₂-selective membranes and is a major component of the solvents that remove CO₂ from flue gas. CO₂ is well known to cause PEG to swell. There is considerable uncertainty about the molecular scale details of the conformation, orientation and packing of PEG molecules, their interaction with the T-O-T layers, and the structural and dynamical behavior of the charge balancing cations and CO₂ molecules. PEG is also a useful model species to understand the role of ether oxygens in the interaction of clays with organic species in the natural environment. Because the interlayer structures are highly disordered, we describe the structural relationships in terms of the distributions of the pair-wise interatomic distances involving the interlayer species and the basal oxygens (OBasal), a variety of the angular relationships among the orientations of various bond vectors and the normal to the basal surface, and the dihedral angles describing the conformations of the PEG molecules.

For the MMT-CO₂ system, the structural arrangement among the CO₂ molecules is similar to that in supercritical CO₂ and is analogous to that of crystalline CO₂. All Na ions remain coordinated by OBasal but are also coordinated by OCO₂ and a few are displaced ~3Å above their surface sites. Cooperative motion of the Na ions and CO₂ molecules increases the Na diffusion and the CO₂ reorientation in the interlayers.

For the MMT-PEG and the MMT-PEG-CO₂ systems, the PEG is highly disordered with many of the molecules lying in a layered parallel to the basal surface of the clay. Some of the PEG molecules span from one basal surface to the other across the interlayer. Many of the Na ions are displaced from the basal surface and are coordinated by both OBasal and OCO₂. Some are completely displaced from the surface and are dissolved in the interlayer PEG. In the MMT-PEG-CO₂ system, the CO₂ molecules occur in well-defined layers parallel to the basal surface and are more commonly dissolved in the PEG. In this system, Na ions have few OCO₂ nearest neighbors. The presence of CO₂ causes the basal spacing to expand, but does not change the conformation of the PEG.

In the MMT-PEG-CO₂ system, the PEG molecules have a disordered conformation with dominantly trans but some gauche C-O dihedral angles, as in molten PEG. The maximum lengths of the PEG molecules are longer in the X-Y direction than in the Z direction. In the MMT-PEG-CO₂ system, the PEG molecules have a similar structural arrangement and conformations, but those that span between the two basal surfaces are extended by about 3Å due to expansion of the interlayer by the CO₂. CO₂ does not change the distributions of dihedral angles of the PEG. The structural environments of CO₂ in the MMT-PEG-CO₂ system are also very similar to those in supercritical CO₂ with the OCO₂ replacing many
of the O\(_{\text{CO}_2}\) in the coordination shell around CO\(_2\). The C\(_{\text{CO}_2}\) are coordinated to the O\(_{\text{PEG}}\) in an arc perpendicular to the local C-O-C linkages of the chain.

The MD simulations were carried out using a model system consisting of 128 crystallographic unit cells of MMT (8a x 8b x 2c) with the structural formula Na\(_{0.75}\)(Al\(_{3.5}\)Mg\(_{0.5}\))\([\text{Si}_{7.75}\text{Al}_{0.25}]\)O\(_{20}(\text{OH})_4\). Each PEG molecule consisted of 11 CH\(_2\)-O-CH\(_2\) units, and the two ends were capped by CH\(_2\)-OH groups. The MMT-CO\(_2\) and MMT-PEG-CO\(_2\) systems contained 4.17 CO\(_2\)/Na. The MMT-PEG and MMT-PEG-CO\(_2\) systems contained 1.04 11-monomer PEG molecules/Na. All PEG chains in the initial structures had identical starting conformations but were translated and rotated randomly to optimally pack the interlayer galleries with few or no hard contacts between the neighboring chains. The MD simulations use the CLAYFF force field\(^1\) for the clay substrate, the CHARMM force field\(^2\) for the PEG, and the force field parameters of Cygan et al.\(^3\) for CO\(_2\). The simulations were performed in the NPT ensemble at a temperature of 318 K and a pressure of 8 MPa, just above the critical point of bulk CO\(_2\) (305 K, 7.4 MPa).
HOW DRY IS A "DRY" SMECTITE

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Water molecules adsorbed on smectite and smectite-type mineral surfaces in 2:1 clay minerals represent one of the most unique and important states of water. The exact quantification of the amount of water adsorbed on smectites and minerals which contain smectitic surfaces i.e. mixed-layered illite-smectite is a crucial issue in porosity measurements of shales, as well as in soil science, and civil engineering. The widely accepted standard drying procedure involves heating a sample at 105°C or 110°C for prolonged time, sometimes under vacuum. This procedure is usually thought to provide a "dry" (completely dehydrated) rock.

A set of four smectites, differing in chemical composition, layer structure, amount and localization of the layer charge were examined with thermogravimetry (TG) and X-ray diffraction (XRD) in order to precisely measure the amount of water adsorbed on the surface and to examine the conditions of a drying procedure that are sufficient to remove the adsorbed water. Each smectite was examined in three homoionic forms (Cs+, Na+ and Mg2+) in order to test the influence of the interlayer cation on the dehydration and dehydroxylation behavior.

Experiment consisted of two steps, both within one TG run. The first step was simulating a widely used drying procedure and involved isothermal drying of the samples at 110°C for 4 hours under high flow of dry N2 to mimic the vacuum conditions that remove the thermally-released H2O molecules. Subsequent ramp heating to 1000°C was performed to examine the amount of water remaining after the first step.

The comparison of the mass loss during dehydroxylation with theoretical mass loss calculated from the chemical formula indicates that noteworthy part of the water remained in all the samples after long drying at 110°C (Figure 1). For Mg-smectites as much as 4 wt.% excess water loss was noted. This corresponds to almost 6 vol.% of water present in the sample after the extensive drying applied. The exchangeable cation hydration enthalpy plays the most important role in water retention in the sample. For all samples the dehydration is not complete even at 300°C (Figure 2), which is the lowest temperature that the dehydroxylation starts at. For the smectites that dehydroxylate at the lowest temperatures (beidellite, nontronite) the residual adsorbed water still exists when the dehydroxylation is advanced.

The calculations based on TG experiments have been confirmed by XRD experiments with an heating chamber. XRD patterns of the samples heated between 110°C and 750°C shows that the d001 value decreases and becomes sharper during heating up to T≈400°C. The d001 peak series indicate that a mixed-layering of the dehydrated and incompletely-dehydrated layers occurs and that the content of the dehydrated end-member increases with the temperature of heating. In-situ heated Mg-smectite shows by far greater effect of the mix-layering than the Na-smectites.

The present study questions the validity of the conventional pre-drying methods to various measurements in geosciences: from isotope analysis of 2:1 clay minerals to total porosity determination with Boyle’s law.

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The present study questions the validity of the conventional pre-drying methods to various measurements in geosciences: from isotope analysis of 2:1 clay minerals to total porosity determination with Boyle’s law.
ADVANCES IN MOLECULAR SIEVES: NEW POTENTIAL FOR UTILIZING THE PROPERTIES OF MINERAL NATURAL ZEOLITES

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Forming the heart of hundreds of processes as catalysts, adsorbents, ion-exchange and purification agents, crystalline molecular sieves (Figure 1) are among the most important and valuable classes of inorganic materials. Utilized in petroleum cracking for gasoline production, for oxygen production from air, for water purification by removing heavy metals and much more, these materials directly impact our lives.

Molecular sieve applications have been dominated by the use of synthetic crystalline materials. Abundant and inexpensive natural mineral zeolites have been a poor step-cousin to their synthetic relatives owing to nonuniformity of materials and properties not only from deposit to deposit but also from sample to sample within a deposit. This nonuniformity generally necessitates over-engineering adsorptive and catalytic processes such that much more expensive synthetic molecular sieves are generally more cost effective when viewed from a whole system cost perspective.

However, unique natural zeolite properties unavailable in synthetic zeolites are beginning to renew interest in these materials. Geomorphic natural zeolites are showing great promise in robust durable membranes for separation of molecules by size including hydrogen from syngas and the deoiling/desalination of contaminated water in oil sands processing. The unique ion exchange selectivities of certain natural zeolites have made them indispensable in the cleanup of Fukushima, Japan and other nuclear applications.

Finally, as the world moves toward the use of heavier oils for energy needs, the application of natural zeolites as cheap disposable cracking catalysts offers a fascinating new possibility.

A brief history, overview and update of natural zeolite applications and promise for the future will be presented.

Figure 1. SEM (left) and TEM (right) micrographs of molecular sieve.
DECONVOLUTION OF TRANSITION-METAL SUBSTITUTION AND INTERCALATION EFFECTS ON LAYER-TYPE IRON MONOSULFIDE (MACKINAWITE) STRUCTURE

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Mackinawite (tetragonal FeS) is a layer-type mineral composed of edge-sharing FeS4 tetrahedral sheets stacked along the c-axis via van der Waals forces. This sulfide structure looks simple, but an interesting question about the structure remains unresolved that cannot be addressed by experiments alone. In sulfide ore deposits, FeS was often reported with a high content of transition metals such as Ni and Co. Based on its layered structure, two possibilities were proposed as transition metal sites in FeS: substitution for Fe site or intercalation between FeS4 tetrahedral sheets. The detailed structures of metal-doped FeS, however, are not clearly defined yet. We have examined the two metal sites in FeS crystal by using density functional theory with dispersion correction (DFT+D), a computational mineralogy method. Before presenting geometry-optimization results of FeS that has substitution or interaction with Co, Ni, or Cu, we show that DFT+D reproduces the experimental structure parameters of pure FeS and Co-, Ni-, or Cu-doped FeSe crystal which is isostructural with FeS. And then we present when more metals are intercalated in FeS, a axis lattice parameter decreases but c axis increases compared to pure FeS. When Fe site in FeS is substituted by a transition metal, metal-specific trends are found: in Co case, a and c axes both tend to decrease with increasing the metal content, but in Cu case they both tend to increase; in Ni case, a axis and c axis respectively tend to increase and decrease when more Ni is substituted. Lastly we discuss possible mechanisms about the metal incorporation into FeS.
APPLYING THE ISOTOPIC COMPOSITION OF CLAY MINERALS TO THE EXPLORATION OF BURIED ORE DEPOSITS

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Clay minerals have been used extensively in the study of paleoclimates, basin evolution and ore deposits because they result from the interaction between fluids and host rocks. In effect, much of what we know about the origin of ore deposits and the fluids involved in alteration and mineralization comes from using the H and O isotopic composition of clay minerals, provided their temperature of formation is known and that they form during the mineralizing process. Oxygen and H stable isotopic compositions of clay minerals can indicate prospective areas for ore deposits, especially when coupled with other geologic information, but not without caveats. To calculate the isotopic compositions of the fluids, the temperature at which the clay minerals formed must be determined, the fractionation factors between the clay and fluid must be known, and it must be demonstrated that the clay formed during the mineralizing process and not under retrograde exchange with later fluids. In addition, isotopic analysis of clay minerals is difficult, expensive and time consuming, thus rendering it unattractive for exploration.

Although the H and O isotopic composition of clay minerals can be used to constrain mineralizing fluids and their character, this is only useful if the clays that reflect these fluids are exposed near the surface and data exist to relate them to either the mineralization or alteration associated with a deposit type. Given that discovery of ore deposits near the surface have become scarce, techniques that can remotely sense deposits at depth are required to shape exploration strategies and find additional deposits.

In contrast to many other minerals in soils, clay minerals have large and diverse surface sites, onto which elements and compounds being transported can adhere as either outer or inner sphere complexes. Thus, clays from soil horizons may reflect element and compound fluxes leaking from the geology below, including those that have migrated from ore deposits at depth. Elements and organic compounds from microbes acting on the deposit or from the deposit itself at depth (see Figure) may also have isotopic compositions that are distinct from those originating in the background geology, making both the concentration of them in soil clays and their isotopic compositions definitive indicators of their origin. In effect, clay minerals in soils are a relatively homogeneous media that can trap elements migrating from below and therefore be useful for detecting undercover deposits. In addition, as with clay minerals associated with alteration zones around deposits, H and O isotopic compositions of the clay minerals can indicate if they originate from regoliths, tills or bedrock and isotopes of the elements and compounds associated with the clays can indicate their origin as well, thus adding value to exploration beyond elemental concentrations.

The clay size fraction from various soil horizons are separated and characterized by X-ray diffraction, short wave infrared spectroscopy, electron microprobe and scanning electron microscopy. In addition to H isotopes, other isotopic compositions such as Li, B, Pb, U of elements incorporated into the clays or adsorbed onto the surfaces are being used to reflect the origin of these elements from ore deposits. Other techniques, such as pyrolysis extraction of volatiles from clay minerals from both soils and drill core are used to verify where within the samples the elements of interest reside and whether there is evidence of elemental mobilization of specific elements from depth. These techniques are being developed for exploration and environmental geochemistry to trace element migration in the near surface environment. Clay minerals offer enhanced targeting of mobile elements relative to media used in previous efforts, especially when coupled with isotopic tracers.

Possible mechanisms involved in the migration of elements from ore deposits at depth and trapped on active surfaces of clay minerals in soils.

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We have developed a model that simulates the abundance and properties of fibrous illite that forms in sandstones from the reaction of kaolin with K-feldspar (or alternatively, K-rich brine). Illite fibers may nucleate on the walls of intergranular pores or pores that form from Kfeldspar dissolution provided that reactants are available. The reaction is considered precipitation rate limited where the rates of nucleation and growth of the crystallites are simulated using Arrhenius expressions that consider saturation state and temperature (as well as the nature of the substrate in the case of nucleation). The model simulates a distribution in illite fibers and tracks the dimensions and volumes of the crystallites through geologic time as well as the dissolved reactant volumes. The bulk KAr date is calculated for the pure authigenic material as well as for a mixture of this material with K-feldspar, muscovite, and illite detrital contaminants. The bulk illite d18O also may be simulated provided that the water d18O is specified through geologic time. We have coupled this model with models of sandstone compaction, quartz cementation, plagioclase albition, and other diagenetic processes. This suite of diagenetic models, in turn, provides input for models of bulk physical properties including porosity, permeability, mineralogy, chemical composition, and elastic bulk and shear moduli. The permeability model for instance considers the effect of illite fiber growth on wetted surface area, flow path tortuosity, and the loss of intergranular pores and concomitant development of micropores and grain dissolution pores. The objective of this coupled suite of models is to accurately predict rock properties away from sample control and through geologic time.

We evaluated the performance of the fibrous illite model on two geologically distinct datasets: (A) Jurassic sandstones from offshore Norway with quartzose compositions that were exposed to maximum temperatures ranging from 108 to 173 °C and (B) Miocene sandstones with abundant metamorphic rock fragments from Southeast Asia with maximum temperatures ranging from 157 to 182 °C (Figure 1). Petrographic observations in both datasets are consistent with the interpretation that illite formed from the in situ reaction of kaolinite and K-feldspar. Both datasets incorporate samples with lower thermal exposures where K-feldspar and kaolinite reactants co-exist as well as higher thermal exposure samples where one reactant or the other has been fully consumed.
The model reproduces the extent of illitization reaction in each dataset using the same kinetic parameters (the 73.2 kJ/mol kinetic case in Figure 2). Predicted KAr ages are consistent with available data in both datasets given uncertainties associated with detrital contaminants. Simulated δ18O values are within 0.5‰ of measurements from the Southeast Asia dataset when the present-day water δ18O value is assumed for the time of illite growth. Additionally, the distributions in modeled fiber dimensions from the Norway dataset are comparable to Atomic Force Microscopy measurements from units with similar ages and thermal exposures from the North Sea.

Figure 2: Comparison of predicted illite abundance (black dots) with data from petrographic analysis where gray circles indicate samples where kaolinite and K-feldspar co-exist and open circles indicate where they do not. The numeric values refer to the activation energy for crystal growth used in the simulation: The 73.2 kJ/mol case reproduces the illitization pattern in both dataset. The 68 kJ/mol scenario predicts a greater extent of reaction than is observed whereas the converse is true for the 76 kJ/mol case. (After Lander and Bonnell, 2010.)
The most recent surge in drilling activity supported at least two broad fields of product development based on the first principles of bentonite-based fluid chemistry and mechanics. Specifically, wire line coring operations in the minerals exploration industry and the ground source heat pump industry both offered significant opportunities for the next generation of drilling products. Keys to unlocking commercial value was an understanding of the desired fluid type required to impart the properties needed for the application. Fluid engineering, in turn, required refreshers for the fluid suppliers in basic bentonite mineralogy, montmorillonite chemistry, basic polymer chemistry, and interactions during the mixing and pumping processes at the drill site. To best meet the technical needs for the application, geothermal grouts were formulated to behave as hybrid fluids at the surface but then quickly thicken as high solids gels in the subsurface after the drilling process was complete. The former product feature was a challenge due to the significant increase in solids content as compared to a standard drilling fluid; e.g., >65.0% to 6.25%, respectively. Additionally, these solids consisted of highly conductive materials that spanned a broad range in grain density and particle size.

For geothermal grouts, the key was to first recognize that the colloidal properties required for these fluids were completely different than those required for a drilling fluid in coring operations. Grouts required the mineralogist to develop a timed “gelling” of the slurry at significantly higher solids content than that of a typical drilling fluid in order to ensure its proper mixing, pumping and finally placement in a geothermal loop system. This was achieved by understanding the interactions between the primary exchangeable cations (Na⁺, Ca²⁺ and Mg²⁺), various alkaline salts (Na₂CO₃, MgCO₃), and various dispersants.

Conversely, fluid suppliers were asked to increase the “yield” of bentonite fluids in order to increase the efficiency of the coring process as well as lower costs. Yield is a term long-known in the industry that describes the number of forty-two gallon barrels one ton of bentonite can produce with given rheological properties. Within the American Petroleum Institute (A.P.I.) system of classifying bentonite, the A.P.I. 13 section 9 products typically yield 90-100 barrels of drilling fluid. This yield is approximately half of the desired target for most coring operations. As the drilling industry globalized in the recent years, it became quickly apparent that local bentonites varied in their yield between regional geological locations, between mines and even in production lots from the same mine. In general, few global bentonites achieved yields to the level of the Wyoming bentonite-based products. The few that were initially comparable behaved differently over time, developing hysteresis or “separation” or thickening if left unattended. These fluids typically developed other measurable differences in their fluid properties; i.e., higher filtrate volumes, higher yield points, and higher low end rheology. Unifying the fluid type of the various global bentonites to the hybrid Bingham-Power law fluid became the key to developing products whose performance became more predictable and consistent in the field. In this case, factors related to clay chemistry and manufacture led to opportunities to differentiate and extend the barrel yield of these products. This paper will report the processes, key findings and comparisons for these two applied research efforts as a reminder that the versatility of montmorillonite consistently delivers opportunity to its markets.
EFFECT OF WATER MOLECULE CONTENT ON SURFACE ACTIVITY OF Na-MONTMORILLONITES

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Water molecule content has a great impact on surface activity and structure stability of Na-montmorillonite used in medicine and industry fields and helps to understand the interaction between water and montmorillonite minerals. Na-montmorillonites from Shandong Province, China, with a series of water contents (0-15.2%) were investigated by adsorption and desorption isotherms of water vapor at 293.15K, adsorption isotherms of nitrogen at 77.15K and differential scanning calorimetry (DSC) and thermogravimetry (TG), respectively. When the water contents of Na-montmorillonites gradually decrease, the adsorption and desorption isotherms of water vapor are not closed completely and the hysteresis phenomena of adsorption isotherms becomes more apparent. As the moisture content reduces, the total specific surface areas of BET (TSSABET) increase from 515.6/g to 619.2/g and then decrease to 466.7/g according to the adsorption isotherms of water vapor. The peak of TSSABET is about 619.2/g at nearly 1.5% water content. Furthermore, the drier samples are, the less consistent with BET theory adsorptive isotherms of water vapor is. With moisture contents decreasing, the external specific surface areas of BET (ESSABET) calculated from adsorption isotherms of nitrogen rise from 20.1/g to 77.6/g and then drop to 68.1/g. The maximum ESSABET, 77.6/g, appears at 4.4% water content. Hence, conserving some water content plays a significant role on maintaining surface activity of Na-montmorillonite. The TG/DSC curves obtained from Na-montmorillonites of various water conditions show a double endothermic peak with the maximum values centered at 106-123°C and 150-171°C, which demonstrates that neither the weakly adsorbed water molecules located in the external surface, mesopores and some part of interlayer space nor strongly adsorbed water molecules in interlayer space do not disappear. Besides, Migration and transformation of two categories of water molecules probably lead to the hysteresis phenomena of adsorption and desorption isotherms of water vapor, the distribution regularity of external specific areas of BET and characters of TG/DSC curves.
According to a report published in 1995 by the Nuclear Energy Agency (NEA) and to today’s broad international consensus on the technical merits of disposal of long-lived radioactive wastes in deep, stable geological formations, safe geological disposal is assured by a system that will (a) isolate the wastes from the biosphere for extremely long periods of time and (b) ensure that residual radioactive substances reaching the biosphere will be at concentrations that are insignificant compared, for example, with the natural background levels of radioactivity. Geological disposal should also provide reasonable assurance that any risk from inadvertent human intrusion would be very small.

These requirements are addressed in most national programs by passive multibarrier repository systems that ensure safety. For meeting the inherently required stability and longevity of these passive multibarrier systems, the design of the repository has to be such that its performance is insensitive to detrimental phenomena or it must be possible to avoid these phenomena.

Passive multibarrier systems typically comprise the natural geological barrier provided by the repository host rock and its surroundings and an engineered barrier system. This multibarrier principle provides overall robustness of the system that ultimately enhances safety by containing the waste in different materials with different properties.

Some of the OECD countries with programs for the disposal of high-level waste can rely on a clay-rich host rock (France, Belgium and Switzerland). Other programs compensate for the absence of a clay host rock by relying on corrosion-resistant waste canisters and elaborate engineered barrier systems (Sweden and Finland). As part of the engineered barrier system concept, bentonite or bentonite-sand mixtures are often selected as the interface to the host rock or as a buffer between the canister and the host rock.

The obvious advantages and safety-relevant properties of clay in the context of waste disposal, such as a high sorption and cation exchange capacity, self-sealing and swelling potential and inherently low hydraulic conductivity, etc. have been extensively studied. This paper proposes to explore the different repository concepts and designs from the perspective of the clay involved and to focus on the different safety relevant functions of clay in the multi-barrier system.
A large stratified deposit of unusual black talc layer between dolomite layers, was found in the late Neoproterozoic Dengying Formation, located in Guangfeng County, Jiangxi Province, southeastern China. The reserve is estimated to be more than half a billion tons. The talc mineral deposit occurs primarily as oolitic structure and mainly consists of talc (30 ~ 70 %), dolomite, quartz, and magnesite. The ooids are composed of pure talc crystals. Most of talc crystals are ultrafine nano-plates. Electron-microprobe analysis (EPMA) revealed its chemical composition close to pure white talc and the infrared spectrum of the black talc is similar to that of white talc from Trimouns (Pyrenees, France). The black talc contains small amount of organic carbon (~0.37-0.68 wt%), which causes the blackness of talc. Z-contrast images show that isolated graphite-like layers in the interlayer positions of talc nano-crystals. It is suggested that precursors of stevesite or kerolite precipitated from locally Al-depleted sea water in shallow marine or lagoon environment. And extracellular polymeric substances from photosynthetic microorganisms enhanced the nucleation or precipitation of the precursors. Further diagenesis resulted in formation of the black talc.
CALCIUM CARBONATE POLYMORPHS ON MICA SUBSTRATES AND THEIR INTERFACIAL FREE ENERGIES: IMPLICATIONS FOR MINERAL TRAPPING MECHANISMS IN GEOLOGIC CO₂ SEQUESTRATION

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Micas are a group of environmentally abundant clay minerals which can serve as substrates for precipitation in aqueous environments. The precipitation process is important because it affects not only the aqueous environment of these micas, but can also impact their surface properties, such as surface roughness and surface hydrophobicity. In many cases, precipitation will be controlled by nucleation rates. Nucleation also influences the fate and transport of contaminants and the permeability of caprocks and formation rocks in the subsurface, including geologic CO₂ sequestration (GCS) sites. In particular, the investigation of carbonate nucleation is needed to better understand mineral trapping mechanisms in GCS. According to the classical nucleation theory, the nucleation process is controlled by many parameters, one of which is the interfacial energy between the substrate and nucleated particles.

Here we present an in situ study of the effective interfacial energy between calcium carbonate (CaCO₃) and the basal surface of a model mica, muscovite. We compared this result with nucleation on the (100) surface of quartz. Nucleation rates on substrates were obtained by grazing-incidence small-angle x-ray scattering (GISAXS) and were applied to the classical nucleation theory to calculate the effective interfacial energy. Complementary techniques included atomic force microscopy (AFM), Raman spectroscopy, scanning electron microscopy (SEM), and contact angle analysis. Thermodynamic calculations of saturation were conducted using Geochemist’s Workbench (GWB, Release 8.0, RockWare, Inc.).

The effective interfacial energy between CaCO₃ and mica was 40.7±0.8 mJ/m² if the formation of calcite was assumed and 24.0±0.3 mJ/m² if the formation of vaterite was assumed. In either case, the effective interfacial energy was less than that between CaCO₃ and quartz (51.1±0.7 mJ/m² and 31.7±1.4 mJ/m² for calcite and vaterite, respectively). The nucleated particles were smaller on mica than on quartz. Calcite and vaterite were identified as the nucleated particles based on results from Raman spectroscopy. No other phase was identified. The CaCO₃ phase also showed that the fraction of vaterite was larger at higher saturation indices, suggesting a slower phase transformation from vaterite to calcite. This phase transformation also impacted the surface property of precipitates: vaterite had rougher surfaces and was reported to be more hydrophilic than calcite. Our findings give key insights and new thermodynamic information which can help in designing pore scale reactive transport models for many subsurface environments, and particularly for geologic CO₂ sequestration field sites. They can also be applied in other systems where CaCO₃ precipitation is a concern, such as industrial scaling, paper surface treatment, and bio-mineralization.

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BIRNESSITE SORPTION OF CONTAMINANT LEAD WITH TRICLINIC AND HEXAGONAL BIRNESSITE
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In the United States, over 300 Superfund sites list Pb as a “contaminant of concern,” typically as a result of industrial 
smelting and mineral processing. Pb is also broadly distributed in soils due to fallout of leaded gasoline exhaust in 
past decades. Many studies have demonstrated that high Pb levels in blood cause long-term neurological damage in 
children, including lowered intelligence and attention deficit hyperactivity disorder. Consequently, the cycling of Pb in 
air, soil, and groundwater is of extreme societal concern. It has long been known that Mn oxides exhibit a particularly 
strong affinity for Pb. For example, molecular modeling and X-ray absorption spectroscopy of birnessite-like phases 
suggest that Pb sorbs as triple corner-sharing complexes at Mn vacancy sites and as double edge-sharing complexes 
on lateral edge surfaces. However, it is not known whether Pb also can exchange with interlayer cations in birnessite, 
and, if so, under what circumstances.

We employed time-resolved X-ray diffraction (TR-XRD) to examine the uptake of Pb by birnessite in a series of flow-
through experiments with and without 0.1 M Pb(NO₃)₂ solution at pH 3. We used synthetic hexagonal H-birnessite 
and triclinic Na-birnessite as our starting materials. XRD patterns of the reacting birnessite were collected every 30–60 
seconds. In the absence of Pb, triclinic birnessite transformed to hexagonal birnessite within 30 min. Rietveld analysis 
of the hexagonal H-birnessite yielded an octahedral Mn occupancy of 0.85, with a concomitant substitution of Mn 
into an interlayer position above the vacancy sites. In the presence of Pb, triclinic Na-birnessite transformed into a tur-
bostratically disordered hexagonal-like phase after ~6 hrs. Batch experiments with the identical chemistry after 7 days 
produced the same result, with no increase in structural order. Surprisingly, hexagonal H-birnessite showed little, if any, 
transformation in the presence of Pb after 6 hrs of TR-XRD observation, despite its high octahedral vacancy concentra-
tion. Seven-day batch experiments using hexagonal H-birnessite with 0.1 M Pb(NO₃)₂ solutions at pH 3 yielded the same 
result. We suggest that dissolved Pb substituted within the triclinic Na-birnessite interlayer upon layer delamination 
during the transition to hexagonal birnessite. In the absence of layer delamination induced by cation exchange, acces-
sibility to the interlayer during exchange with hexagonal birnessite was inhibited and Pb sorbed only to surface sites.

ABSTRACTS
Determination of the Solid Acidity of Montmorillonite Based on Single NH₃ Adsorption System

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Great attention has been paid to the montmorillonite acidity, due to the roles of acid sites of montmorillonite in the geological process and application in industry catalysis. Various determination methods have been proposed to obtain the acidity parameters of montmorillonite, such as the Hammett indicators, temperature-programmed desorption (TPD) and Fourier transform infrared spectroscopy (FTIR) methods. However, the used probe molecules and determination conditions in the previous studies are not based on a one probe and single test system, and thus the obtained results are poorly comparable, which influences the understanding of montmorillonite acidity.

In this work, a novel method based on single NH₃ adsorption system was set up for the characterization of the solid acidity of montmorillonite. This method combined TPD and FTIR for the determination of the amount, type, and strength of montmorillonite acid sites. The total solid acid amount was obtained by using back titration and curve deconvolution methods during TPD analysis, which avoided the influence of physically adsorbed and hydrogen bound NH₃ on the determination of acid amount. The specific amount of the Brønsted and the Lewis acid site was calculated according to the total amount of the solid acid sites and the ratio of Brønsted/Lewis sites obtained by TPD and FTIR methods. The strength of each acid site and the mechanism of heating on the acidity were proposed based on these obtained results.

The total amount of acid sites of montmorillonite was 1.15 mmol/g, which was higher than that obtained by the Hammett indicators method because of the detection of solid acid sites in the montmorillonite interlayer space. These acid sites contained 1.00 mmol/g Brønsted and 0.15 mmol/g Lewis acid sites. The acidity of montmorillonite was mainly derived from the interlayer polarized water, Si-OH, the H₃O⁺ adsorbed by the negatively charged tetrahedral AlO₄ and unsaturated Al³⁺ ions, all of which were attributed to the Brønsted acid sites with the exception of unsaturated Al²⁺ ions (Lewis acid sites). Heating led to an increase in the acid strength and the acid amount, and changed the type of the partial acid sites. The interlayer polarized water after heating at 120°C provided more protons and exhibited higher acid strength than that in raw montmorillonite. After heating at 400°C, the interlayer polarized water acted as very strong acid sites. The H₃O⁺ adsorbed by tetrahedral AlO₄ was attributed to weak-strength acid sites and transformed to Si-O(H)-Al after dehydration, while displaying very strong-strength acidity. Unsaturated Al³⁺ ions showed medium-strength Lewis acidity, although some adsorbed water molecules and exhibited weak Brønsted acidity. After dehydroxylation at 600°C, abundant unsaturated Al³⁺ ions appeared and the amount of Lewis acid sites increased.

The acidity of montmorillonite was mainly derived from the interlayer polarized water, Si-OH, the H₃O⁺ adsorbed by the negatively charged tetrahedral AlO₄ and unsaturated Al³⁺ ions, all of which were attributed to the Brønsted acid sites with the exception of unsaturated Al²⁺ ions (Lewis acid sites). Heating led to an increase in the acid strength and the acid amount, and changed the type of the partial acid sites. The interlayer polarized water after heating at 120°C provided more protons and exhibited higher acid strength than that in raw montmorillonite. After heating at 400°C, the interlayer polarized water acted as very strong acid sites. The H₃O⁺ adsorbed by tetrahedral AlO₄ was attributed to weak-strength acid sites and transformed to Si-O(H)-Al after dehydration, while displaying very strong-strength acidity. Unsaturated Al³⁺ ions showed medium-strength Lewis acidity, although some adsorbed water molecules and exhibited weak Brønsted acidity. After dehydroxylation at 600°C, abundant unsaturated Al³⁺ ions appeared and the amount of Lewis acid sites increased.
MECHANICAL AND GAS BARRIER PROPERTIES OF RUBBER/KAOLIN NANOCOMPOSITES

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Clay minerals, as an important natural phyllosilicate material, have many attractive structural features. Especially the layered structure and high-aspect ratio characteristic can considerably improve the gas barrier property of polymer composites. Thus, clay minerals usually are recognized as a natural barrier in polymers. Previous works on improvement to gas barrier property of rubber polymer composites have greatly focus on montmorillonite, but a little on kaolin. Kaolin is mainly composed of kaolinite, which as one of important clay minerals can be used as functional filler due to its light color, special stratified structure and availability.

A kind of fine kaolin, so called nanokaolin, with average thickness of 20-50nm and average diameter of 300-500nm, was manufactured through a series of procedures of purification, size separation, exfoliation, surface modification and spray dry. The nanokaolin(NK) was applied in various rubbers by traditional method of melt mixture process and compared with the precipitated silica(PS). The results show that the tensile strength of NK is close to that of PS in SBR composite, and exceeds the PS in NR, BR and EPDM composites. For the elongation at break and rebound elasticity, NK is obviously superior to PS. But for modulus and tear strength, NK is dominant in NR, and there is some difference compared with PS in SBR, BR and EPDM.

A series of SBR composites filled with modified kaolin were prepared by melt blending and the gas permeability of the composites was measured. The influence of kaolin powder size, contents, and structure types of filler on the gas barrier property of SBR composite were investigated and discussed. The gas barrier model based on kaolin was established to evaluate and predicate the gas permeability of rubber composites. There are three main factors of filler that affect the permeability of the filled composite: the volume fraction of the clay, the aspect ratio of clay and clay orientation relative to the diffusion direction.

According to the barrier mechanism of clay, the author has established the gas model of SBR/kaolin composite based on the Nielsen model and other previous works. The barrier model formula can be expressed as follows:

\[ \text{Relative Permeability} = \frac{1}{1 + \xi} \]

**\xi** is the combination parameter. Assumed that **\xi**=1 before the calculation of model due to it is difficult to determine in the experiment, and it can be analyzed by the comparison between the prediction value and the measured value.

The comparison between prediction value of model and measured value of experiment indicated that the orientation angle of kaolin platelet is 45° when the volume fraction at low level (20~40phr), and when the volume fraction at high level(50~70phr), the orientation angle of kaolin platelet is 45° when the volume fraction at low level(20~40phr), and when the volume fraction at high level(50~70phr), the orientation angle of kaolin platelet ranged between 30°~45°. Based on the above result, the author defined that the orientation angle of kaolin platelet located at lower level, while it trend to lower angle when the volume fraction located at higher level. The overall orientation angle of clay platelet in filled composite trend to high angle when the volume fraction located at lower level, while it trend to lower angle when the volume fraction located at higher level. The overall orientation angle of clay platelet is 45° when the volume fraction at low level (20~40phr), and when the volume fraction at high level (50~70phr), the orientation angle of kaolin platelet is 45° when the volume fraction at low level (20~40phr), and when the volume fraction at high level (50~70phr), the orientation angle of kaolin platelet is 45° when the volume fraction at low level (20~40phr), and when the volume fraction at high level (50~70phr), the orientation angle of kaolin platelet is 45°.
angle is chosen as 30°. The fitting of prediction value and measured value was shown in the Fig. 1, which presented the prediction value is lower than the measured value at low volume fraction and opposite results at high volume fraction, the ratio of prediction value and measured value at high volume fraction can be expressed the combination parameter $\xi$, which increased as the volume fraction increased due to the aggregation of kaolin platelets in the composite matrix.

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Understanding Acid-Base Chemistry of Clay Minerals Using First Principle Molecular Dynamics

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Knowledge on clay-water interfaces is essential for both understanding interfacial biogeochemical processes and providing guidance for developing advanced materials. Because of the layered structures, the surfaces of clay minerals can be divided into basal surfaces and edge surfaces. Due to dangling bonds, the edge surfaces represent more active chemistry than basal surfaces. Edge surfaces are responsible for acid-base chemistry of clays, such as surface charging, complexation of heavy metal cations and organics. However, the microscopic structures and pristine acidity of edge sites are still not accessible to experiments. With FPMD (first principles molecular dynamics) and free-energy perturbation techniques, we have investigated the hydration structures, acidity constants, and metal cation complexation of clay edge interfaces.

In this presentation, we will talk about the following topics.

1) Hydration structures. With FPMD based free energy calculation techniques, the hydration structures of edge surfaces are revealed. The stable edge groups include Si-OH, Al-(OH)2(OH) and Mg-(OH)2 sites. For Al in octahedral sheets of (010) surfaces, the 5-fold coordination, i.e. wAl(OH) is also a stable state which has a higher free energy than the 6-fold coordination.

2) Acidity constants. Acidity constants of the acidic sites are derived by FPMD based vertical energy gap technique. The results indicate that wSi-OH and wAl-(OH)2(OH) are major acidic sites, which are responsible to the observed pH-dependent phenomena. In contrast, wMg-(OH)2 sites are found very inert.

3) Fe2+ complexes adsorbed on edges. The derived pKas indicate that wSi-O- and wAl-(OH)(OH) sites are potential sites for complexing heavy metal cations. With FPMD simulations, we show that stable monodentate and bidentate Fe2+ complexes form on wSi-O- and wAl-(OH)(OH), respectively.
The structure of water films at charged clay surfaces is an essential factor in understanding and predicting the physicochemical properties of the aqueous adsorbed species which can provide fundamental insights into mobility of contaminants in soils and subsurface environments. Concurrently, the ion-water interactions strongly depend upon the substrate structure and the nature of the charge compensating ions. The ion transport in porous media is strongly influenced by the interactions occurring at the mineral-water interfaces. In particular, the retention properties of aqueous ions through clay minerals is pivotal in understanding, since clays are considered as geochemical barriers for the containment of toxic wastes. At the same time, surface specific results obtained from advanced experimental techniques are often difficult to quantitatively interpret without having a reliable molecular scale picture of the underlying physical and chemical process. Meanwhile, molecular computer simulations have become one of the most important tools in the study of such interfacial systems and phenomena by providing invaluable atomistic information on the underlying physico-chemical process.

Classical molecular dynamics (MD) computer simulations using CLAYFF force field were performed for the adsorption of Cs⁺ ion at hydrated muscovite surface. The layer charge distributions in muscovite were represented more realistically than in earlier studies by using a large surface area for the substrate. Atomic density profiles and the topology of the hydrogen bonding network were analyzed in detail for the interfacial solution structure. The random distribution of isomorphic Si/Al substitution in the tetrahedral layer leads to the formation of three different adsorption sites at the basal surface. Potential of mean force (PMF) calculations were performed, in order to quantify the energetics of Cs⁺ ion complexation at each of the three adsorption sites. A series of NVT-ensemble MD simulations were carried out under ambient conditions with the application of the umbrella sampling algorithm to pull the Cs⁺ ion and constrain its distance from the muscovite surface. The adsorption free energy profiles thus obtained clearly indicate that the inner sphere surface complex of the ion is highly stable at three different adsorption sites. Irrespective of the adsorption sites, the adsorption free energy is found to be around 10 kcal/mol. The simulation results are compared with available experimental data and other simulations to provide reliable comprehensive molecular view of the structure and energetics of aqueous ion at hydrated muscovite surface.

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EFFECT OF THE ISOMORPHIC SUBSTITUTION DISORDER ON THE INTERFACIAL WATER STRUCTURE AT ILLITE SURFACES: MOLECULAR DYNAMICS SIMULATION STUDY

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The investigation of mineral-water interfaces plays a crucial role in the study of various environmental and geochemical problems. The prime reason for exploring the mineral-water interactions lies in the fact that it determines various phenomena ranging from ion transport, weathering, swelling, and so on. It is important to highlight that the mineral-water interactions are controlled by various factors such as mineral substrate structure and composition, hydration structure of aqueous metal ions and surface charge distribution. At the same time, the near surface structure and dynamics of aqueous species strongly depends upon these factors which are not always possible to probe experimentally. In addition, the results of such experiments are often difficult to quantitatively interpret without having a reliable molecular scale picture of the underlying physico-chemical processes. Meanwhile, molecular computer simulations can be highly efficient in providing these invaluable atomistic details in the investigation of interfacial systems.

Classical molecular dynamics (MD) computer simulations using CLAYFF force field were performed for a series of hydrated monovalent cations at two different models of muscovite surfaces. In the first model the isomorphic Si/Al substitutions were disordered. The larger surface area of the disordered model allowed for a more realistic representation of the layer charge distributions in muscovite than in earlier studies of this interface. Near surface structure was quantitatively analyzed in terms of atomic density profiles, surface atomic distribution and the topology of hydrogen bonding network. The local structural disorder of the substrate charge distribution is clearly responsible for the significant redistribution of water molecules at the interfacial region. The dynamics of aqueous species at the interfacial region were examined by diffusion coefficients obtained from mean square displacement of water oxygen atoms. Furthermore, the hydrogen bond dynamics for the aqueous species were calculated with the help of autocorrelation functions of H2O reorientational motions. The simulation results are compared with available experimental data and other simulations to provide reliable comprehensive molecular view of the structure and energetics of aqueous ion at hydrated muscovite surface.

A pictorial representation of the disorder isomorphic Si/Al substitution at the basal surface of muscovite mica is illustrated in the figure. Color codes: red—O, pink—Al, yellow—Si, white—H, cyan—metal ions (K+, Li+, Rb+, NH4+, H3O+). For the sake of simplicity, only one tetrahedral surface is shown in the figure.
The unique shape and selectivity properties of zeolites have been extensively used as molecular sieves in various technological studies ranging from biochemical to nuclear and energy storage industries. The interaction between the guest molecules and the substrate makes it a perspective tool to be used in purification process in biomedical applications like hemodialysis due to uremia syndrome. It is characterized by the inability of the human renal system to purify blood from metabolic waste. Urea being a nitrogen bound toxin is efficiently removed during conventional dialysis method which is not effective for the removal of toxic substances like paracresol (p-cresol) and creatinine. Many phenolic compounds accumulate in uremia and there has been longstanding interest in separating them during the process of hemodialysis. Recent experimental studies clearly report an enhanced p-cresol removal using porous materials like zeolites. In particular MFI and Faujasite zeolites seem to exhibit better performance than conventional polymeric materials. However, the fundamental interactions on molecular scale level are not well understood. Meanwhile, molecular computer simulations have become one of the most important tools in the study of such adsorption process and corresponding energetics by providing invaluable microscopic information on the underlying physico-chemical process.

Monte Carlo (MC) computer simulations were performed for the adsorption of p-cresol in MFI, NaX and NaY faujasite zeolites. Grand canonical monte carlo (GCMC) simulations using configurational biased algorithm were used throughout the adsorption of p-cresol and in coadsorption of water molecules while the energetics data were obtained from Canonical NVT simulations. The coadsorption of water molecules was studied with and without the presence of p-cresol in the substrate in order to understand the influence of the toxin on aqueous environments during the adsorption process. Our simulation results clearly indicate that there are four p-cresol molecules adsorbed per unit cell of MFI whereas ~35 in the case of NaX and NaY faujasite. The angular distributions of the p-cresol molecule were studied in detail to depict the preferred orientation of the p-cresol molecules at their adsorption sites.

The most important results obtained from these simulations are as follows. The comparison of the adsorption isotherm of water in zeolite with that of water in presence of toxin evidences a cooperation phenomena: p-cresol seems to facilitate the penetration of water into zeolite during coadsorption process. All the results were compared with available experimental data to provide reliable comprehensive molecular view of the adsorption process and energetics at ambient conditions.
EVALUATING THE ROLE OF ZETA POTENTIAL IN A NATURAL ANTIBACTERIAL CLAY FROM THE COLOMBIAN AMAZON

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The emergence of antibiotic-resistant bacteria and increasing accumulations of antibiotics in reclaimed water, drive the quest for new natural antimicrobials. We are studying the antibacterial mechanism(s) of clays that have shown an ability to destroy bacteria or significantly inhibit their growth. One possible mode of action is from soluble transition metal species, particularly reduced Fe, capable of generating deleterious oxygen radicals (ROS). Yet another possibility is related to membrane damage as a consequence of physical or electrostatic interaction between clay and bacteria. Both mechanisms could combine and reinforce each other to produce cell death.

This study addresses a particular antibacterial clay from the NW Amazon basin, South America (AMZ clay). The clay mineral fraction (<2µm) is composed of disordered kaolinite (28.9%), halloysite (17.8%) illite (12%) and smectite (16.7%).

Mean particle size is 1.6µm, the total area is 278.82 and specific surface area is 51.23 m²/g. The pH of a suspension (200mg/ml) is 4.1 and its Eh is 361mv after 24h of equilibration. The ionic strength of the water in equilibrium with the clay after 24 hrs is 0.5M. These conditions, affect the element solubility, speciation, and influence the interactions between clay and bacteria.

Standard microbiological methods were used to assess the viability of two model bacteria (Escherichia coli and Bacillus subtilis) after incubation with clay at 37°C for 24 hrs. The chemical composition of bacteria was analyzed before and after clay treatment, using Inductively Couple Plasma Mass Spectroscopy. The cells were separated from the clay using Nycodenz gradient media achieving partial separation. Results showed elevated concentrations of Al, Fe and Cu on treated cells relative to control. However, unlike other antibacterial clays, the solution chemistry of its aqueous leachate does not affect cell viability. It appears that physical or electrostatic interactions between cells and clay surfaces are required for the AMZ bactericide.

Experiments showed that exchanging AMZ clay with KCl caused loss of antibacterial property. Among the exchangeable ions that are potentially toxic are Al³⁺, Cu²⁺, Zn²⁺, Ba²⁺ and Co²⁺. Besides exchangeable cations, the cation exchange neutralizes the surface charge thus modifying the interaction between the charged cell surface and the clay. Therefore, we evaluated the clay and bacteria zeta potential (ζ) as an index for possible electrostatic interaction. Results show that at pH 4, the ζ of clays is -14mV while it is ~ -33 for bacteria. The high ionic strength (0.5M) plus the Al³⁺ and Ca²⁺ present in the electrolyte, affect the thickness of the hydration shells, which allow the clay particles and bacteria to come into closer contact. The proximity increases the probability of attractive forces, thus binding clays and cells.

In summary, results indicate that a process other than simple chemical transfer from clay to bacteria is operating. The electrostatic attraction and physical proximity may enhance the toxic action of metals and interfere with the membrane properties or processes.
Kerolite is present in microbiobes formed in the photic zone of basaltic caves in Kauai. The kerolite develops early in the mineralization of the microbial mats, commonly with aragonite ± calcite. Precipitation of hydromagnesite, magnesite, hydromagnesite, monohydnocalsite, dolomite and gypsum follows as the microbial deposits become completely calcified. Nucleation of the kerolite has been attributed to development and subsequent dehydration of Mg- and Si-rich gels on extracellular polymeric substances (EPS) produced by cyanobacteria in the mats (Léveillé et al., 2007). Kerolite is typically the only inorganic phase found in actively growing microbial mats.

The kerolite contains up to 4% occluded carbon, likely remnants of polysaccharides. It has an average carbon isotopic composition of –28.4 ‰, a few permill lower than the average measured for the microbial mats. Most of the occluded carbon is released from 250 to 1000°C upon heating under vacuum; this fraction ranges in isotopic composition from –35 to –26 ‰. Smaller quantities released from 90 to 250°C range to higher carbon isotopic compositions (–29 to –14 ‰). The small amounts of carbon released from 25 to 90°C have a very wide scatter in isotopic composition, ranging from –29 to +14 ‰.

The isotopic compositions of the small quantities of hydrogen released from the kerolite at 25-90°C (under vacuum) range from –127 to –64 ‰; yield measurements suggest that much of this hydrogen may originate from occluded organic matter. DTA-TG patterns suggest that most hydrogen is released at 250-1000°C. Some hydrogen is also lost at 90-250°C, overlapping the interval in which hydrogen from organic matter and possibly also residual interlayer water is released. Contributions from the interlayer water, however, are likely minimal. PXRD patterns for the kerolite show little to no expandability upon ethylene-glycol vapour solvation. The hydrogen isotopic composition at 90-250°C is slightly higher (avg. –78 ‰; –86 to –70 ‰) than at 250-1000°C (avg. –86 ‰; –99 to –70 ‰). Assuming equilibrium with cave water at the ambient cave temperature, the average hydrogen-isotope kerolite-water permill fractionation is –80 ‰ at 211°C.

The kerolite oxygen-isotope compositions show unexpectedly high variation, ranging from +16.3 to +23.5 ‰. This variation was not correlated with the range of pretreatment temperatures tested for removal of adsorbed water. Possible explanations for the wide range of oxygen isotopic compositions include: (i) contributions from organic oxygen, (ii) contributions from residual water retained between layers in this turbostratic structure, (iii) thin-film and related evaporative effects and exchange during transformation of the Mg- Si gels to poorly crystallized kerolite, and (iv) non-equilibrium isotopic effects. Nonetheless, assuming oxygen isotopic equilibrium with cave water, an average oxygen-isotope kerolite-water permill fractionation of +22.7 ‰ is obtained for 211°C. This value matches very closely with the permill fractionation calculated for the kerolite-water system (+22.7 to +23.0 ‰) using Savin and Lee bond-type empirical methods.

The microbiobly mediated formation of kerolite in these basaltic caves allows us to understand clay-water-organic interactions associated with basaltic rocks at low temperatures in extreme terrestrial (and extraterrestrial?) environments in ways that are otherwise not possible. It offers a special opportunity to investigate isotopic behavior in clay-water systems that are not so easily explored in short-term, bench-top experiments. Finally, it allows evaluation of the active versus passive roles played by microbial activity in catalyzing Mg-clay formation in such an unconventional environment.


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IN SITU STUDIES OF MONTMORILLONITE HYDRATION IN DRY TO WATER-SATURATED SUPERCRITICAL CO$_2$: IMPLICATIONS FOR CAPROCK INTEGRITY

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In geologic carbon sequestration, carbon dioxide is injected as a supercritical fluid into a geologic reservoir for long-term storage. Supercritical CO$_2$ (scCO$_2$) is buoyant and it will rise to meet the caprock barrier. The dominant fluid in contact with caprock minerals could become scCO$_2$. Caprock formations often contain high concentrations of clay minerals, including montmorillonite, illite, chlorite, kaolinite, and glauconite. Montmorillonites are of particular interest because they swell or shrink by the uptake or release of species in their interlayer. Clay expansion could lead to closure of caprock fractures, preventing leakage of CO$_2$ to the Earth’s surface. However, clay shrinkage could open fractures, compromising the caprock seal and allowing CO$_2$ to escape.

Here, we report results of in situ infrared (IR) spectroscopic, X-ray diffraction (XRD), and quartz crystal microbalance (QCM) experiments on sodium, calcium, and magnesium saturated Wyoming bentonites at 50°C and 90 bar. The goals of our studies are (1) to quantify concentrations of water and CO$_2$ partitioned into these clays, (2) to correlate interlayer spacing with water and CO$_2$ uptake, and (3) to obtain direct molecular-level information to help understand the reactions of water and CO$_2$ uptake by the clay. XRD provides the interlayer spacing as a function of the total water concentration. Transmission IR spectroscopy is used to measure water concentrations in the scCO$_2$ or incorporated into a clay. The combination of QCM and transmission IR data allows quantification of adsorbed CO$_2$ concentrations. Attenuated total reflection (ATR) IR spectroscopy is used to monitor water and CO$_2$ intercalation reactions at a molecular level. Polarized IR radiation with this ATR-IR technique gives geometric information about the CO$_2$ molecules residing in the interlayer.

We compare titration curves generated from the transmission IR spectroscopic and QCM measurements for each type of cation-saturated clay. The trends in the curves are correlated to interlayer spacing determined by XRD. We also compare ATR-IR spectra from the titrations of each clay type. These molecular level data demonstrate that the interlayer spacing is a complex function of partitioning of water and CO$_2$ between the clay and the supercritical fluid. Furthermore, polarization IR results show that there is at least one type of intercalated CO$_2$ molecule that is oriented perpendicular to the clay sheets.

The experimental research presented here provides fundamental knowledge that will reduce risks of the geologic carbon storage. Our results are helpful for constraining thermodynamic models and molecular dynamic simulations used to predict and explain volume changes in a high clay content caprock.
PRACTICAL APPLICATIONS FOR CLAY-DERIVED ZEOLITE N: AN AMMONIUM-SELECTIVE ION EXCHANGER FOR INDUSTRY USE

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Over the past ten years, scaled-up utilisation of a previously under-exploited zeolite, Zeolite N, has been demonstrated for selective ion exchange of ammonium and other ions in aqueous environments. As with many zeolite syntheses, the required source material should contain predictable levels of aluminium and silicon and, for full-scale industrial applications, kaolin and/or montmorillonite serve such a purpose. Field, pilot and commercial scale trials of kaolin derived Zeolite N have focused on applications in agriculture and water treatment as these sectors are primary producers or users of ammonium. The format for the material—as fine powders, granules or extrudates—depends on the specific application albeit each has been evaluated.

Zeolite N is a convenient, stable framework within which appropriate ions such as K+ and NH4+ are transferred from one medium to another based on chemical equilibria of the specific environment. The type zeolite, produced by either low temperature ambient or hydrothermal conditions, is potassic with the specific formula |K10(H2O)8Cl2| [Al12Si12O40]–EDI. Other compositional forms of Zeolite N, which allow for cation and anion substitution such as |KxNa1-x(H2O)8Cl2| [Al12Si12O40]–EDI. At production scale, bulk density of the powder is ~0.3 g/cm3, with average particle size ~2.5 μm, pH~10.8 (in 20% slurry) and average brightness L=94.9. Granules or beads for fixed bed reactors are prepared as 1.6mm–3.0mm size fraction with 9wt% to 15wt% sodium silicate binder. In general, the cation exchange capacity (CEC) of Zeolite N powder produced from kaolin is greater than 500meq/100g (or ~65g NH4+ per kg zeolite). In beads or granules, this capacity is reduced by the quantity of binder and in practice, results in effective loadings of between 45–55g NH4+ per kg zeolite.

Fertilisers based on ammonium can often be inefficiently utilised by horticultural crops or high-value applications (e.g. golf turf), particularly when grown on low quality or sandy soils. In some environments, the lost nitrogen in highly leached soils can be an environmental hazard or may constrain use of aquifers5. Glasshouse trials show that plants grown in sandy soils with moderate levels of Zeolite N powder reduced the loss of added ammonium by 90% compared with an unamended soil5. An added advantage of a Zeolite N amendment is that exchanged potassium is released into soil solution and is available to plants5.

Pilot plant and commercial use of Zeolite N is demonstrated for wastewater sidestreams in sewage treatment plants and for treatment of mature landfill leachate solutions. A range of ammonium ion concentrations from <100mg/L to >600mg/L have been reduced to defined breakthrough conditions by ion exchange using Zeolite N, often in the presence of competing cations such as Na, Ca, Mg, and Fe. These applications are in fixed bed reactors using beads or extrudates as described above and with pre-treatment to reduce total suspended solids to < 100mg/L. Generic sites for which Zeolite N has been used to reduce ammonium concentrations to target levels include: digestor sidestream and tertiary flows from wastewater treatment plants; mature landfill leachates and stormwater run-off.

Use of Zeolite N to treat anaerobic digester sidestreams resolves a significant operational problem by reducing overall nutrient load in the effluent. However, the dominant market for this type of product is more likely to be focused on streams with 50mg/L < [NH4+] < 250mg/L and little or no BOD. These waste streams are common in manufacturing plants, mature landfills and smaller sewage treatment plants. Regeneration of the media is simply effected via caustic or caustic + salt solutions and can result in beneficial re-use of the ammonium by-product. Ammonium exchange efficiency after many cycles of regeneration is retained with limited loss of loading capacity on subsequent cycles.
Other applications have been trialled with this robust material and include comparisons with natural zeolites and Zeolite A. In these latter cases, the selectivity for ammonium ion is compromised by a larger pore size that exchanges more readily with divalent ions. The effective pore size for Zeolite N is <0.3 nm compared with 0.41 nm for Zeolite A. For fixed bed reactors under similar conditions, Zeolite N reduces ammonium to a specific breakthrough value through ion exchange by factors of more than ten compared with natural zeolite and a factor of three times that of Zeolite A. In all applications, Zeolite N loading capacity for ammonium is significantly higher than natural zeolites.
INFRARED STUDY OF THE INTERACTION OF PYRIDINE WITH ACID-TREATED MONTMORILLONITE

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Infrared (IR) spectroscopy in the middle (MIR) and near (NIR) regions was used to gain a better insight onto the active groups at the surface of acid-treated montmorillonite using pyridine, the most employed probe molecule in IR studies. Na-saturated montmorillonite SAz-1 (Cheto, Arizona) was treated with 6M HCl at 80 ºC for 2, 4, and 8 hours. Acid treated samples are denoted as SAz-2h, SAz-4h and SAz-8h. Overnight dried samples were placed in desiccator and exposed to pyridine vapor for 48 h at 25 ºC. After that the spectra were measured in both IR regions to determine the presence of acid sites and to follow the interaction of pyridine with montmorillonite surface. To examine the strength of the pyridine bonding the samples with adsorbed pyridine were heated for 1 h at 110, 170, 230 ºC and consequently the spectra were collected.

Upon acid treatment the montmorillonite was gradually decomposed and protonated amorphous silica was created. The MIR spectroscopy confirmed that structure of SAz-1 montmorillonite was partly disturbed after 2 h treatment and only fragments of the layers were present in SAz-4h. The spectrum of SAz-8h showing the bands at 1096, 968, 880 and 466 cm⁻¹ assigned to vibrations of SiO groups arranged in three-dimensional framework indicated, that solid reaction product contained only amorphous silica. Creation of acid sites in partly decomposed samples confirmed the bands appearing after pyridine adsorption in the 1700–1400 cm⁻¹ range. They were related to the ring stretching vibrations of different pyridine species formed at montmorillonite surface. Only physically adsorbed (1573 cm⁻¹) and H-bonded (1593, 1441 cm⁻¹) pyridine was detected for acid-untreated montmorillonite and amorphous silica. In contrast, a diagnostic band at 1539 cm⁻¹ assigned to deformation vibration of N-H groups in pyridinium cation was observed for SAz-2h confirming the presence of strong Brønsted acid sites. Due to high polarizing power of H⁺ and Al⁺⁺ cations (extracted upon dissolution from SAz-1 octahedra) pyridine was able to accept proton from water molecules and to create pyridinium cation. Similar band but of evidently lower intensity detected for SAz-4h revealed that only small portion of montmorillonite layers persisted the 4 h treatment in HCl. The MIR spectra indicated complete release of H-bonded pyridine upon heating at 170 ºC but strongly bonded pyridinium cations were able to bear up heating even at 230 ºC.

Changes in chemical bonds upon dissolution of SAz-1 montmorillonite approved also NIR spectra showing the first overtone (2νOH) and combination (ν+δOH) modes of XH groups (X=O, C). Gradual decrease of the intensities of 2νOH (7057 cm⁻¹) and (ν+δOH) (1651 cm⁻¹) bands of structural OH groups reflected less octahedral atoms. A new band occurring near 7315 cm⁻¹ in the spectra of dissolved samples was assigned to νSiOH. The increase of its intensity with time of acid treatment confirmed the formation of a protonated silica phase. The NIR spectra of the samples after pyridine adsorption showed the first aromatic CH overtone and combination bands in the 6200-5800 cm⁻¹ and 4700-4000 cm⁻¹ regions, respectively. The complex shape of the 2νOH band resulted from the overpopulate contributions of the CH groups occurring at different positions in relation to the nitrogen. The profile of the Na-SAz-1 band was significantly changed for SAz-2h indicating a marked perturbation of CH vibrations after pyridinium cation was formed. The shape of the 2νOH band of SAz-4h and SAz-8h resembled to some extent the band of acid-untreated sample, however, the position was shifted to higher wavenumbers. All this features proved considerable variability in pyridine bonding onto montmorillonite with different degree of decomposition. The adsorption of pyridine on acid-treated samples modified also the first OH overtone region. While the position of the 2νOH band remained nearly unchanged the 2νSiOH band at 7315 cm⁻¹ almost completely disappeared in all acid treated samples. Silanol groups as a weak acid sites formed hydrogen bonds with pyridine-nitrogen. As a result, the SiOH overtone was shifted to lower wavenumbers and contributed to broad complex band near 7100 cm⁻¹. Upon heating the pyridine molecules are progressively released and the SiOH band at 7057 cm⁻¹ almost completely disappeared in all acid treated samples. Silanol groups as a weak acid sites formed hydrogen bonds with pyridine-nitrogen. As a result, the SiOH overtone was shifted to lower wavenumbers and contributed to broad complex band near 7100 cm⁻¹. Upon heating the pyridine molecules are progressively released and the SiOH band at 7057 cm⁻¹ almost completely disappeared in all acid treated samples. Silanol groups as a weak acid sites formed hydrogen bonds with pyridine-nitrogen.
overtone re-appeared near 7315 cm$^{-1}$. Its intensity increased with temperature, i.e. with decreasing amount of adsorbed pyridine. Gradual vaporization of pyridine confirmed also decreasing intensities of the CH overtone and combination bands. Similarly as in the MIR region, almost complete disappearance of pyridine band was observed for Na-SAz-1 and amorphous silica heated above 170 ºC, while well-resolved 2nCH and (n+d)CH bands were still present in the spectra of 2 and 4 hours treated samples. The obtained results showed that NIR spectroscopy can also provide valuable information on pyridine bonding with montmorillonite surface.
Kaolin is an important and widely used industrial mineral. It plays an integral part in our everyday lives since it is ubiquitous in many products we use daily such as printing and packaging paper products including magazines and catalogs as well as food and beverage packaging, paints, plastics, ceramics, rubber, ink, high strength concrete, catalysts, pharmaceuticals, proppants for extracting natural gas and oil, etc. Approximately 23.6 million metric tons of kaolin were used worldwide for various applications in 2010. The paper industry is by far the largest consumer of kaolin (Figure 1) although the overall demand for paper is progressively decreasing due to the internet and the growth of other electronic media.

For most modern industrial applications, kaolin as mined and in its crude state is practically unusable. It has to be refined using a series of processing technologies before it can be used. These technologies are selected to beneficiate the crude kaolin as well as improve and develop new products to match specific performance attributes and applications.

There is an ever-increasing demand on the kaolin industry for improved product quality and productivity, which will further intensify in the future. The demand for kaolin from the paper and paperboard industries has been steadily decreasing due to decline in production and consumption of paper combined with an intense competition from other mineral substitutes such as ground calcium carbonate and precipitated calcium carbonate. This has heightened the pressure on kaolin companies to develop innovative and tailored kaolin product solutions with improved performance, cost effectiveness, and increased diversity in their product portfolios.

Properties such as brightness/whiteness, particle size distributions, surface area, morphology, surface charge, surface chemistry, chemical composition, crystal structure, abrasivity/hardness, refractivity index, relative inertness, thermal and electrical properties, rheological properties, etc., make kaolin a unique material suitable for many diverse applications. Many of these properties can be tailored through various processing and product engineering technologies to improve desired attributes. Examples will be presented to demonstrate how kaolin can be modified to develop high-performance products for paper and paperboard coating and filling, high strength concrete, paper denking and recycling, and polymer-composite applications.

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CLAY MINERALOGY RESEARCH FOR HYDROCARBON EXPLORATION: WHAT TOOLS DO WE NEED?
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In the last 50 years research on clay minerals applied to hydrocarbon exploration resulted in a number of potential applications which have been attempted with varying success. This presentation is an attempt to briefly review how clay mineralogy has been applied to solve problems facing HC exploration and to highlight current challenges where clay research may yield useful information to reduce risk in HC exploration.

Textural relationships between authigenic and detrital minerals are a powerful tool to determine the relative order of formation of mineral cements and shed light on the relative timing of fluid changes in a sedimentary rock. Geochronometry based on the absolute age dating of authigenic minerals is challenging for a number of reasons. We are often constrained to use very small samples and these are prone to contamination by older material. The use of clay minerals as a geo-thermometer has been attempted using different approaches on different types of data. The techniques give non unique solutions or only locally calibrated and qualitative relationships with temperature. Stable isotope (O & H) geochemistry has provided valuable information on the conditions of formation of diagenetic clays in reservoirs, thereby helping constrain diagenetic fluid sources. One common impediment to quantifying the paragenesis of clay minerals in sedimentary rocks has been the difficulty in characterization of the samples.

Sample preparation and analytical procedures and equipment have improved and now we routinely provide mineralogy data on shales to constrain quantitative log interpretation. XRD allows us to characterize clay sized particles but natural samples are most commonly mixtures including artifacts from sample processing. The decomposition of XRD patterns is a method to more accurately characterize the main types of closely related phases in complex samples but combining analytical data (XRD, XRF, bulk density, etc.) and modeling techniques is even further improving our understanding. A major advance would be to develop techniques of isotopic (dating and stable isotopes) characterization of clays at the thin section scale where textural relationships between analyzed points is known. Shale petrophysics (log response, acoustic response and poro-perm/fracture pressure gradient) is an important topic which impacts seismic interpretation and basin models. A problem is the nature of the samples we analyze. In situ, deeply buried clay-rich sedimentary rocks from HC bearing basins are still lacking. Well cuttings are the most commonly available types of samples but they are poor representatives of the original sediment, particularly in recent wells where aggressive drill bits and stable mud emulsions destroy samples.

Low salinity pore water in a number of sedimentary basins comes from clay transformations. Predictive models are needed. When does dehydration dominate and when does transformation dominate the driving mechanism for release of water from hydrated clays? The impact of water from clay transformations on overpressure development needs to be better understood.

Unconventional HC resource plays: gas shales, oil shale and shale oil has renewed interest and added new questions in applying clay characterization to HC exploration. Understanding the thermal maturity of organic shales, predicting HC fluid type and petrophysical properties (porosity and permeability) are questions common to both conventional and non-conventional settings. New questions include: distribution of different fluids (liquid and gas HC and water), mechanical properties / link between mineralogy and fracability, OM preservation, OM distribution in mature source rocks.
The remediation of sites contaminated with heavy metals is of environmental importance. Among others clay mineral-based sorbents, raw and modified zeolites, and activated carbons are used to immobilize or reduce the content of toxic metals in soils and waters. Although kaolin group minerals do not have high specific surface area, their ability to efficiently remove carcinogenic chromate was shown earlier (Matusik & Bajda, 2013). The goal of the research was to obtain grafted derivatives of halloysite which are stable in aqueous solutions and test their affinity to sorb selected heavy metals. For the experiments a halloysite sample (H) from Polish Dunino deposit was selected. The modification procedure consisted of 2 steps. Firstly, the mineral was intercalated with dimethyl sulphoxide. Secondly, the formed intercalate was reacted with diethanolamine (DEA) or triethanolamine (TEA) at 180°C for 24 h under argon flow (Letaief & Detellier, 2008). The obtained products HDEA and HTEA, respectively were washed with isopropanol and water, and dried at 65°C for 24 h. The materials were examined by XRD, IR, and CHNS elemental analysis. The equilibrium sorption experiments were conducted at 22°C for the concentration range of 0.005-5.0 mM/L of Pb(ii), Cd(ii), Zn(ii), or Cu(ii) introduced as nitrates. The sorbent/solution ratio was set to 20 g/L and the applied pH was in the 2.0-6.5 range. For the kinetic experiments the suspension samples were collected after 0.5, 1.0, 1.5, 2, 3, 4, 5, 6, 8, 10, 15, and 20 min of the reaction. The filtered samples were analyzed for heavy metals using AAS method and colorimetric azo dye-based method was used for nitrate determination. The XRD patterns confirmed the formation of HDEA and HTEA with d001 values equal to 10.3 Å and 10.8 Å, respectively. The presence of interlayer grafted aminoalcohol molecules was reflected in changes of bands in the OH stretching region (3700-3600 cm⁻¹) as well as the appearance of bands in the C-H stretching region (3000-2800 cm⁻¹) in the IR spectra. Assuming that the nitrogen lone electron pair of grafted aminoalcohol is the sole sorption center which attracts the cations the sorption capacity of the materials was calculated from CHNS elemental analysis. It was equal to 248.4±23.0 mM/kg (HDEA) and 330.2±35.6 mM/kg (HTEA), respectively. The affinity to sorb heavy metals increased significantly in the case of modified halloysite as compared to raw halloysite (Table 1). The sorption on raw halloysite is exclusively possible due to the presence of deprotonated alumino and silanol groups on the particles edge. The sorption capacity observed for the H sample for the examined cations followed the trend: Pb(ii) < Cu(ii) < Cd(ii) < Zn(ii). The increase of sorption for the HDEA and HTEA samples was connected with the accessibility of the interlayer space for the cations in which they were attracted by nitrogen lone electron pair. The most significant increase of sorption capacity was noticed for Cd(ii) and Zn(ii). Apart from the sorption experiments with Cu(ii) the metals were sorbed in greater amount on HDEA sample in contrast to HTEA sample. This may be attributed to a hampered access of metals to TEA nitrogen due to steric hindrance effect. A rapid increase of the initial pH was noticed in the experiments with HDEA and HTEA materials due to protonation of nitrogen lone electron pair and this undoubtedly lowered the overall sorption capacity. The experiments carried out at different pH
values revealed that the heavy metals sorption increased along with increasing pH as the concentration of competitive protons decreased. In turn, the opposite trend was observed for the nitrate ions which were introduced to starting solution. The N(V) sorption was the highest at low pH where the lone electron pair was protonated and thus capable to attract anions. With the pH increase their sorption was lowered. The sorption was best described using Langmuir equation as compared to Freundlich and Dubinin-Radushkevich models. The kinetic experiments showed that the sorption on raw halloysite took place almost instantly with the equilibrium achieved after ~1 minute from the start of reaction. On the other hand, for the grafted HDEA and HTEA materials the sorption increased gradually and the equilibrium was reached after ~6 minutes. This was due to slower diffusion of sorbate into the interlayer space. The kinetics followed the pseudo-second order model in the whole time range. The experimental data fit the pseudo-first order equation only in the first few minutes of the reaction. The applied Weber-Morris plot allowed to distinguish two steps of the reaction connected with external mass transfer and intra-particle diffusion.
CHROMATE AND ARSENATE REMOVAL BY KAOLINITE INTERCALATED WITH AMMONIUM SALTS

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Chromium in the hexavalent and arsenic in the pentavalent ionic forms are toxic and highly mobile in aqueous environment. Moreover, the Cr(VI) has carcinogenic properties which make it in particular hazardous to humans. The use of zeolites modified with ammonium salts was proved to be effective for the removal of the mentioned anions. Recently, the synthesis of kaolinite intercalates with selected ammonium salts trapped in the interlayer space was reported (Kuroda et al., 2011). In connection to this the objective of the study was to investigate the capability of the obtained intercalates to immobilize Cr(VI) and As(V) ions.

A well ordered kaolinite sample from Polish Maria III deposit was selected for the experiments. The Hinchley index of the mineral was calculated to 1.31. The intercalation procedure consisted of 3 experimental steps. Firstly, the mineral was pre-intercalated with dimethyl sulphoxide. Secondly, the formed intercalate was washed with methanol at room temperature which led to formation of a methoxy-kaolinite (KM) (Matusik et al., 2012). Finally the KM sample was mixed with 1 M ammonium salt/methanol solution for 24 h at room temperature. For the intercalation reactions 4 different ammonium salts were chosen: benzytrimethylammonium chloride (B1), tetramethylammonium chloride (TMA), and benzylidimethylhexadecylammonium chloride (B5). The obtained products MB1, MTMA, and MBS, respectively were centrifuged. The MB1 and MTMA samples were washed with isopropanol to remove the excess of salts which crystallized on the mineral surface. Washing was not possible in the case of MBS as the intercalate could be destroyed. Afterwards the materials were dried at 65°C for 24 h and characterized by XRD, IR, and CHNS elemental analysis. The sorption experiments were performed at room temperature for the Cr(VI) and As(V) concentration range of 0.02-50.0 mM/L. The sorbent/solution ratio was set to 20 g/L and the applied pH was in the 3-11 range. For the kinetic experiments the suspension samples were collected after 0.5, 1.0, 1.5, 2, 4, 6, 8, 10, 15, and 20 minutes of the reaction. The filtered samples were analyzed for Cr(VI) using 1,5-diphenylcarbazide method and for As(V) using AAS method with hydride generation.

The XRD patterns of MB1 and MTMA revealed the peaks with d001 equal to 14.4 Å and 12.6 Å, respectively. The observed interlayer spacing suggested monolayer arrangement of organic molecules. In contrast to MBS sample where the d001 value equal to ~35 Å indicated a tilted arrangement of organic chains in relation to the kaolinite 1:1 layer. The IR bands related to stretching (3100-2800 cm−1) and bending (1080-1300 cm−1) vibrations of ammonium salts were noticed in the IR spectra. The CHNS analyses allowed to calculate the chemical formulas of the intercalates which showed that the content of salts in the MB1 and MTMA samples was in agreement with theoretical maximum capacity of kaolinite. In turn, for the MBS an excess of salts was present as the sample could be not washed with isopropanol.

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Table 1. Parameters of Freundlich and Langmuir sorption isotherms for the reactions with Cr(VI) and As(V) at initial pH 5.

<table>
<thead>
<tr>
<th>Anion –&gt;</th>
<th>Cr(VI)</th>
<th>Langmuir</th>
<th>As(V)</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model –&gt;</strong></td>
<td>Freundlich</td>
<td>Langmuir</td>
<td>Freundlich</td>
<td>Langmuir</td>
</tr>
<tr>
<td>Sample</td>
<td>$1/n$</td>
<td>$K$ (mM/kg)</td>
<td>$R^2$</td>
<td>$q$ (mM/kg)</td>
</tr>
<tr>
<td>M</td>
<td>0.453</td>
<td>1.987</td>
<td>0.955</td>
<td>1.664</td>
</tr>
<tr>
<td>MB1</td>
<td>0.702</td>
<td>12.391</td>
<td>0.993</td>
<td>81.301</td>
</tr>
<tr>
<td>MTMA</td>
<td>0.672</td>
<td>4.306</td>
<td>0.963</td>
<td>22.371</td>
</tr>
<tr>
<td>MB5</td>
<td>–</td>
<td>–</td>
<td>0.500</td>
<td>–</td>
</tr>
</tbody>
</table>

With the exception of Cr(VI) sorption on the MB5 material the experimental sorption isotherms were best described using Langmuir equation in terms of modelled equilibrium sorption capacity ($q$) which should be close to experimental data (Table 1). In agreement with earlier studies the results showed that anions sorption capacity of raw kaolinite was very low and did not exceed 5 mM/kg. The sorption of Cr(VI) and As(V) on MB1 and MTMA materials was comparable and equal to ~80 mM/kg and ~23 mM/kg, respectively. In the case of As(V) sorption on the MB5 material the $q$ reached ~322 mM/kg, while for Cr(VI) the Langmuir and Freundlich equations did not model the data appropriately ($R^2 < 0.95$). The experimental data revealed a large Cr(VI) uptake equal to ~980 mM/kg. This was due to rapid precipitation of yellow color organic chromate as a result of B5 salt reaction with Cr(VI) ions as attested by the IR spectroscopy. The formation of precipitate was not observed in the case of As(V). The increase of initial pH generally lowered the sorption capacity due to competition with hydroxide ions. The kinetic experiments revealed that the reactions were of pseudo-second order. The uptake of Cr(VI) in the reaction with MB5 material was very fast with equilibrium achieved just after 0.5 min, while gradual uptake was characteristic for the MB1 and MTMA materials. On the other hand in the experiments with As(V) only the reaction with MTMA proceeded gradually with equilibrium achieved after 10 min, while these with MB1 and MB5 took place instantly. The XRD and IR analyzes confirmed that the intercalates structure was destroyed during reactions in aqueous media.
Victor Drits is a true pioneer in clay and mineral science. Over his distinguished career he has specialized in physical methods, including spectroscopy, diffraction, and computing methods to characterize the real structure of a wide variety of minerals, including mixed-layered clays and disordered lamellar structures in general. This high precision work made it possible to reveal the evolution and transformation mechanisms of this family of compounds in geological environments.

In 1996 he was awarded Distinguished Member of The Clay Minerals Society. Among Professor Drits’s many achievements, he and Bob Reynolds independently were the first to calculate full XRD patterns for mixed-layered illite-smectite. In a long and productive collaboration with clay and mineral scientists around the world, many of the mysteries have been resolved, which contribute to better understanding of clay minerals. Many of Victor’s publications begin with the words, “New insights into…”. Victor has always taken the broadest and most rigorous and quantitative approach to structural problems based on modern methods of solid state physics as reflected in two of his eight books, Electron Diffraction and High-Resolution Microscopy of Mineral Structures, and X-Ray Diffraction by Disordered Lamellar Structures, published with Cyril Tchoubar. In addition to XRD, electron diffraction, and HRTEM, Victor is a master of selected area electron diffraction (SAED), oblique texture electron diffraction (OTED), Mössbauer, FTIR, XANES, EXAFS, SANS, thermal analysis, and other synchrotron methods used to characterize structure composition relationships in a wide range of natural materials.

Victor held a position as Head of the Laboratory of the Physical Methods for the Study of Rock-forming Minerals, Geological Institute of the Russian Academy of Sciences, Moscow from 1970 to 2005, and is currently a principle scientist at the same institute. Victor has been honored with an honorary degree from Orleans University, an Honorary Membership in the Mineralogical Society of Great Britain, and Ireland, and the Gold Medal of AIPEA. He continues to conduct high level research and mentor students and colleagues from many countries around the world. After so many years of productive work, he has not lost his enthusiasm for discovery and enjoyment of life.
ABSTRACTS

TRACKING CYCLIC STEAM INJECTION IN OIL SANDS USING OXYGEN AND HYDROGEN ISOTOPIC COMPOSITIONS OF CLAY MINERALS

Jennifer L. McKay and Fred J. Longstaffe

Because of its high viscosity and relatively deep burial (450-500 m), in-situ thermal recovery methods such as cyclic steam stimulation (CSS) are used for bitumen extraction from Clearwater Formation oil sands in Alberta, Canada. Injection of hot fluids during CSS alters the sands, causing loss of some minerals and precipitation of others. High temperatures and high water-rock ratios associated with CSS have the potential to change the isotopic composition of pre-existing phases even in the absence of mineralogical changes. We explore this possibility here for the Clearwater Formation reservoirs through an examination of pre- and post-steaming core samples obtained at ≤10 m (near-injector) and >10 m (distal-injector) from the location of the steam injection well. Clay minerals are ideal for this purpose given their susceptibility to oxygen and hydrogen isotopic exchange at high water-rock ratios and elevated temperatures.

Clearwater Formation reservoirs are unconsolidated, rock fragment-dominated (volcanic, chert), fine- or medium-grained (feldspathic) litharenites, which also contain lower quantities of quartz, feldspar, highly altered grains, and dolomite. Ilite-smectite and illite are the dominant detrital clay minerals. These disseminated clays are most abundant in the lower part of the reservoir, along with shale laminae containing diocahedral smectite and illite-smectite. Shale clays containing smectite and siderite are also present. Berthierine is the most abundant diagenetic clay mineral and likely crystallized from brackish to fresh water (Hornibrook and Longstaffe, 1996). Diagenetic smectite and chlorite-smectite are generally restricted to discrete intervals, and likely formed in a more marine environment (McKay and Longstaffe, 1997). Kaolinite is limited in abundance and typically restricted to sands near the base of the Clearwater Formation in the Cold Lake area. Calcite cements comprise abundant carbonate-cemented zones. Disseminated, pore-filling siderite and rare siderite nodules are also present.

In near-injector cores, CSS produced substantial mineralogical changes, including dissolution of volcanic glass and disseminated carbonates, and neof ormation of zeolites, pore-lining calcite and hydroxy-interlayered smectite (HIS). Berthierine was preserved and remains the most abundant clay in the post-steaming sandstone even after 18 cycles of steam injection. The oxygen and hydrogen isotopic compositions of berthierine from near-injector samples decreased systematically because of partial isotopic exchange with the injected fluid at ≤110 °C. The oxygen isotopic compositions of smectitic clays in near-injector cores also decreased because of isotopic exchange and/or formation of HIS. A systematic change in hydrogen isotopic compositions of near-injector smectitic clays was generally not observed. The highly variable isotopic composition of pre-steaming smectitic clays, together with the particular combination of fluid composition and temperature during CSS, appears to have resulted in post-steaming hydrogen isotopic compositions similar to pre-steaming compositions.

The hydroxy-interlayered smectite (HIS), which was a product of CSS in many near-injector cores and, less commonly, in distal-injector cores, appears to have formed by addition of interlayer material to pre-existing smectitic clays during the earlier stage of CSS when reservoir temperatures were relatively low (≤110°C). This may explain why HIS is less abundant in berthierine-rich portions of the reservoir. The grain-coating berthierine may also have isolated and insulated reactive rock fragments from injected fluid, thus restricting HIS formation.

In distal-injector cores, berthierine and smectitic clays were generally unaffected by oxygen or hydrogen isotopic exchange during CSS, thus indicating limited interaction with injected fluids. One exception involves a distal-injector core in which isotopic exchange was detected at the same depth as the injection zone. In this case, injected fluids were able to move horizontally further into the reservoir within the injection zone, probably along injection-related fractures. Whether or not hydrogen isotopic exchange occurred between clay minerals and bitumen in reservoir regions that were heated, but which had no direct contact with injected fluid, is difficult to assess.

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Two fuel spills at Australia’s Casey Station (66°17’ S 110°31’ E) in Antarctica, in 1999 and 2010, resulted in contaminant migration downstream through permafrost. Elevated hydrocarbon levels were detected in soil surrounding both sources. On-site remediation techniques were required to clean the soil within its natural environment and meet obligations to the Protocol on Environmental Protection to the Antarctic Treaty. An active treatment method was specifically tailored to the site and risks associated with Antarctic operations and environment. Soil was excavated in 2011 through 2013 and placed in biopile treatment cells with nutrient addition and aeration systems. The six biopiles were designed with a geosynthetic composite liner system using geosynthetic clay liners (GCLs), high density polyethylene (HDPE) geomembranes and geotextiles. Different combinations of GCL types are used in the biopiles and compared to investigate the ideal barrier design for Antarctic environments.

This is the first time geosynthetics have been used in field applications in Antarctica. Research is focused on the long-term performance of these geosynthetics to impede contaminant migration with exposure to the Antarctic’s cold and dry climatic conditions and freeze-thaw cycling. Sample extraction pipes were positioned in the barrier system to monitor for any outward contaminant migration. Results after the first season of biopile operation show no hydrocarbon migration below the GCL liner.

Sacrificial GCLs coupons were placed within the barrier system and samples were exhumed after one and two years in the field. These underwent material performance testing in the laboratory: hydraulic conductivity, water content, peel strength, swell index and fluid loss. Results from GCL coupons exhumed after one year in the field show that one of the GCL types is functioning well within the design criterion. Despite the arid environment and high permeability subsoil, the extracted samples of GCL have maintained moisture, maintained their hydraulic performance, and shown no significant decrease in their physical peel strength. Additional monitoring continues in order to show longer-term performance, of GCLs in the Antarctic environment.
The markets for sodium montmorillonite, commonly known as bentonite, are based on the intrinsic structural and chemical properties of this clay mineral. These properties include its laminar structure of nanometer scale. The montmorillonite crystallites also have negative charged defects in its octahedral and tetrahedral structural layers. These clay crystallites can be dispersed in water to approach individual sheets. Positively charged broken bonds on the edges of these sheets are attracted to the negative structural charges when a clay slurry is at rest, forming a card-like structure that can suspend solids and form gels.

Major commodity markets and value for bentonite in the USA have generally increased over the last two decades, with some decrease during the recent USA recession. New uses for bentonite are now dominate major markets. Other commodity markets increased or decreased as changes occurred in each industrial application. Major commodity markets include absorbents (predominantly pet litter), adhesives, animal feed, ceramics, civil engineering, drilling fluids, extenders and fillers, foundry sand binders, iron ore pelletizing, refractories, water proofing and sealing, and other minor uses.

Many markets are tied to the economy, while other markets are tied to the USA population. For example, clumping pet litter, one of the two largest bentonite markets of a million metric tons or more per annum, will not change significantly with economic recession or expansion because we are now an urban society. However, oil and gas drilling, the other major market of over one million tons per annum, decreased significantly during the last USA ands world economic recession, but has dramatically increased in recent years. Other major markets for iron ore pelletizing and foundry sand binding decreased significantly with the recent recession, but have recovered in recent years.
The Amargosa Valley at the southwestern edge of Nevada has a unique geological environment that contains soluble silica and is rich in soluble magnesium, while low in soluble aluminum. This environment produced sepiolite, a trioctahedral clay mineral, that has a lath structure extending in one direction to about 1 μm in length and constrained in the other directions to 12 by 18 Angstroms. As a trioctahedral clay mineral, sepiolite disperses in both fresh and saline water, giving unique application characteristics.

Sepiolite has an API specification for salt water drilling where it imparts non-Newtonian shear thinning and particle suspension. Other major commercial markets for sepiolite include: absorbents, adhesives, animal feed, carriers of pesticides and fertilizers, ceramics, extenders and fillers, and pet litter. These markets are tied to the USA economy and population, and will grow during recovery from the recent USA recession and the increasing demand for oil and gas on a world basis.
FROM EMPIRICAL METHODS TO MODELING, HOW TO MEASURE THE SEALING CAPACITY OF CAPROCKS

Edesio Miranda-Barbosa*
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The capacity of CO₂ storage in some aquifers is related to the quantity of CO₂ stored and also the residence time for the injected CO₂. This is due to the sedimentary origin of aquifers or due to the stratified layers of sediments that compose this aquifer, we will find a varying permeability in sandstones and lower permeability in shales.

To determine the maximum CO₂ column necessary to induce the capillary failure of the seal we can use empirical methods base on mineralogy and make a coupling with geochemical/modeling.

The caprocks of some reservoir/aquifer are constituted mainly by shales that can function as sealing against eventual leakage of CO₂. However, there are still many questions about the measurement of capacity of caprock to seal. To predict this sealing capacity Kuskhin (1997) suggested an equation in displacement pore throat diameters which in turn is related to its mineralogy, particularly about quartz content. This equation is resumed as:

\[ \text{displacement pore throat diameter (nm)} = 1.4 \frac{(\text{Ṣ quartz in matrix})}{\text{γ hydrocarbon and γ brine}} - 20.5 \]

But this is limited to non-smectitic and non-organic shales. So it's not applicable to many caprocks used as sealing for CCS proposals (average ≥ 2% of smectite). A correction or simplification of this problem was suggested by Lindberg (1997). He considered a pressure difference for CO₂ and water wet shale pore as in the following equation:

\[ Δp = 2 \frac{(\text{γ hydrocarbon and γ brine})}{r}, \]

where Δp = pressure difference in Mpa and γ = water wet shale pore in mN/m. The prediction of pressures of capillarity for Nordland shale (Sleipner field), show the trapping of CO₂ column for this formation varying from 11469, 1063 and 1188 m high. Other measurements of sealing capacity of caprock were done by Dewhurst et al. (2002) for Muderong Shale in the northern Carnarvon Basin, northwest shelf of Australia. They have used this equation:

\[ \text{Pc} = \left(\frac{\text{γ hydrocarbon and γ brine}}{\cos θ}\right), \]

where γ is interfacial tension and θ is the contact angle between fluid and solid. The nature smectitic of this shale (28% of smectite, it is the main clay mineral of this rock) impose a contact angle of 140° as described by Diamond (1970). If the shale was more illicic or kaolinitic the contact angle would have been 150°. Then for Muderong shale an adaptation of the last equation has been created. Pbh = \( \text{Pc} \times (\text{γ hydrocarbon and γ brine})/(\text{cos θ}) \), where Pbh is a pressure sub-surface brine-hydrocarbon and γ and θ are interfacial tension and contact angles for the rock-brine-hydrocarbon system. Updating the last equations and focaling on Nordland shale (Sleipner field) we have noted a diminution of the column height of CO₂ but not meaning an inefficacy of the sealing.

Geochemical modeling:

The modeling software used here is diaprase-gas (Bildsten, 1998). This is based on thermodynamic equilibrium constants and on kinetic description of precipitations and dissolutions but it's limited to open diagenetic systems, so we worked in closed system.

Other tests were made using a version of diaprase and adapted to open but simple diagenetic systems.

Unfortunately and until that time we had no formation water data from the Nordland Shale (caprock for Sleipner field), so we need to simulate our mineralogical data with water formation from Utsira Formation (CO₂ injection site). Therefore it was used data from Nordland Shale and formation water from Utsira Sand. The best results considering

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only smectite (like clay mineral) the system will be in equilibrium after 10,000 years. More complex mineralogy will obviously take more time for the system to reach the equilibrium.

Perspectives:
Nowadays and since it is very difficult to measure mainly clay porosity in the laboratory, we are proceeding molecular modeling of some clays to understand the hydrodynamics in nanopores, example on effect of pore size, velocity profile, slip length.

Effects of pressure, pore size, surface type on fluids in interparticle pores and then to accurate knowledge on clay behaviours and measure better their capacity to seal.
BENTONITE EROSION PROCESSES AND LONG TERM PERFORMANCE OF THE ENGINEERED BARRIER IN A NUCLAR WASTE REPOSITORY: EXPERIMENTAL STUDIES WITHIN THE EC-BELBAR PROJECT.

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Highly compacted bentonites are envisaged as engineered barrier for high level radioactive waste (HLRW) repositories: they provide low hydraulic permeability, which minimizes the water income to the waste, high sorption capacity for most cations and a stable environment where radionuclides (RN) can be transported only by diffusion. The integrity of the properties of the bentonite barrier is fundamental for the safety functions of these repositories.

The main mineral component in bentonites belongs to the smectite clay group. In contact with the water coming from the geological formation where repository is placed, smectite will swell and form a gel able to penetrate into open rock fissures, joints or other available pore space. If the chemical conditions ensure colloidal stability, the gel can be transformed into a stable sol; erosion processes of different origin may take place at the gel front and colloidal particles can be released.

To understand and quantify bentonite erosion processes, under different physico-chemical conditions, is important for establishing the functionality of the bentonite barrier at the long-term, which could be compromised if a significant clay loss occurs. Furthermore, if the eroded material is colloidal, these colloids might be a vehicle for RN transport of towards the geosphere.

Studies are still needed to point out under which conditions compacted bentonite is able to produce colloidal particles, free to move in groundwater. Additionally, colloid-RN and colloids-rock interactions, as well as the potential relevance of the clay colloids presence on RN transport must be thoroughly analyzed.

The possible effects of bentonite erosion on the long term performance of the engineered barrier and on radionuclide transport are being evaluated, both experimentally and theoretically, in a collaborative Project within the Seventh Framework Programme of the European Community (Euratom), the BELBar Project, which has fourteen partners from seven European Countries.

In this work, the main experimental results obtained so far in the BELBar Project will be summarized and discussed. Several potential physico-chemical factors which can contribute or hinder the bentonite erosion processes are being experimentally analyzed.

1) The characteristics of the bentonite clay: smectite content; presence of certain accessory minerals as calcite or gypsum; the nature of the cations present in the interlayer; the total charge and charge distribution between the tetrahedral and octahedral sheets; the compaction density;

2) The chemistry of the groundwater: ionic strength, pH, chemical composition (concentration of monovalent vs. divalent cations, ...). This point is highly related to the stability and mobility of colloids in groundwater;

3) Clay—groundwater interactions: dissolution processes and ionic exchange; kinetics of the interactions; effects of the solid to-liquid ratio; effects of hydrodynamic conditions;

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3) Clay—groundwater interactions: dissolution processes and ionic exchange; kinetics of the interactions; effects of the solid to-liquid ratio; effects of hydrodynamic conditions;
4) Groundwater velocity: the presence of a hydraulically active fracture at the bentonite surface may play a role in bentonite erosion and has to be accounted for. Erosion could be mechanically produced by drag forces, caused by the flow along the bentonite surface, exceeding the bond particle forces;

5) The characteristic of clay extrusion paths: porosity of the rock, fracture dimensions.

Furthermore considering that if clay colloids can be “generated” by erosion processes and they are stable under the groundwater chemical conditions, they could be RN carriers, the following topics must be addressed:

1) Analysis of the main mechanisms controlling colloid mobility processes for their appropriate description.

2) Understanding of RN/colloid interactions: the mobility of clay colloids will not necessarily enhance the mobility of strong sorbing radionuclides, if the sorption is reversible.

3) Understanding of colloid retention processes.

The joint analysis of laboratory studies (and in-situ data) is expected to provide realistic inputs for the models used in the performance assessment of HLRW repositories.
The acid-activated and pillared acid-activated catalysts were used as catalyst for alkylation of benzene with 1-decene and 1-dodecene in a batch-slurry reactor at different temperatures of 388, 403, and 488 K. Benzene to olefin molar ratios of 8.75, 12, and 15 with 1 wt% of catalyst were studied. The alkylation products were analyzed by GC.

It was found that acid-activation of clay prior to pillaring increased the meso-microporosity, total specific surface area, total pore volume (TPV), and surface acidity of the catalyst. Figure 1 shows N2 adsorption desorption isotherms of samples.

Table 1: BET specific surface area ($S_{BET}$), total pore volume (TPV), micropore volume (Vμ), TPD acidity and basal spacing ($d_{001}$) of the solids indicated

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m²/g)</th>
<th>TPV (cm³/g)</th>
<th>Acidity (meq NH₃/g)</th>
<th>$d_{001}$ (Å)</th>
<th>Vμ (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>60</td>
<td>0.20</td>
<td>0.05</td>
<td>12.3</td>
<td>nd</td>
</tr>
<tr>
<td>H-Clay</td>
<td>162</td>
<td>0.22</td>
<td>0.82</td>
<td>13.4</td>
<td>0.11</td>
</tr>
<tr>
<td>H-Al-PiLC</td>
<td>238</td>
<td>0.23</td>
<td>1.31</td>
<td>18.4</td>
<td>0.13</td>
</tr>
</tbody>
</table>

* Total pore volume at a relative pressure of 0.99.
* Obtained from XRD data.

It was concluded that under optimized conditions, conversion yields of 98% and 77% were respectively obtained for 1-decene and 1-dodecene. New catalysts were prepared by acid treatment and pillaring of natural bentonite. Pillared intercalated clays (PiLCs) prepared with inorganic polycations have high thermal stability, good rigidity, uniform micropores, and excellent acidity. Acid activation of montmorillonite prior to pillaring strongly influences the performance and activity of the clay and resulting new material with physicochemical properties intermediate between those of conventional pillared clays and acid activated clays. Specific surface area, pore volume and acidity of pillared acid-activated clay were enhanced compared to natural clay. More than 98% of conversion was achieved in the alkylation of benzene by 1-decene. Catalysts exhibited desirable selectivity towards linear alkylbenzene (LAB).
Our small piece of the huge amount of accumulating understanding of the world around us is the product of the interaction and leadership of a relatively small group of personalities. Chances are that these individuals never see themselves as guiding lights. None-the-less, we owe them huge debts of gratitude for our intellectual heritage and pushing the boundaries of our understanding of things in the nano-world. Looking behind us gives us the confidence that we will continue to solve the evolving mysteries of this world of clay and clay-like materials.
**MINERALOGICAL AND CHEMICAL SPECIATION OF ARSENIC–BEARING NANOPHASES IN ORIGINAL AND OXIDIZED MINE TAILINGS IN A LIMESTONE ENVIRONMENT**

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Metals such as Pd, Ag, Cu and Zn are commonly mined in Zimapán, Hidalgo state, Mexico, producing sometimes large heaps of tailings that are potentially an environmental hazard due to high concentrations of heavy metals. Near Zimapán, arsenic occurs naturally, but mining uncovers and concentrates As in areas where their tailings are left. After weathering of mine tailings, it is not uncommon to find acid mine drainage (AMD) being produced and accelerating the already present problems. A complete characterization of the complex, ongoing geochemical processes will give insight for the most feasible and practical remediation products and strategies. This research examines AMD at the molecular level and aims to uncover the mineralogical speciation and chemical phenomena with As and present minerals, regularly iron oxyhydroxides. The objectives of this study are to determine mineralogical and chemical constraints and patterns associated with As mineral interactions and their speciation during different weathering stages.

Previous experiments characterized As-containing nanoparticles formed during the oxidation of the acid mine tailings, whereas emphasis is on ferrihydrite, goethite, lepidocrocite, jarosite, and pyrite. Scanning electron microscopy has shown signs of As inhibiting mineral growth and crystal nucleation when added to synthetic iron oxides.

X-ray absorption near edge spectroscopy (XANES) and x-ray fluorescence mapping (XRF) was used to obtain elemental speciation, distribution, and quantification information on oxidized samples from Zimapán’s As-rich mine tailings. Bulk, sand, silt, and clay fractions were examined, in addition to synthetically produced jarosite, ferrihydrite, goethite, arsenopyrite, and schwertmannite for reference minerals.

X-ray diffraction and XANES experiments unanimously indicated that arsenic occurred in the form of arsenopyrite in the original tailing, but was oxidized to form As(V) in an intimate association with nanometer-sized iron oxides. Microbeam XANES suggested the presence As in the arsenopyrite form in the sand particles, which were due to the unoxidized raw tailing materials. The presence of two different oxidation stages is especially noticeable by the abundant difference of sulfide minerals, S, gypsum, iron oxides, and residual silicate minerals. After oxidation, several minerals such as jarosite and iron oxides contained As.

It was determined that the majority of the As in the samples persist as As(V). There is also evidence of the samples having both common forms of Arsenic (As(III) and As(V)) together. All methods confirmed an unsurprising abundance of iron oxides, although goethite is identified to be the main sorption mineral of As(V) in the samples. Arsenic has an intrinsic relationship and behavioral tendencies with iron (oxy)hydroxides, principally sorbent and desorption characteristics.
Antibacterial mineral deposits, which are effective in killing antibiotic resistant bacteria, have recently been identified. The mineralogical and geochemical variables in these deposits could lead to discovery of new antibacterial mechanisms. This study focuses on the main hydrothermal alteration zones identified in an antibacterial clay deposit near Crater Lake, Oregon. We hypothesize that smectite interlayers in the mixed-layered illite-smectite (I-S) serve as a reservoir for transition metals generated during the oxidation of iron sulfides. The I-S buffers the water added to hydrate the clays to low pH (< 4) ultimately producing metal and sulfate-rich solutions that generate reactive oxygen species effective in killing human pathogenic bacteria.

The antibacterial effectiveness of four clay samples and leachates (aqueous solutions equilibrated with the clays for 24 hours) from reduced (blue) and oxidized (red and white) zones from the deposit were tested against model pathogens (Escherichia Coli ATCC 25922 and Staphylococcus Epidermidis ATCC 14990). The geochemistry of the mineral samples and leachates was measured using quantitative X-ray diffraction (XRD), cation exchange capacity (CEC), inductively coupled plasma mass spectrometry (ICP-MS), ferrous/ferric iron assay, hydrogen peroxide (H$_2$O$_2$) assay, along with pH and Eh measurements.

XRD results reveal that mixed-layered illite-smectite (70-80% illite) is present in all the samples. The antibacterial susceptibility testing indicates that the reduced blue zones containing pyrite were the most bactericidal. However, the white leached zones containing no measurable pyrite were still antibacterial and released Fe$^{2+}$ indicating that smectite interlayer spaces may serve as a reservoir for ferrous iron. CEC values for the bulk mineral samples averaged 15 meq/100g. The red oxidized zones were not antibacterial. ICP-MS elemental analysis and Fe$^{2+}$/Fe$^{3+}$ assay of mineral leachates shows that samples containing mM levels of soluble Fe$^{2+}$, Fe$^{3+}$, Al$^{3+}$, and Ca$^{2+}$ and SO$_4^{2-}$ are bactericidal. The clay minerals and pyrite buffer aqueous solutions to pH 2.5—3.1 and Eh above 630mV, in the stability field for Fe$^{2+}$. The H$_2$O$_2$ assay revealed that the blue reduced samples containing pyrite are undergoing oxidation and generating H$_2$O$_2$. The ferrous and ferric iron assay revealed that all of the antibacterial samples contain Fe$^{2+}$, which in the presence of hydrogen peroxide forms hydroxyl radicals that are toxic to biomolecules. These minerals may be useful in treating chronic non-healing wounds infected with antibiotic resistant bacteria by buffering the pH and Eh to levels that promote wound healing while killing invading pathogens.
MOLECULAR DYNAMICS SIMULATIONS OF TURBOSTRATIC HYDRATED MONTMORILLONITE WITH AND WITHOUT INTERCALATED CARBON DIOXIDE

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In nature the structures of the expandable clay minerals can deviate from ideal layer-stacking and form turbostratic structures, where layers can be twisted by a certain degree relatively each other. Rotation of one layer relative to the adjacent layer creates an interlayer structure that is defined by the Moiré pattern formed by the ditrigonal rings in the sheets of basal oxygen atoms belonging to adjacent layers, which could in turn impact the distribution of interlayer cations, water, and CO2. Turbostratic montmorillonite systems, with the rotational angle varied from 0 to 12 degrees, were studied computationally using a flexible interatomic potential for CO2 combined with the Clayff force field. The energies, one and two-dimensional density distributions of the interlayer species (ions, water, and carbon dioxide), radial distribution functions, and the d-spacing as a function of the rotational angle were computed. The simulations show that the initial change from 0 to 30 is an endothermic process that is accompanied by a small (0.1 Å) expansion of the d-spacing. Subsequent rotation proceeds with small or no energy barriers and without sizable expansion of the interlayer distance. Increasing water content facilitates rotation by making the energy requirement lower for the initial shift. Rotation of clay layers induces structural rearrangement of the interlayer species. In particular, the 2D density distributions reveal that molecules and ions form concentric circles reminiscent of a Moiré pattern. At the same time the radial distribution functions remain almost unperturbed in response to rotation suggesting that internal distances between the intercalated species are preserved. Increase of the rotational angle and/or carbon dioxide concentration leads to adsorption of sodium and calcium ions at the clay surfaces causing multidirectional energy changes that also depend on the initial humidity level.

This technical effort was performed in support of the National Energy Technology Laboratory’s ongoing research in Subtask 4000.4.641.061.001.255 under the RES contract DE-FE0004000.
The dissolution rate of montmorillonite in the hyperalkaline condition is important parameter for estimating the performance assessment of radioactive waste disposal. Generally, the actual dissolution rate of montmorillonite in compacted bentonite are different from that determined through batch or flow-through experiments. However, the difference has not been clarified yet in detail. Bentonite/hyperalkaline-fluid interaction has also been investigated by reactive transport models. The experimental results with different conditions are therefore necessary for verifications and comparisons of the models. The modelling results have been verified with experimental observations. However, careful experimental methods are needed for the accurate prediction of the performance of barrier system. The conventional experimental methods on the verification of the model in bentonite/hyperalkaline-fluid interaction have several drawbacks, which is difficult to simulate the experimental results or predict the performance of barrier system. Therefore, the objective of this study is to develop a microstructural analysis method by x-ray CT for tracing the alteration process in bentonite/hyperalkaline-fluid as function of time.

In bentonite/hyperalkaline-fluid interactions, the secondary formed analcime was observed in x-ray CT images in the bentonite. The formation pattern of the secondary mineral with time can verify the one dimensional reactive transport model results. As a result, it can be inferred that the actual dissolution rate of montmorillonite in compacted bentonite is one order lower than that of the montmorillonite in powder bentonite. This is due to limiting the reactive surface area and departure from equilibrium. Therefore, the dissolution rate of compacted montmorillonite needs to be used for the prediction of the long-term performance of barrier system.
Arsenic contamination of groundwater aquifers results from both the oxidation of arsenic-containing sulfide minerals and the reduction of arsenic-bearing iron hydroxides. Both processes can occur in aquifers undergoing managed aquifer recharge (MAR). This study focuses on the oxidation of arsenopyrite due to recharge with highly treated wastewater, during which there is simultaneous arsenic release and oxidized iron layer formation. We studied the effects of anion identity (e.g., chloride vs. nitrate) and dissolved oxygen presence on arsenopyrite dissolution and secondary mineral phase precipitation.

We found that in the presence of chloride, iron hydroxides underwent faster phase transformation, resulting in hematite formation after seven days. Furthermore, differences in secondary mineral phase between model MAR systems were related to their aqueous arsenic mobility, indicating a dynamic relationship between arsenic mobilization from arsenopyrite and attenuation by oxidized iron precipitates. Results can be used to establish safer MAR operations and make recommendations for injection water pretreatment.
Iron-containing clay minerals represent a major source of redox equivalents in natural environments. Microbial and chemical reduction of structural Fe in clay minerals were shown to occur in significant amounts of Fe(ii) in the clay mineral structure, which in turn is capable of reducing organic compounds, metals as well as nutrients. Despite the importance of Fe-bearing clay minerals as potential source of renewable redox equivalents in subsurface environments and the ubiquitous presence of dissolved Fe(ii) in these environments, little is known about the heterogeneous reactions between aqueous Fe(ii) and structural Fe(iii) in clay minerals. Here we evaluate whether the new conceptual framework describing heterogeneous reactions between aqueous Fe(ii) and Fe(iii) oxides which has recently emerged is applicable to clay minerals. Fundamental processes contributing to this framework are electron transfer between aqueous Fe(ii) and structural Fe(iii), bulk electron conduction, and Fe(ii)-Fe(iii) atom exchange.

We recently showed that interfacial electron transfer between aqueous Fe(ii) and structural Fe(iii) occurs in several clay minerals (NAu-1, NAu-2) [2, 3]. Adsorption of aqueous Fe(ii) was a prerequisite for heterogeneous electron transfer to occur. We investigated the effect of solution pH on interfacial Fe(ii)-Fe(iii) electron transfer and were able to distinguish between electrons being transferred from Fe(ii) adsorbed to basal planes versus from Fe(ii) bound to edge OH groups. Isotope specific Mössbauer spectroscopy was applied to determine the extent of reduction of structural Fe in smectites after exposure to aqueous 56Fe(ii), which is invisible in Mössbauer spectra. In combination with a sequential extraction procedure which selectively targets Fe(ii) sorbed to basal planes and subsequently edge OH-group bound Fe(ii), we were able to distinguish the structural environments of Fe(ii) resulting from electron transfer via basal planes or through edge OH-groups.

Experiments with aqueous Fe(ii) enriched in 57Fe and depleted in 54Fe were carried out to determine the exchange of stable Fe isotopes between aqueous Fe(ii) and structural Fe(iii) in clay minerals. We observe rather striking results that up to 20-40% of structural Fe in clay minerals mixes with aqueous Fe(ii). Experiments with high aqueous 56Fe enrichment suggest no dependence of Fe atom exchange on the initial aqueous Fe enrichment. We found that after reaction with Fe(iii), 20-30% of clay mineral Fe was accessible to the sequential extraction procedure, suggesting a redox-driven mobilization of structural Fe in clay minerals. More extensive Fe atom exchange as well as structural Fe mobilization were observed at higher pH values, where also more extensive interfacial electron transfer occurred. Our observations of both interfacial electron transfer between sorbed Fe(ii) and structural Fe(iii) in clay minerals and significant mixing of Fe atoms between the aqueous phase and bulk structure require us to develop a new conceptual model to describe redox reactions involving Fe-bearing clay minerals.

Iron-containing clay minerals represent a major source of redox equivalents in natural environments. Microbial and chemical reduction of structural Fe in clay minerals were shown to occur in significant amounts of Fe(ii) in the clay mineral structure, which in turn is capable of reducing organic compounds, metals as well as nutrients. Despite the importance of Fe-bearing clay minerals as potential source of renewable redox equivalents in subsurface environments and the ubiquitous presence of dissolved Fe(ii) in these environments, little is known about the heterogeneous reactions between aqueous Fe(ii) and structural Fe(iii) in clay minerals. Here we evaluate whether the new conceptual framework describing heterogeneous reactions between aqueous Fe(ii) and Fe(iii) oxides which has recently emerged is applicable to clay minerals. Fundamental processes contributing to this framework are electron transfer between aqueous Fe(ii) and structural Fe(iii), bulk electron conduction, and Fe(ii)-Fe(iii) atom exchange.

We recently showed that interfacial electron transfer between aqueous Fe(ii) and structural Fe(iii) occurs in several clay minerals (NAu-1, NAu-2) [2, 3]. Adsorption of aqueous Fe(ii) was a prerequisite for heterogeneous electron transfer to occur. We investigated the effect of solution pH on interfacial Fe(ii)-Fe(iii) electron transfer and were able to distinguish between electrons being transferred from Fe(ii) adsorbed to basal planes versus from Fe(ii) bound to edge OH groups. Isotope specific Mössbauer spectroscopy was applied to determine the extent of reduction of structural Fe in smectites after exposure to aqueous 56Fe(ii), which is invisible in Mössbauer spectra. In combination with a sequential extraction procedure which selectively targets Fe(ii) sorbed to basal planes and subsequently edge OH-group bound Fe(ii), we were able to distinguish the structural environments of Fe(ii) resulting from electron transfer via basal planes or through edge OH-groups.

Experiments with aqueous Fe(ii) enriched in 57Fe and depleted in 54Fe were carried out to determine the exchange of stable Fe isotopes between aqueous Fe(ii) and structural Fe(iii) in clay minerals. We observe rather striking results that up to 20-40% of structural Fe in clay minerals mixes with aqueous Fe(ii). Experiments with low aqueous 56Fe enrichment suggest no dependence of Fe atom exchange on the initial aqueous Fe enrichment. We found that after reaction with Fe(iii), 20-30% of clay mineral Fe was accessible to the sequential extraction procedure, suggesting a redox-driven mobilization of structural Fe in clay minerals. More extensive Fe atom exchange as well as structural Fe mobilization were observed at higher pH values, where also more extensive interfacial electron transfer occurred. Our observations of both interfacial electron transfer between sorbed Fe(ii) and structural Fe(iii) in clay minerals and significant mixing of Fe atoms between the aqueous phase and bulk structure require us to develop a new conceptual model to describe redox reactions involving Fe-bearing clay minerals.
A comprehensive understanding of the fate of radioactive cesium (Cs) in soils and sediments has acquired new urgency in light of the accident at the Fukushima Daiichi Nuclear Power Plant in March 2011. The strong association of Cs with micaceous minerals, specifically the edge sites of these minerals, is well known. Yet an atomistic description of these sorption sites has remained elusive due to the inherent difficulties of isolating these sites via experiment. Moreover, the edge surfaces rarely occur as well-defined mineral faces and often are highly disordered. In part, this disorder is a manifestation of the low surface energy of the materials.

Atomistic simulations provide a means of investigating the 2:1 phyllosilicate edge that overcomes the difficulties of isolating the edges in experiments. The three components necessary for an atomistic simulation are a model that describes the initial positions of the atoms; an energy expression to describe the interactions between molecules; and an algorithm to sample the energy surface. Energy expressions define atomic interactions parametrically for a specific set of atoms under specific thermodynamic and model constraints. The application of these parameters to a different set of thermodynamic or model constraints requires that they be validated for this new application. The CLAYFF forcefield has been used extensively to model the bulk structures of hydroxide, oxyhydroxide, and aluminosilicate minerals. Despite success in modelling a range of bulk mineral structures for which the forcefield was developed, only recent atomistic simulations have validate pyrophyllite edge structures predicted by CLAYFF.

The disordered nature of the edge structure can be attributed, in part, to the chemistry of aluminium (Al). The predicted edge structures are sensitive to the choice of edge face, particle geometry, and pore size. In response to increasing local charge, the edge Al assume decreasing coordination environments (i.e. octahedral, square pyramidal, trigonal bipyramidal, and tetrahedral). This reduced Al coordination parallels the reduced coordination predicted by ab initio cluster calculations of Al dimers with bridging hydroxyls. Atomic simulation of Cs surface complexation at pH \( \gg K_a1 \) identify three strong adsorption sites at the edge face associated with the exposed vacancies in the tetrahedral and octahedral sheets. Coincident with the development of the Al trigonal bipyramid, an edge silica (Si) tetrahedron rotates 90 degrees. This inverted Si tetrahedron is reminiscent of the Edelman-Favejee model of 2:1 phyllosilicate structure. Thus our atomistic simulations with the CLAYFF forcefield predict 1) edge structures that are consistent with previous higher-level ab initio simulations and 2) the presence of three strong adsorption sites at the edge face.
Clay minerals used as natural and engineered barriers in geological nuclear waste repositories are able to considerably reduce the mobility of radionuclides in the environment. The radionuclide retention happens through a combination of various physical and chemical processes taking place at the clay-water interface, but their molecular mechanisms are still insufficiently understood.

To obtain detailed microscopic scale information on the structure and energetics of the adsorption of cesium (Cs+) and strontium (Sr2+) ions at the smectites clay surfaces we have performed a series of classical molecular dynamics (MD) computer simulations with hydrated Cs- and Sr- montmorillonites. Clay and ionic interatomic interactions were described using partial charges and van der Waals parameters taken from the CLAYFF force field.

The structures of both ions on the montmorillonite clay surface were probed in terms of atomic density distributions in the direction normal to the clay surfaces, pair-correlation functions, and coordination numbers. The 2-dimensional and 3-dimensional diffusion coefficients were calculated to probe the ionic mobility at the clay surface. The potential of mean force of Cs+ and Sr2+ ions adsorption on all the possible clay adsorption sites was determined to probe the energetic criteria governing the binding of these species onto the montmorillonite surface.

The atomic density distributions of the two investigated ions show a significant layering in the distribution of aqueous species at the interfacial region. However the different charges and sizes of the two ions, as well as their different affinity to water, lead to a strong binding of Cs+ ions with the clay surface whereas Sr2+ ions prefer to stay hydrated. Pair correlation functions and coordination numbers indicate that Cs+ and Sr2+ can adsorb either on ditrigonal or triangular sites located on the montmorillonite surface.

These findings are to be confirmed with the potential of mean force calculations that may show energetically favorable position for Cs+ and Sr2+ from the clay surface, as well as the energetically preferable adsorption site on the clay surface. Cs+ and Sr2+ mobility is considerably reduced by substrate adsorption, but the diffusion coefficients tend to get closer to bulk solution values when the ions are removed from the surface.
INVESTIGATION OF THE GENESIS OF AHİRÖZÜ KAOLIN DEPOSITS (ESKİŞEHIR, TURKEY) USING MINERALOGICAL, PETROGRAPHICAL AND GEOCHEMICAL ANALYSES

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Hydrothermally originated kaolin deposits, located in Ahırözü-Mihalıççık district, Eskişehir-Turkey, were developed within the granite and granite-serpentinite contact. The purpose of this study is to explore the genesis of kaolin deposits through mineralogical, petrographical and geochemical analyses.

There were some evidences acquired associated with the existence of mineralizations in the region during the field study. According to the field investigations, XRD analyses and thin-section analyses were performed in order to confirm these observations in association with the mineralization traces. Therefore, as a result of these analyses, locally distributed cubic and spherical crystals were determined as pyrite and magnetite minerals, respectively. To discover the origin of the kaolin deposits situated in the area, XRD, SEM-EDX, geochemical and microscopic studies were conducted by means of examining the mineralogical and petrographical properties of these deposits which also have an economical potential.

The presence of natarolinite was determined in the pink coloured rock samples by XRD and SEM-EDX analyses. These minerals were observed as rhombohedral shaped and dominantly distributed in the images. While studying the morphological features of clay minerals in the samples through SEM-EDX analyses, platy kaolinite aggregates and tubular halloysite minerals were identified as well.

In the scope of the study, XRD diagrams were generated by comprising analysis results for each rock sample to determine the type of clay minerals and the other mineral phases of the whole rocks. An overview was constituted related to the characteristic of rocks in the study area depending on the results obtained from these analyses. Furthermore, XRD results proved the presence of kaolin minerals in our samples with definite and characteristic peaks. Quartz and feldspar were observed as the dominated non-clay minerals in the samples. However, there were rock samples detected by using XRD and thin-section analyses mainly consisted of plagioclase crystals altered into kaolin minerals and dolomite. Considering the geochemical analyses, there were samples enriched by Ni (app. 300 ppm) implying a basic/ultrabasic source rock whereas the samples including high percentage of SiO2 (app. 60%) introducing the presence of acidic parent rock in the area. Moreover, the samples which were altered to clay minerals mostly were enriched with respect to Al2O3 and SiO2.

Consequently, the origin of kaolin deposits in the region was investigated in association with metallic mineral enrichments. According to the results, two types of parent rocks were identified in the study area where one is acidic and the other is basic depending on the presence of rock-forming minerals and abundance of elements acquired by geochemical analyses. Natarolinites defined by both XRD and SEM analyses were originated due to the reaction of sulphate rich hydrothermal solutions with clay minerals in the study area.
CLAY DERIVED MATERIALS FOR ENVIRONMENTAL MANAGEMENT
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The crave for growth of technology and increased development to improve the quality of life has created an imbalance in the environment by way of increased hazardous and toxic wastes generated by industries into the environment. This concern has directed researchers' effort towards developing effective treatment technologies and/or effective and environmentally friendly scavengers for these generated wastes. In recent years, a lot of work has been driven towards obtaining new adsorbents that may be used to remove organic anionic pollutants from wastewaters. Hydroxide (HT), a clay based material is a promising sorbent for undesirable inorganic and organic compounds. HTs, anionic clays with the general formula \([M^{2+} \cdot M^{3+}(OH)_{2}]^x[ A^n \cdot n] \cdot mH_2O\) can intercalate a variety of anions.

Recently, modification of HTs with organic anions has received considerable attention with applications in adsorption, catalysis, photochemistry and electrochemistry. We have successfully synthesised a series of MgAl and ZnAl hydroxide-like compounds (HTLcs) by co-precipitation method. All the compounds exhibited characteristic patterns of well crystallised layered structure of hydroxide confirmed by PXRD and FT-IR. The HTLcs have been modified (based on the memory effect property) by structural reconstruction of the calcined compounds by intercalating sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS) into their structure [Fig. 1(a)] with an expectation that these novel compounds will take up phenol and phenolic compounds from aqueous solution [Fig. 1(b)].

Fig.1: (a) Powder diffraction patterns of (top to bottom), Mg\textsubscript{2}Al\textsubscript{CO}_3HTlc, calcined Mg\textsubscript{2}Al\textsubscript{CO}_3-[500°C], Mg\textsubscript{2}Al\textsubscript{CO}_3-SDS HTlc and Mg\textsubscript{2}Al\textsubscript{CO}_3-SDBS HTLCs (b)Uptake of 2CP at the various pH by Mg\textsubscript{2}Al\textsubscript{CO}_3-HTLc modified with (SDS) \([2CP] = 0.078\text{mM/L} \) and \([\text{Mg}_2\text{AlCO}_3_{-SDS}] = 0.5\text{g/L}\) at ambient conditions.
Recent archeological investigations revealed the use of a novel clay-based hybrid composite in some ancient Chinese structures. This ancient material technology uses lime, clay, and biopolymer such as starch (from cooked sticky rice) as well as sand or gravel as non-reactive filler to prepare a hybrid clay-based bio-nano-composite. Samples of this material obtained from an intact ancient tomb are remarkably tough, strong, acid resistant, and reportedly blast resistant. Understanding its mechanical properties and the underlying physical and chemical mechanisms controlling the mechanical behavior can help revitalize this ancient material technology and motivate its reuse in modern constructions for sustainability.

In this paper, nano/micro microstructural characterization using scanning/transmission electron microscopy (SEM/TEM) was conducted to understand the morphology, texture and packing density of the individual mechanical phases in the composite.

SEM images reveal a highly heterogeneous microstructure consisting mainly of fully activated phase with a frozen-gel-like morphology, partially activated and unreacted clays, silt and sand inclusions (Figure 1). While fully activated phase transformed into globular mass, partially activated clay tend to retain tubular or platy structures. Closer examination of the partially activated or unreacted aggregate under higher magnification showed reaction along the edges as well on the surfaces. Therefore, it can be inferred that reactivity of aluminosilicate minerals was mostly influenced by particle size rather than mineralogical composition. It is, thus, highly likely that these cement mix were prepared by simply mixing non-pulverized clays, coarse aggregates, starch and lime using high water/cement (w/c) ratio for workability. High-resolution TEM images show a complex web-like network with dense nano-crystallites formed along the voids and within the matrix (Figure 2). It is, thus, highly likely that these cement mix were prepared by simply mixing non-pulverized clays, coarse aggregates, starch and lime using high water/cement (w/c) ratio for workability. High-resolution TEM images show a complex web-like network with dense nano-crystallites formed along the voids and within the matrix.

**Figure 1:** a) SEM image showing dense, fully activated cementitious binder b) frozen gel like morphology revealed in high resolution, c) partially activated clay aggregates coated with gel-type matrix
nano-crystallites formed along the voids and within the network, and the calcium-silicate-hydrate (C-S-H) phase consisting an inner dense nano-crystalline core extending outward forming less dense and fibrous phase (figure 2). The microstructure of C-S-H phase is similar to that reported for product obtained in ordinary Portland cement. The matrix also possesses micrometer to nanometer sized pores. Relics of the organic polymers (rice starch) were also observed. A dense, intercalated C-S-H and clay aggregates (figure 2c) suggests the active physical-chemical interaction between organic polymer, clay and/or C-S-H to produce hybrid nanocomposites.

Based on this study, we propose that slow and weak pozzolanic reaction between clay and lime produces cementitious binder consisting of C-S-H phase with an overall low packing density. Characteristic mechanical property of this hybrid composite is, therefore, attributed to binding mechanism of C-S-H phase. However, the role of nano-crystallites, particularly those formed within the voids, and intercalated composites in the binding mechanism cannot be underestimated. Detailed structural and chemical analysis of the binder phase is planned for future studies.
The exchangeable cation composition in one of the most laborious analyses in smectite characterization. This is usually carried by wet chemical methods with low degree of precision (reproducibility and repeatability). Although difficult, it is very important in defining the proper application of a bentonite. This is also a challenge in Brazil because most deposits in the country exhibit a wide range in the exchangeable cation composition. Until now, the main control parameter used in the exploration is the Swell index or Free Swell test procedure (Na⁺ favors swelling while Ca²⁺ and Mg²⁺ not).

In modified interlayer smectites, e.g. pillared smectites, it is difficult to characterize the nature and disposition of the pillars introduced in order to increase the micro- (and meso-) porosity. Meanwhile, one knows that the nature of interlayer species influence in the elementary layer size, in the tactoid size, and in the arrangement of tactoids, which define the porosity of the material as a whole.

In general, the porosity of a both natural and modified smectite is evaluated by N₂ adsorption-desorption at 77 K, BET SSA and BJH PV. On the other hand, Particle Size Distribution (PSD) analysis by light scattering has not been used so frequently as a complementary tool in such textural evaluation.

This work aims to present a preliminary proposal to evaluate the interlayer species of smectites based on the particle size distribution analysis using light scattering (green and red lasers) and the Mie theory. The equipment used was an Analysette 22 Micro Tec Plus (Fritsch) using the spherical particle model, the montmorillonite refractive index (n = 1.560) and water as the dispersant agent (n = 1.333). One hundred scans were carried out (shots per scan 2ⁿ=4, maximum time=7s) in the measured range of 0.08 to 2000 μm and beam obscuration between 13 and 18%. Ten Brazilian smectites have been used in this work, including a Mg-montmorillonite and two smectites from the Source Clays Repository of The Clay Minerals Society: SWy-2 (Na-montmorillonite) and SAz-1 (Ca-montmorillonite). All the samples were previous dehydrated for 2 h at 400 ºC.

The results show that for the particle-size analysis, the mean cumulative frequency distributions curves were completely different for each cationic type according to the following sequence: Na < Mg < Ca, while the Mg, Ca bentonites curves fall between the Mg and Ca curves (Fig. 1A).

For the Al-pillared smectites, distribution curves pointed to a greater similarity between the pillared Na- and Mg-smectites, and different from the Ca-smectite, showing the effect of the cationic type in the synthesis process (Fig. 1B). It also depicts the great importance of this technique in the textural evaluations of the porous materials obtained, besides the evaluation of the interlayer species characterization of the starting clayey materials.
METHODS FOR HANDLING AND STORING OXYGEN-SENSITIVE CLAY MATERIALS

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Reliable investigations of oxygen-sensitive clay samples require adequate methods and techniques for minimizing exposure of the sample to oxygen. Such samples include Fe-rich smectites in which the effects of reduction of structural Fe(III) to Fe(II) are being probed. The purpose of the present report is to describe the methods for special handling and storage of redox-sensitive smectites that are used in the authors’ laboratory, and to illustrate the effectiveness of such methods by appropriate measurements of changes in redox status of the structural Fe.

The key apparatus for this purpose are a controlled-atmosphere liquid exchanger (CALE), an inert-atmosphere reaction tube (IRT), and a glove box equipped with freeze-drying capability. The <2 µm size fraction of ferruginous smectite in a citrate-bicarbonate (C-B) buffered solution at 70 °C for 4 h. Lower levels of reduction were achieved by using shorter reduction times. Reduced samples were taken through a series of washing and freeze-drying steps using the IRT in combination with the CALE, with 0.005 M NaCl as the washing solution. The samples were then analyzed at the various stages along the way for Fe(II) and total Fe using the 1,10-phenanthroline/Uv-vis chemical method, for color by Uv-Vis spectroscopy, and for Fe(II):Fe(III) ratios and other properties using Mössbauer spectroscopy. Another set of reduced samples was taken through a parallel sequence without protection from the atmosphere, and results were compared with those which were protected.

The maximum extent of reduction observed gave a Fe(II):total Fe ratio of 0.91129 ± 0.0047. As reduction progressed, the color changed from yellow-brown in the unaltered sample through green-yellow in the partially reduced sample and then to dark grey in the totally reduced sample. The Fe(II) content decreased slightly with each stage of handling with the IRT and CALE apparatus. The final Fe(II):total Fe ratio after extensive washing and freeze drying was still greater than 0.8. Without protection, on the other hand, this value decreased to less than 0.4, demonstrating the necessity of protecting these redox-sensitive samples from the atmosphere. Once freeze-dried, reduced samples are less susceptible to reoxidation than samples left in suspension. These results illustrate the high efficiency and suitability of the CALE, IRT, and glove-box freeze drying apparatus for oxygen-sensitive clay redox systems.
Contamination of surface and ground water by nitrate, chromate, and many other redox-active anionic compounds creates health risks for various forms of life on Earth, but in situ methods for their remediation are difficult to find. Redox-active clay minerals have the potential to serve in this role, but their natural negative surface charge inhibits their reactivity with anionic species. Recent studies have shown, however, that the negative charge of the clay mineral layer can be reversed by the exchange of polymeric cations, which decreases the coulombic repulsion of clay mineral surfaces toward anionic pollutants. One recent study exploited this phenomenon using reduced ferruginous smectite exchanged with polydiallyldimethylammonium chloride (PDADMAC) to reverse its surface charge. The reversed-charge, redox-activated clay-polymer composite was then reacted with nitrate and succeeded to reductively remove nitrate from solution, demonstrating that such a clay–polymer composite could be a solution for nitrate pollution removal.

The purpose of the present study was to build on that earlier study by exploring the possibility of using naturally occurring polymeric cations as the means for reversing the surface charge from negative to positive. The fine fraction (<2µm) of Na-saturated and freeze-dried ferruginous smectite (SWa-1) and five different loadings (0, 0.075, 0.25, 0.5 and 1.0 g.L-1) of a linear polysaccharide, poly-(D) glucosamine (chitosan), a naturally occurring polymeric cation, were used. The resulting composites were reduced by sodium dithionite in an oxygen-free environment, then washed free of excess salts and reacted with sodium nitrate in an oxygen-free environment. The final supernatants obtained after reaction with nitrate were analyzed by accelerated diffusion methods to determine NH4+-N, NO3-–N, and (NO3− + NO2−)-N. The corresponding extent of reoxidation of structural Fe(ii) to Fe(iii) as a result of nitrate reduction was also measured, using the 1,10-phenanthroline/Uv-light method (Komadel and Stucki, 1988).

In all except the lowest loading of chitosan, the surface charge was reversed from negative to positive. Results further revealed a substantial loss of NO3− from solution, accompanied by an increase in NO2− content. Structural Fe(ii) was also reoxidized to Fe(iii), confirming a redox interaction between the structural Fe in the clay mineral and the nitrate in solution. These findings are consistent with the hypothesis that polymeric organic cations in natural soils and sediments have the potential to reverse the surface charge of constituent clay minerals and thereby provide a means by which remediation of redox-active anionic contaminants can proceed via redox reactions with structural Fe(ii) in the clay minerals.

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SYNCHROTRON X-RAY DIFFRACTION

A REFINED STRUCTURE FOR HYDROHEMATITE BASED ON TIME-RESOLVED SYNCHROTRON X-RAY DIFFRACTION

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In 1936, Hüttig and Strotzer proposed the term “hydrohematite” to distinguish stoichiometric hematite [Fe2O3] from isostructural ferric oxide phases that incorporate high concentrations (up to 8 wt%) of H2O. Since that time, the existence of “hydrohematite” has been a source of contention. Several supporters have cited anomalies in the evolution of infrared spectra during the dehydration of goethite [FeOOH] to hematite to argue for the appearance of intermediate hydrous hematite-like phases (Wolska and Szajda 1985; Kustova et al. 1992; Burgina et al. 2000; Chernyshova et al. 2007). These researchers posit that OH- groups substitute in an ordered fashion for O in the hematite framework, and the requisite charge balance is achieved by iron vacancies. On the other hand, several researchers have countered that anomalies in infrared and X-ray diffraction data simply reflect a variety of defect structures, twins, and even particle morphologies for end-member hematite (Derie et al. 1976; Löffler and Mader 2006).

In the course of measuring the crystallization of hematite from aqueous Fe chloride solutions at 200 °C using time-resolved powder X-ray diffraction at the Advanced Photon Source, we observed evidence for intermediate hematite-like phases during the transition from akaganéite [Fe3O4] to hematite. In our experiments, diffraction peaks that should have been singlets for the A-3c space group of hematite were split, indicating a violation of the 3-fold rotational symmetry. We therefore refined the intermediate structure in the various subgroups of R-3c. As the fit using I2/a was statistically no worse than that in lower symmetry groups, we selected this space group for our final refinement. A monoclinic unit cell with parameters of a = 7.3951(10) Å, b = 5.0117(5) Å, c = 5.4417(7) Å, and β = 95.666(5)° provided a good fit and significant reduction in χ2 and Rw relative to S.G. R-3c. Moreover, our refinements revealed a gradual increase in Fe occupancy of the octahedral site from 0.72 to ~1.00 with increased reaction time, and we observed the coalescence of split to singlet peaks. We conclude that our experiments captured the precipitation of hydrohematite as an intermediate phase with monoclinic symmetry before its transformation to stoichiometric hematite.
My interest in silicate intercalation chemistry was stimulated through an initial collaboration with Professor Max Mortland who, in 1972, had just discovered an unusual electron transfer reaction between Cu²⁺-montmorillonite and benzene that afforded a new clay intercalation compound with a deep red color and an unusual infrared spectrum. In helping Max unravel some of the details of his reaction, I became fascinated by the possibility of changing the pathway of a chemical reaction by confining the reactants to intra-crystalline two-dimensional space with a vertical length scale only slightly greater than the kinetic diameter of the reactants themselves. This curiosity led my students and me to two decades of studies on "Chemistry Between the Sheets...", so to speak. These included investigations of hydrated metal ions embedded in discrete layers of intercalated water, pillared forms of smectites and related layered silicates, collaborative studies with Physics colleagues on the transverse rigidity of the layers, numerous catalytic studies, and other topics which will be briefly reviewed in describing the first half of my odyssey.

In the early 1990s, our investigations of surfactant—intercalated silicic acids led us to contribute to the development of new families of surfactant-templated mesoporous silicas and various other metal oxides. Owing to their very large surface areas, pore sizes, and pore volumes, silica mesophases are promising materials (even commercially proven materials in some cases) for a number of applications, such as chemical catalysis, selective adsorption, and polymer reinforcement, to name a few. A brief summary of our two decades of work on these latter materials and their applications will complete the overview of my forty-year venture into the field of silicate intercalation chemistry.

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WINNING THE 6TH REYNOLDS CUP—AN EDUCATED GUESS OR MORE?

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The qualitative and quantitative analysis of the mineralogical composition is one of the basic tools in geo- and material science. Most common is the application of different XRD quantification methods together with some complementary tools like FTIR spectroscopy and results of chemical analyses, either of bulk samples or with electron microprobe on single grains. The access to measurement devices and the availability of commercial and free/academic software for quantitative evaluation and their developments that even enable the analysis of disordered or interstratified clay minerals allows and encourages more and more people to use them. However, the qualitative and quantitative determination of the mineral composition of clays is still a challenge. Participation in round-robin tests allows to test the own proficiency and that of others. The biennial Reynolds Cup competition, established by Douglas McCarty, Jan Srodon and Dennis Eberl in 2002 rapidly became a success story, which goes now in its 7th edition. The number of participants increases from 15 to over 70. Nevertheless, among the three top-placed in all the competitions are only 10 participants/groups and only one in all. This is a sign that in addition to the technical possibilities the appropriate skills and experience are necessary.

Our lab has placed in the top 10 in 4 of 6 competitions with a third place in 2006 and the first in 2012. The applied method in all contests was the XRD with Rietveld analysis using the program AutoQuan (GE Seifert). We tried to hold the effort low to be comparable with our routine analysis in the lab. This means, beside the XRD and the related preparation of the samples and XRD specimen no further exhaustive methods were applied. This talk will give information about these procedures and techniques to encourage to follow and not to deter new users with the necessity to apply additional comprehensive methods but also to show where are some pitfalls. At the conclusion the 7th Reynolds Cup will be announced.
The type and amount of exchangeable cations are important properties of clays. They strongly influence parameters such as the retardation behavior and hydraulic conductivity as well as the shearing properties of clays. Furthermore, they are very sensitive parameters for detecting changes in mineral properties e.g. in bentonite-alteration. The cation exchange capacity (CEC) is related to the layer charge as the sum of the permanent charge from substitutions or vacancies in octahedral and tetrahedral sheet and the pH-dependent coordination of cations at the edges. However, the values depend on measurement conditions and material properties. Consequently, the CEC is defined as the quantity of cations available for exchange at a given pH. Several methods were developed to measure the CEC using so-called index cations replacing the originally adsorbed exchangeable cations, e.g. NH₄⁺ (Mackenzie 1951) and Cu(ii)-trien (Meier & Kahr 1999). The common feature of all of these techniques is the application of aqueous exchanging solutions. Therefore, all these common CEC methods fail in determination of the amount of exchangeable cations in clays containing water soluble phases like calcite, dolomite, gypsum or halite by chemical analysis of the exchanging solution. The dissolution of these phases in the aqueous exchanging solutions leads to an overestimation of the actual amount of exchangeable Mg²⁺, Ca²⁺ and Na⁺. A number of techniques has been developed to overcome this problem, e.g. the use of a calcite-oversaturated Cu(ii)-trien exchanging solution (Dohrmann & Kaufhold 2010) or an 80% ethanolic NH₄Cl exchanging solution. However, still “A complicated CEC analysis using different CEC methods, anion analyses, and mineralogical analyses is needed to obtain more accurate and plausible results” (cit. Dohrmann et al. 2012).

A new method, based on a non-aqueous (ethanolabs) exchanging solution of an ammonium salt is presented in this work. The main purpose of this approach is to prevent the dissolution of water soluble phases preserving the original pool of exchangeable cations of the clay. The use of the NH₄⁺ as index cation should make the CEC results comparable to those of the NH₄⁺-Ac technique. Several samples were measured: commercial bentonites, clays from the work Dohrmann et al. (2012), and a sodium montmorillonite Cloisite Na⁺ (Southern Clay Products INC.) with a 10 wt% admixture of finely milled calcite and gypsum. The CEC as the sum of exchangeable cations in the exchanging solution shows a good agreement with the CEC measured after Mackenzie (D 0.1-3 cmol+/kg). Slightly higher variations (D 0.4-6 cmol+/kg) were found in comparison to the data in Dohrmann et al. (2012). However, the amount of exchangeable cations Ca²⁺ and Mg²⁺ in the same range or lower suggesting a suppressed dissolution of such phases. The amount of the exchangeable Ca²⁺ and Mg²⁺ for the pure cloisite and the cloisite + calcite sample are similar and only a slight overheating of the exchangeable Ca²⁺ (2 vs. 0.5 cmol+/kg) was found for the cloisite-gypsum sample but significantly below the values from Cu-trien or NH₄⁺-Ac exchange (80-100 cmol+/kg). The results indicate the possible applicability of this new method for the determination of exchangeable cations in calcareous and gypsum containing clays.

The NH₄⁺-Ac method as well as the beforehand presented method are time consuming in determination of the CEC. The Cu(ii)-trien method was introduced as a fast and simple method for CEC measurement. However, this method suffers from a significant underestimation of the CEC in high charged and vermiculite-bearing clays where excessive mechanical and chemical pretreatment and a longer exchange reaction time would be necessary to measure CEC values effectively (Senadel et al. 2009). A fast method was developed to measure the CEC of vermiculites by exchanging the cations by the highly adsorbing organic cation guanidinium C(NH₂)₃⁺ after Na-intercalation by dry grinding with NaCl. Guanidinium (Gdn) concentrations in the exchange solution were measured by fluorescence spectroscopy (Xinder & Plötzle 2010). This method was further simplified and enhanced. The application of a guanidinium-selective electrode to measure the Gdn concentrations in the exchange solution allows easier and faster measurements and gives more accurate data.
reliable results because of the avoidance of time dependent effects in the fluorescence spectroscopic registration. The usage of Gdn-carbonate and of Gdn-acetate in the exchanging solutions allows the CEC measurements at two different pH (Gdn-carbonate pH 10.5 and Gdn-acetate acetate-buffered to 4.5). This makes it possible to investigate the "fix" and the pH-dependent CEC with the same exchanging cation.
**TIME-RESOLVED SYNCHROTRON X-RAY DIFFRACTION STUDY OF DEHYDRATION BEHAVIORS OF PHYLLOMANGANATES**

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There has been considerable interest in recent years in the structures and behaviors of manganese oxide phases having layer structures, so-called phyllomanganates, e.g. chalcophanite, lithiophorite, ranciérite, birnessite and related phases. It has been shown that cations are preferentially adsorbed or incorporated into phyllomanganates in aqueous environments and in soils (McKenzie 1976), and therefore, they play an important role in the sequestration and release of nutrients and toxic elements into the environment. They are also used as cathode materials in rechargeable Li batteries and are being developed as ion-exchange materials and catalysts for industrial use (Bach et al. 1995; Cai et al. 2002). Despite their importance as materials and their active role in geological systems, it has been challenging to investigate the crystal structures and behaviors of many phyllomanganate phases, because they tend to occur as fine-grained, poorly crystalline masses.

The phyllomanganates consist of sheets of edge-sharing $\text{Mn}^{4+\text{,}3+}$-$\text{O}_6$ octahedra, alternating with layers of cations and water molecules. In chalcophanite, one out of every seven octahedral sites in the Mn-O sheet is vacant, and the Zn cations are located above and below the vacancies. The vacant Mn sites are fully ordered. Ranciérite is a Ca-rich birnessite that is a commonly associated with biologically precipitated Mn oxides, and also occurs in oxidized zones of Mn deposits. It has a hexagonal structure similar to that of chalcophanite, but with disordered vacancies in the Mn-O octahedral sheets. Synthetic birnessite phases crystallize in both triclinic and hexagonal forms, depending upon pH and composition. In the triclinic phases, typically Mn$^{3+}$ cations rather than vacancies offset the charges of the interlayer cations.

In situ infra-red spectroscopy studies of the dehydration behaviors of various cation-exchanged birnessite phases by Johnson and Post (2006) suggest that cation hydration energies, and consequently, cation-water interactions are important factors in stabilities and exchange behaviors of phyllomanganate phases. Detailed descriptions of the interlayer region, however, and particularly of the roles played by the water molecules, are severely limited by the generally poor crystallinity of the materials. Furthermore, as water loss occurs at typically <200 °C, structural changes related to dehydration directly impact the material properties and their behavior in near surface natural environments.

In the current study we used time-resolved synchrotron powder X-ray diffraction and Rietveld refinements to better explore the interactions among the water molecules and interlayer cations and the Mn/O octahedral sheets in chalcophanite, lithiophorite, ranciérite, and synthetic birnessite phases with Na, K and Li as the interlayer cations. We will present the results of a series of refinements for these phases over the temperature range 300 to ~825 K that provide, a direct look at structural changes with increasing temperature as they undergo dehydration and consequent phase changes, including formation of stable intermediate anhydrous layer structures for chalcophanite and K-birnessite.
The Clay Minerals Society is an international organization devoted to the study of clays and clay minerals. The National Museum of Natural History (NMNH) is part of the Smithsonian Institution, the world’s preeminent museum and research complex. The Museum is dedicated to inspiring curiosity, discovery, and learning about the natural world through its unparalleled research, collections, exhibitions, and education outreach programs. At the center of the Museum’s exhibition and research programs are its expertly documented collections: more than 126 million natural science specimens and cultural artifacts.

The DMS-NMNH-SI catalog presently contains records for over 1000 clay- and clay-related mineral specimens (Table 1). Through its research, collections, education and exhibition programs, NMNH serves as one of the world’s great repositories of scientific heritage.

We propose the establishment of a partnership between The Clay Minerals Society and the Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution (DMS-NMNH-SI). This partnership would guide and implement planning to enhance the link between scholarship on important clays as recognized by the scholarly community and the permanent preservation of the samples on which the research is based in the existing DMS-NMNH-SI collection. Preservation of ~50 g each of the CMS Source Clays and CMS-Specialty Clays, for example, would serve as a permanent repository for these important materials. Such repositing would be archival and thus not commercial competition with CMS. An early high-priority effort would be to recover now-depleted CMS Source and Specialty Clays that may be presently available only as unused allocations in user laboratories. The joint CMS-NMNH enterprise could also be expanded to include well-studied scientifically important clays in addition to CMS Source and Specialty Clays, that the community collectively recognizes as important. CMS would help establish criteria for screening and accession of such materials for possible inclusion in the CMS-NMNH holdings, helping decide what makes a specific clay sample scientifically important enough to preserve. The CMS collection at DMS-NMNH-SI would also serve as a permanent repository in case the CMS Source Clays Repository ever closes. We propose as an initial step the establishment of a working group including CMS and Smithsonian representatives to discuss a possible collaborative initiative to enhance and expand the Smithsonian’s clay mineral research collection.

**Table 1. Clay- and related minerals at the Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution**

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Secondary surface layers may form by replacement of rock-forming minerals during chemical weathering. Such phenomena may be investigated using Pilling-Bedworth criteria, which involve the calculation of the ratio of the volume of the secondary weathering products (V_p) replacing a primary weathering mineral to the volume of primary mineral replaced (V_r). When V_p/V_r ≥ 1, the surface layer of secondary minerals will occupy at least the same volume as the portion of the reactant mineral replaced. Such a surface layer has negligible porosity, assumes conservation of the least mobile elements such as iron, aluminum, and manganese, and is termed a protective surface layer (PSL). Surface layers are unprotective (USL) when the volume of the products formed by replacement is less than the volume of the reactants replaced (V_p/V_r < 1), with accompanying voids through the surface layer.

Hornblende-product molar volume calculations of USLs from the Southern Appalachian Blue Ridge Mountains of northeastern Georgia, USA, found that aluminum must be imported into the hornblende-surface layer system during early-stage weathering. Although aluminum is typically considered negligibly mobile during weathering, it has been suggested that the source of the imported aluminum in the hornblende USL is from garnet weathering known to occur in the same rock unit. Micromorphologic observations of weathered almandine garnets in Appalachian Southern Blue Ridge regolith reveal PSL formation, potentially reflecting conservation of aluminum.

Pilling-Bedworth criteria and natural almandine garnet-PSL molar volume calculations are used to determine the potential quantity of aluminum available for export from the almandine garnet-PSL system. The results are presented for varying natural almandine compositions and replacement PSL mineralogies. Natural almandine garnets with relatively high aluminum and high iron, relatively high aluminum and low iron, relatively high iron and low aluminum, and those from Southern Appalachian Blue Ridge regolith are specifically investigated. Early work reported hematite, goethite, and gibbsite as the only weathering products for almandine garnet in the Southern Appalachian Blue Ridge. Despite the release of silicon and aluminum during almandine dissolution, there were no studies which identified kaolinite as a weathering product. Secondary products investigated in this study are hematite, goethite, gibbsite, kaolinite, and pyrophyllite. These minerals are ubiquitous in the Southern Appalachian Blue Ridge regolith. Based on Pilling-Bedworth criteria, surface layers are more likely to be protective over a broad range of reactant-mineral compositions when they contain goethite, kaolinite, and pyrophyllite. However, to form a PSL of goethite and kaolinite, an almandine garnet must have a minimum aluminum stoichiometric coefficient of ~3.75 apfu, and a minimum iron stoichiometric coefficient of ~2.7 apfu. Production of PSLs when V_p/V_r = 1 during almandine garnet replacement, and subsequent possible excess aluminum available for export (Al_ex), are a function of the primary almandine garnet's aluminum and iron stoichiometric coefficients, and molar volume as outlined in equation (1).

**Abstr Acts**

**THE CLAY MINERALOGY OF NATURAL ALMANDINE GARNET REPLACEMENT SURFACE LAYERS AND ITS POTENTIAL INFLUENCE ON ALUMINUM MOBILITY DURING EARLY-STAGE CHEMICAL WEATHERING**

Jason R. Price*1 and Michael A. Velbel2

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2Department of Geological Sciences, Michigan State University, East Lansing, MI 48824-1115, USA

*Jason.Price@millersville.edu;

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\[ Al_e = \frac{Al_{Gt} - \left( V_{Gt} - Fe_{Gt} \cdot V_{Gt} + Al_{Gbs} \cdot V_{Gbs} \right)}{0.5 \cdot V_{Kln}} \]  

(1)

where,

- \( Al_{Gt} \) = aluminum stoichiometric coefficient of the garnet
- \( Fe_{Gt} \) = iron stoichiometric coefficient of the garnet; assume all iron conserved in PSL goethite
- \( V_{Gt} \) = molar volume of goethite
- \( Al_{Gbs} \) = moles of aluminum in gibbsite of PSL
- \( V_{Gbs} \) = molar volume of gibbsite
- \( V_{Kln} \) = molar volume of kaolinite

As the proportion of gibbsite in a PSL increases relative to kaolinite, the quantity of aluminum available for export decreases. Almandine garnets with relatively high iron and low aluminum stoichiometric coefficients are capable of yielding more excess aluminum than an almandine garnet with relatively high aluminum and low iron stoichiometric coefficients. A reduction in the quantity of kaolinite in a PSL resulting from the presence of pyrolusite increases the quantity of aluminum available for export from the garnet-PSL system. For the almandine garnet compositions investigated, it is possible that up to 35% of the aluminum produced during almandine garnet weathering could be exported. There is no need to import any other element into the garnet-PSL system to produce the observed weathering-product mineral assemblages.
CLAYS AND DIAGENETIC IRON OXIDES IN THE CENTRAL OKLAHOMA AQUIFER: SURFACE AREA, TRACE ELEMENTS, AND COLLOIDAL TRANSPORT

Virginia G. Priegnitz, Andrew L. Swindle, Jeffrey P. Westrop, Molly R. Sexton, and Andrew S. Madden*  
School of Geology and Geophysics, University of Oklahoma, Norman OK 73019, USA:  
*amadden@ou.edu

The Central Oklahoma Aquifer (COA) provides a needed source of water for municipalities throughout central Oklahoma, including Norman. Groundwater in the Permian sand, silt, and clay comprising the aquifer frequently contains arsenic, chromium, and uranium at unusually high levels, often above 20 ppb (As) or 50 ppb (hexavalent Cr). Current hydrogeochemical models rely on associations between arsenate/chromate and sediment iron oxides, but fail to predict the spatial distribution of trace metals. Two forms of investigation explored trace metal distributions and aquifer mineralogy at the nano- to microscales, in hopes of developing more robust explanations for trace element distributions in sediment and groundwater.

The first form of investigation involved the collection of 50 sediment samples from the USGS/EPA Norman Test Hole Core spanning the productive zones of the aquifer. These samples were analyzed for BET surface area, micromorphology with SEM, color, texture, and grain size with optical microscopy, and whole-rock trace elements geochemistry. Initial results demonstrated anomalously high surface areas in many samples, ranging up to ~60 m\(^2/g\). High surface area values were obtained in both clay-rich and clay-poor intervals. SEM imaging of samples from these intervals revealed the presence of abundant microscale hematite rosettes assembled from nanoscale platelets, in addition to clay minerals and other nanoscale iron oxides. Trace element concentrations followed a general power-law relationship with surface area, with much scatter.

The presence of abundant nano-to microscale clays and iron oxides in contact with groundwater of neutral to basic pH suggests the possibility for colloidal transport. In the second form of investigation TEM grids were deployed in monitoring wells associated with a City of Norman municipal drinking water supply well using an in-house designed subsurface nanoparticle holder. After exposure to groundwater for one week, TEM analysis revealed abundant iron oxides, quartz with or without surface-bound iron oxides, gypsum, and other trace phases.

The links between diagenetic iron oxides, detrital and neoformed clays, and colloidal iron minerals that can serve as vectors for the transport of elements of concern will be explored in future studies. Initial work suggests a correspondence between the spatial distribution of diagenetic and colloidally transported iron oxides. Future investigations of core sediments will explore fine details responsible for the data scatter, including with bulk and clay fraction powder XRD analyses, SEM/TEM, and chemical extractions. Also, future field investigations of colloids collected from groundwater will explore the depth-dependence of colloids and their trace element geochemistry.
An image of a page is provided with the following extracted text:

**ADSORPTION OF LACTATE AND CITRATE ON MONTMORILLONITE**

M. Elena Ramos and F. Javier Huertas*

Instituto Andaluz de Ciencias de la Tierra (CSIC-Universidad de Granada), Avda. de las Palmas 4, 18100 Armilla, Granada, Spain

*javierhuertas@ugr.es

Low-molecular-weight (LMW) organic acids can absorb onto mineral surfaces either by specific chemical interactions (chemisorption) to form inner-sphere complexes or by nonspecific interactions (physisorption) via hydrogen bonding and/or electrostatic interactions to form outer-sphere complexes. Among the LMW organic acids, lactate and citrate play a significant environmental role because of its prevalence in soil, sediments and aerosols resulting from its exudation by plant roots, production by fungi, and discharge by microorganisms.

Spectroscopy methods are a well suite for probing the structure and binding in metal-carboxylate complexes in aqueous solutions and at interfaces. Carboxylate groups of organic ligands have characteristic infrared-active vibrational bands that are sensitive to changes in proton and metal coordination. Attenuated Total Reflectance Fourier transform infrared (ATR-FTIR) spectroscopy is one of the most direct methods used to distinguish different structures of organic adsorbents at mineral/water interfaces under in-situ conditions.

Lactate and citrate were adsorbed on montmorillonite surface from aqueous solutions from pH 2 to 12 in the presence of 10 mmol L⁻¹ KNO₃. The adsorbed molecules were characterized using ATR-FTIR spectroscopy at pH 4, 6 and 8. Macroscopic adsorption measurements indicate that the adsorption of both ligands is highly pH-dependent.

Macroscopic adsorption measurements indicate that the adsorption of both ligands is highly pH-dependent. ATR-FTIR results indicate that lactate is likely adsorbed by nonspecific electrostatic interactions, since no changes were found in peak position and shape of carboxyl group stretches. Nevertheless, ATR-FTIR results suggest that citrate is adsorbed in the >AlOH groups as an inner-sphere surface complex at low pH. The macroscopic adsorption behavior of the ligands was modeled as a function of pH by using the Diffuse Layer Model (DLM) for lactate and the Triple Layer Model (TLM) for citrate. Surface complexation of lactate is represented by the following reaction:

\[ >\text{AlOH} + \text{Lac}^- + \text{H}^+ \rightarrow >\text{AlLac} + \text{H}_2\text{O} \]

\[ \log K = 11.25 \]

Speciation diagram for 0.15 mmol L⁻¹ lactate adsorbed onto montmorillonite is shown in Figure 1. At first, the infrared data apparently do not agree with the proposed model, since the spectra suggested the formation of outer-sphere edge data; black dashed line: overall model fit to experimental data for ligand sorption.

![Figure 1. Speciation diagram of lactate (Lac) and citrate (Cit) adsorption at 25°C from 0.15 mmol L⁻¹ solution onto montmorillonite, calculated from the surface complexation model. Solid circles: experimental adsorption edge data; black dashed line: overall model fit to experimental data for ligand sorption.

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Low-molecular-weight (LMW) organic acids can absorb onto mineral surfaces either by specific chemical interactions (chemisorption) to form inner-sphere complexes or by nonspecific interactions (physisorption) via hydrogen bonding and/or electrostatic interactions to form outer-sphere complexes. Among the LMW organic acids, lactate and citrate play a significant environmental role because of its prevalence in soil, sediments and aerosols resulting from its exudation by plant roots, production by fungi, and discharge by microorganisms.

Macroscopic adsorption measurements indicate that the adsorption of both ligands is highly pH-dependent. ATR-FTIR results indicate that lactate is likely adsorbed by nonspecific electrostatic interactions, since no changes were found in peak position and shape of carboxyl group stretches. Nevertheless, ATR-FTIR results suggest that citrate is adsorbed in the >AlOH groups as an inner-sphere surface complex at low pH. The macroscopic adsorption behavior of the ligands was modeled as a function of pH by using the Diffuse Layer Model (DLM) for lactate and the Triple Layer Model (TLM) for citrate. Surface complexation of lactate is represented by the following reaction:

\[ >\text{AlOH} + \text{Lac}^- + \text{H}^+ \rightarrow >\text{AlLac} + \text{H}_2\text{O} \]

\[ \log K = 11.25 \]

Speciation diagram for 0.15 mmol L⁻¹ lactate adsorbed onto montmorillonite is shown in Figure 1. At first, the infrared data apparently do not agree with the proposed model, since the spectra suggested the formation of outer-sphere edge data; black dashed line: overall model fit to experimental data for ligand sorption.

![Figure 1. Speciation diagram of lactate (Lac) and citrate (Cit) adsorption at 25°C from 0.15 mmol L⁻¹ solution onto montmorillonite, calculated from the surface complexation model. Solid circles: experimental adsorption edge data; black dashed line: overall model fit to experimental data for ligand sorption.
complexes at all the pH values studied. This can be due to a weak nature of the proposed complex $>\text{AlLac}$, which formation does not alter the IR bands position of absorbed lactate with respect to those found for aqueous free lactate.

The TLM fit for citrate sorption to montmorillonite was achieved when citrate sorption is represented by a single reaction:

$$>\text{AlOH} + \text{Cit}^3- + \text{H}^+ = >\text{AlCit}^2- + \text{H}_2\text{O} \quad \log K = 10.58$$

This reaction supports the hypothesis that citrate sorption to montmorillonite is dominated by specific sorption to amphoteric aluminol edge sites in the whole pH range studied (2-9). The ATR-FTIR data agree with the proposed model in acidic conditions, since the spectra suggested that the formation of an inner-sphere monodentate complex is favored at low pH. However, modeling results indicate that this complex exist in the whole pH range studied, with a maximum concentration at pH 5.5. This complex involves one surface Al atom to form a mononuclear, monodentate complex. The infrared spectra also suggested the formation of an outer-sphere complex at near neutral pHs. However, the introduction of outer-sphere complexes in the model led to poor convergence. Speciation diagram for 0.15 mmol L$^{-1}$ citrate adsorbed onto montmorillonite is shown in Figure 1. Although FTIR results indicated that the inner-sphere citrate complexes were favored at low pH and outer-sphere complexes were favored at near-neutral pHs, the model indicates that only one inner-sphere complex is formed in the pH range studied.

These findings are of relevance for the evaluation of the catalytic effect that takes place during the dissolution of clay minerals in presence of low-molecular-weight organic ligands.

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Iron oxide nanoparticles are abundant and serve many functions in natural and complex aqueous systems. Because hematite acts as an important and abundant aid in aqueous contaminant sequestration, and is widely used in industrial applications, it is beneficial to gain a better understanding of hematite nanoparticle formation. The 6-line ferrihydrite iron oxyhydroxide phase is a precursor phase to hematite formation. As 6-line ferrihydrite and hematite nanoparticle nucleation occur simultaneously, it is important to understand how in situ nanoparticle properties, governed by nanoparticle formation conditions, affect ex situ nanoparticle behavior. Understanding 6-line ferrihydrite formation and subsequent transformation to hematite could provide key insight into tuning desirable hematite nanoparticle properties for use in these applications.

In this study, we systematically examined the effects of varying forced hydrolysis synthesis conditions on the in situ and ex situ iron oxide nanoparticle properties. In addition to extensive physicochemical characterization using dynamic light scattering, high resolution X-ray diffraction, transmission electron microscopy, and diffuse reflectance infrared Fourier transform spectroscopy, we also tested the effects of the varied synthesis conditions on the nanoparticles ability to absorb arsenic. Interestingly, enhanced nanoparticle aggregation during drying in fast-cooled samples promoted 6-line ferrihydrite conversion to hematite. As a result there were differences in the in situ and ex situ mineral phase identities and the extent of the hematite and ferrihydrite composition among each sample. Arsenic sorption experiments also revealed that the extent of hematite and 6-line ferrihydrite present in each tested sample affected the rate at which arsenic was adsorbed. The results reveal the significance of investigating both in situ and ex situ nanoparticle property dependencies and relationships.
Silanization of Phyllosilicates Type Montmorillonite for Silver Adsorption

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In this work a commercial montmorillonite (MMT) was used as a clay material for silver ion exchange with and without functionalization by using 3-aminopropyltriethoxysilane (AMPS) by means of a reflux in toluene for 16 h. For the cation exchange capacity, the montmorillonite was dispersed in a solution of ammonium acetate and later on the ammonium ions were titrated with sodium hydroxide.

The aim of this work was to increase the antibacterial capacity of systems based on silver ions supported in clays type MMT, by controlling the dispersion and availability of silver species. The functionalized MMT has the capacity to retain silver ions, not only in the interlayer space, but also in the amine group from the AMPS, which could improve the dispersion and facilitate its reduction.

The materials were characterized by XRD, FTIR, SEM, TGA and microbiological test. The graphic 1 (left) shows the FTIR spectra for MMT before and after AMPS treatment, it is possible to see new bands at 2932 and 2863 cm⁻¹ due to the antisymmetric and symmetric stretching of C-H from the organic moieties. It is also possible to see a good dispersion of silver species on MMT (right) on MMT.

The results show an increase in the interplanar space in MMT by silver incorporation corroborated by XRD and an important improvement in the antibacterial activity on the material functionalized.
In the context of sustainable soil management it is of prime importance to better understand the cycles of major nutrients such as potassium (K). K is abundant in most soils but the overwhelming majority of soil K is unavailable to plants, the available fraction corresponding essentially to K⁺ in solution and to exchangeable K. Clay minerals like smectite or vermiculite have the ability to retain water and cations, including K⁺, in their interlayer spaces and to exchange them rapidly with other cations of the soil solution. The unavailable fraction corresponds to K in feldspars and micas, soil parent minerals. Under the action of plants, part of non-exchangeable K can be released from mica/illite interlayers however when exchangeable K is insufficient (Badraoui et al., 1992). Clay minerals, including micas, thus play a pivotal role in K soil processes (Barre et al., 2008; Simonsson et al., 2009). Despite growing interest in K fate in soils investigations, no precise and quantitative information has been proposed so far as to the distribution and speciation of K in soils at a micron scale and on its relations with clays and some soil elements, like roots. To retrieve this information, we used a combination of micro X-ray fluorescence (µXRF) and micro X-ray absorption near edge structure (µXANES).

Soil samples come from the Morrow Plots (U. of Illinois at Urbana-Champaign), one of the oldest continuous agricultural experimental plots in the world (150 years). Samples were picked in fields cultivated with different crops and amendments. XRD on bulk samples evidences the presence of kaolinite, mica, illite and illite-smectite. Although chemical analyses indicate similar K values for the different samples, extractable K amounts increase with the presence of fertilizers. For synchrotron γ-analyses and to preserve soil organization, undisturbed mottles of soils were impregnated with resin and self-supporting 30 µm thin sections were prepared to allow the collection of XANES spectra in transmission mode. µXRF and µXANES data were collected at the X-ray microscopy beamline ID21 (Susini et al., 2002) at the ESRF, France. In a first experiment, the beam was focused down to 0.3×0.5 µm² using a KB mirror system. XRF maps (300×300 µm²) were collected with a 1 µm step above the K K-edge (3.7KeV) to evidence the location of the K-bearing minerals and of quartz, based on K, Al and Si elements distribution. Maps at Fe K-edge evidence the location of higher elements of the soil like Ca and Fe. µXANES were then collected on points of interest (POI) and bulk analyses of soil samples (top). Black lines = experimental spectra, gray lines = fitted spectra, dotted lines for PI p1 = components of the fit.

Figure 1. K K-edge XANES of K-bearing reference minerals (bottom) and of POI and bulk analyses of soil samples (top). Black lines = experimental spectra, gray lines = fitted spectra, dotted lines for PI p1 = components of the fit.
position of the white line (3618 or 3619 eV) and of the oscillations at 3627 or around 3645 eV. The spectral signature of illite-smectite remains indistinguishable however from that of a mixture of illite and smectite.

In soil samples, pure feldspar spectra were recorded (figure 1, p.3). By contrast, clays were often observed as a mixture of phases at the micron scale. Linear combination fitting are needed to determine the contribution of each phase (figure 1, p.1 and 2). These fits evidence the diversity of the clay associations and the strong heterogeneity at the micron scale. In a second experiment, the new XANES full-field imaging station, recently developed at the ID21 beamline (Fayard et al. 2013), was used to further study K speciation, but over a full 2D field of view of a few hundreds of microns. Using an unfocused beam, a transmission image of thin sections is recorded at each energy step (0.2 eV) along the K XANES spectral range (figure 2a). In these conditions, up to $4 \times 10^6$ XANES spectra can be recorded simultaneously, preserving the sub-micron spatial resolution. After data processing, a XANES spectrum can be extracted corresponding to each pixel of the map. The distribution of K is obtained from the difference between images below and above the edge (figure 2b). More interestingly, the distribution of each of the K-bearing mineral can be obtained by applying statistical analyses on extracted XANES spectra. Thus the clay distribution in the root vicinity allows unraveling the ability of plants to access the different K pools (in particular exchangeable and non-exchangeable K in clays) and better understanding the influence of amendments on this availability.

Figure 2. a) One of the transmission maps of a stack (800×500 µm² map size, 0.3×0.3 µm² pixel size, 3.618 keV). b) K repartition map derived from the difference between images below and above the K edge (white corresponds mainly to the feldspars, gray to the clays and black to the absence of K).
Molecular Explanation for Why Talc Surfaces Can Be Both Hydrophilic and Hydrophobic

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While individual water molecules adsorb strongly on a talc surface (hydrophilic behavior), a droplet of water beads up on the same surface (hydrophobic behavior). To rationalize this dichotomy, we investigated the influence of the microscopic structure of the surface and the strength of adhesive (surface–water) interactions on surface hydrophobicity. We have shown that at low relative humidity, the competition between adhesion and the favorable entropy of being in the vapor phase determines the surface coverage. However, at saturation, it is the competition between adhesion and cohesion (water–water interactions) that determines the surface hydrophobicity. The adhesive interactions in talc are strong enough to overcome the unfavorable entropy, and water adsorbs strongly on talc surfaces. However, they are too weak to overcome the cohesive interactions, and water thus beads up on talc surfaces. Surprisingly, even talc-like surfaces that are highly adhesive do not fully wet at saturation. Instead, a water droplet forms on top of a strongly adsorbed monolayer of water.
Elimination of the single variable between analogous equations for any two water properties yields an equation which
in a clay-water system is described by a common exponential equation containing a single variable, namely, the average
in an exciting synthesis of his studies clay-water interaction, Phil discovered that all the properties of interparticle water
molar absorptivity, O-H stretching and H-O-H bending. A careful analysis of the data indicated that the exchangeable
supercooling, viscosity, heat and entropy of compression, specific volume, specific heat capacity, specific expansibility,
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what Phil's early work was in the main interactions of water with soils and clays, with the main interest in the water phase including
between the surfaces of clay particles and the interparticle water lowers the potential energy of the water and, thereby,
When Phil began his professional career, it was generally believed that water next to surfaces of all solids behaves like
Dr. Peterson was a man of great vision and believed in giving young scientists the freedom to develop their interests
and capitalize on their abilities. Thus Phil was able to develop his own research program that interested him. Phil's early
work was mainly in the interactions of water with soils and clays, with the main interest in the water phase including
movement of water in soils, diffusion rate of water in soils, density of adsorbed water in bentonite, viscosity of water in
clay systems, heat capacities of water in clay systems, and many other water properties. By the mid 1970 Phil's research
started to indicate that to understand the water interactions with clays it would be best to more fully understand the
clay mineral structures. It was at this point that Phil and I started a very fruitful collaboration that lasted after his retire-
When Phil began his professional career, it was generally believed that water next to surfaces of all solids behaves like
normal bulk water and that all colloidal phenomena, including those involving clays, could be described adequately by
electrical double-layer theory. This theory had the advantage of being quantitative and intellectually satisfying. One of its
most useful application was in the prediction of swelling pressure of clays. When Phil hypothesized that the interaction
between the surfaces of clay particles and the interparticle water lowers the potential energy of the water and, thereby,
contributes to the swelling pressure, his hypothesis was given little credence. In view of the complexity and controver-
sial nature of the subject, few researchers joined Phil in these investigations. Therefore, it took more than 35 years of effort
for Phil to succeed in showing that interparticle water differs appreciably from bulk water in the following properties:
supercooling, viscosity, heat and entropy of compression, specific volume, specific heat capacity, specific expansibility,
specific compressibility, free energy, enthalpy, and entropy. Moreover it differs in the following spectroscopic properties:
molar absorptivity, O-H stretching and H-O-H bending. A careful analysis of the data indicated that the exchangeable
cations could not account for these differences.
In an exciting synthesis of his studies clay-water interaction, Phil discovered that all the properties of interparticle water
in a clay-water system is described by a common exponential equation containing a single variable, namely, the average
thickness of the water films on the particle surfaces, and a constant that is characteristic of the property involved.
Elimination of the single variable between analogous equations for any two water properties yields an equation which
allows one property to be calculated from the other provided the respective values of the characteristic constants are
known. Since these constants are determinable, the calculation of every property of the water in a clay-water system from the measured value of a single property is feasible.

Subsequent experiments using X-ray diffraction techniques it was determined the swelling pressure of expanding clays is described by an exponential equation containing two universal constants and a single variable, i.e., either the interlayer distance or the water content. Since the properties of the interlayer water were also functions of the water content, it was evident that these properties and the swelling pressure are related. Now double-layer theory does not predict the equation that relates the swelling pressure to the interlayer distance. Nor does it predict the relation between this pressure and the properties of interparticle water. Thus Phil showed that the double-layer theory of clay swelling is untenable.

In some of the last experiments that Phil did before he retired he was able to show that the frequency of the Si-O stretching vibrations in the clay layers changed with the water content over the entire range of swelling. Further, the Si-O stretching frequency was found to depend exponentially on a single variable—the water content. Farther work suggested that the Si-O stretching vibrations in the clay were coupled to the H-O-H bending vibrations of the interlayer water and that, as these vibrations change with interlayer distance (water content), the energy of the system changes. This, in turn, affects the swelling pressure of the clay.

As a young undergraduate and as a MS student at the University of Missouri, I had some interaction with another pioneer of the Clay Minerals Society. It was C. E. Marshall that introduced me to the new Clay Minerals Society when he took me with him to attend the first meeting of the Clay Minerals Society in Madison, Wisconsin. I had already accepted a Graduate Assistantship from M.L. Jackson and would start my work in Madison the following March after my wife graduated. I will try to relay some of my personal observations of Dr. Marshall as a teacher in Soils and in Agriculture Biochemistry. He was a member of my graduate committee so I had a little more interactions with him than many of my fellow students. In July of the year that I went to the University of Wisconsin, Dr. Marshall moved over to University Administration as Dean of the Graduate School.
The Earth’s crust is composed of rocks with varying degrees of porosity at the nm to millimeter scale, and is both a source and reservoir of geofluids, as well as a target for geologic carbon storage (GCS). Fluid-rock interactions control compositions of fluids, subsurface fluid mobility and mixing, and enhanced recovery processes. Caprocks comprised of thick layers of clay or mudstones that are thought to be impenetrable to CO2, often overly the porous reservoir and serve to retain buoyant plumes of CO2. To quantify the interactions of caprock with CO2, we measured the excess sorption of supercritical CO2 to Na-montmorillonite clay, a proxy for cap rock materials. At low fluid densities, limited amounts of CO2 adsorbed to the clay. Using neutron diffraction, the change of the clay interlayer spacing was measured as a function of the CO2 density. An immediate increase of the sub-1W hydrated clay interlayer spacing upon CO2 addition was found at low pressures, and the d-spacing remained constant as CO2 density increased. Furthermore, changes in the intensity of the d(001) interlayer peak upon addition of CO2 prove that CO2 enters the interlayer space. Combination of the excess sorption and neutron diffraction results enables calculation of the CO2 density in the interlayer spaces. In GCS environments, the limited swelling of sub-1W clay upon contact with CO2 could assist in the sealing of small fractures and enhance storage security. Using FTIR, the reactivity of the Na-montmorillonite clay—CO2 system was studied. No signatures of reaction products were identified, indicating that CO2 adsorption to sub-1W Na montmorillonite is a physical process and that CO2 does not interact chemically with the clay.
Fe-rich kaolinites and halloysite (both spherical and tubular) in soils of a terrace chronosequence in the dry tropics of Costa Rica (Nicoya Peninsula) are derived from the transformation of smectite via interstratified kaolin-smectite (K-S). The smectite is iron-rich (13.2 ± 1.6 % Fe₂O₃, anhydrous basis) and forms early during pedogenesis from beach sediments rich in basaltic-andesite clasts and shell fragments. Smectite is the dominant mineral in Holocene terrace soils; with time, pedogenic smectite evolves to interstratified K-S that inherits flaky smectite crystal form. In late Pleistocene (50 ka) soils, K-S is the dominant soil mineral, comprising ~90 % of soil clay in the C-horizon of 50 ka terrace soils. In upper B-horizons of 50 ka soil, the K-S has begun to undergo transformation to Fe-rich kaolinite and halloysite. The oldest soils in the chronosequence (120 ka) are dominated by subequal amounts of Fe-kaolinite and halloysite (4.9 % Fe₂O₃). Kaolinites in the C-horizon of 120 ka soils have flaky morphology and 10.2 % Fe₂O₃ whereas the upper B-horizon contains hexagonal kaolinites with < 3 % Fe₂O₃ (as well as spheroidal and tubular halloysite).

K-S is indicated by X-ray diffraction (XRD) data that reveal an asymmetric 001 peak at 16.2 Å (ethylene glycol-solvated) and irrational 00h peaks (7.6, 3.5 Å) that exhibit Mering-like behavior, and by transmission electron microscopy-analytical electron microscopy (TEM-AEM) data that document single crystals of K-S (Figure 1) with compositions intermediate to those of end-member crystals of smectite and kaolin. Changes in the compositions of tetrahedral and octahedral sheets, notably decreases in octahedral Fe and Mg and increases in Al, indicate that the smectite to K-S reaction is accompanied by localized dissolution of smectite 2:1 layers that likely proceeds laterally along the 2:1 layers. TEM, Fourier transform infrared (FTIR) and XRD indicate presence of kaolinite and both forms of halloysite, and XRD (e.g. incomplete expansion and collapse) and O TA indicate the development of Al-hydroxy-interlayers in K-S with time. The oldest soils contain hexagonal kaolinites with low iron content (< 3 % Fe₂O₃).
Changes in crystal chemistry over time (Figure 2) likely reflect two reaction mechanisms. The first is the layer-by-layer, cell-preserved reaction of smectite layers to kaolin layers that results in transformation of smectite to K-S and eventually kaolinite — this mechanism has been observed in previous studies of K-S from soils and volcaniclastic deposits, and in these soils results in Fe-rich kaolinites. The second mechanism involves dissolution of K-S crystals followed by crystallization of tubular and spheroidal halloysite. The likely sequence of transformations, based on the changes in chemistry shown in Figure 2, is as follows: (A) smectite ➞ K-S ➞ Fe-kaolinite (solid state, cell-preserved), simultaneous with (B) smectite ➞ K-S ➞ spheroidal halloysite ➞ tubular halloysite. The origin (from smectite via K-S) of Fe-bearing kaolinite and halloysite has potentially important implications for clay mineral reactions and elemental cycling in tropical soils.

Figure 2. Changes in crystal chemistry from TEM-AEM analysis. Data are arranged from youngest soil (left) to oldest (right), with idealized end-member kaolinite on far right.
Organic dyes are aromatic molecules where conjugated double bonds form large \( \pi \) orbitals. The energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (thus, the \( n \pi^* \) transition energy) is a function of the dimension and shape of the molecular orbital. Hence, the larger the chromophore, the smaller the energy needed for a \( n \pi^* \) transition—yielding light absorption in the visible range 400-700 nm.

A molecule which has absorbed a photon should eventually release its excess of energy. Relaxation mechanisms include internal conversion (heat), photon emission (luminescence) or, in the case of a photolabile molecule, a photodegradation reaction that might partly decompose the molecule, decreasing the size of the \( \pi \) orbital, yielding molecules that will no longer absorb in the visible range (color fading). Adsorption to clay minerals avoids in some cases the photo-degradation. Mayans combined the pigment Indigo with the acicular clay mineral palygorskite, obtaining a compound named "Maya Blue", that conserved the color over centuries, whereas indigo not bound to clay or bound to other minerals (even though similar to palygorskite, as sepiolite) fade.

A recent research investigated whether adsorption of the cationic dye methylene blue to different clays may avoid its photodegradation, as the mineral palygorskite stabilizes the indigo. Fig. 1a shows absorption spectra in the visible range for the different MB-clay complexes. MB complexed with clinoptilolite, sepiolite or vermiculite show absorption spectra almost identical to free dye \((\lambda_{\text{max}}=660\text{ nm})\); whereas complexes with palygorskite and montmorillonite show a maximum absorption band hypsochromically shifted to 570 nm. This spectroscopic phenomenon is known as metachromacy, and usually ascribed to formation of dye aggregates. In dye-clay complexes an alternative mechanism suggested for metachromacy is the interactions between the oxygen plane of the mineral and the dye \( \pi \) orbitals. Since the amount of dye in this study is very low compared with the adsorption capacity of the clays, the second mechanism seems more feasible. Furthermore, in dilute solutions MB can enter the channels of sepiolite and palygorskite, as indigo entrance was reported. Dye aggregation is not possible in such narrow channels.

Fig. 1b shows that photodegradation of free dye is linear with time, indicating a zero-order process \((R^2=0.996)\). MB adsorbed on sepiolite, clinoptilolite and vermiculite exhibits faster decomposition, with more than 80% photodegradation, in a...
process suitable to a first order equation ($R^2 > 0.98$). On the other hand, MB adsorbed on montmorillonite and sepiolite exhibits almost complete stabilization.

The connection between metachromacy and photostabilization of MB may not be coincidental, though no literature specifically reports it previously. Studies with Maya Blue ascribed stability of indigo with palygorskite to the tight structure inside the channels of the mineral, resulting in stronger bonding through C=O groups. It is obvious that channels are not essential for the stabilization of methylene blue, which is observed not only in palygorskite, but also in the smectitic montmorillonite. In this presentation we will report additional results that show that the effect is not unique to methylene blue, and it appears in other cationic adsorbed dyes, when irradiated with different wavelengths. Further studies are needed to elucidate the interactions that yield photostabilization on some clay minerals, whereas fast catalyzed photodegradation is measured on others.
INTERACTIONS BETWEEN ORGANICS AND WATER MOLECULES WITH SILICATE SURFACE BY THEORETICAL ATOMISTIC METHODS

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Interactions between organic molecules and mineral surfaces are not easy to be determined experimentally and the Computational Mineralogist methods can be a good tool for this study. Interesting connections between this approach and some experiments, such as, microcalorimetry, spectroscopy and kinetic studies can be found. Some examples are presented in this work.

The interactions between organics and water molecules within the silicate surfaces can determine the crystallographic structure of organoclays. These interactions can determine the formation of water clathrates of organics on the phyllosilicate surfaces. Heterogeneous reactions of atmospheric volatile organic compounds (VOCs) on aerosol particles may play an important role in atmospheric chemistry. Silicate particles are present in air-borne mineral dust in atmospheric aerosols, and free-radical reactions can be different in the presence of these mineral particles. The spectroscopic properties of these systems during the reaction can be calculated, and interesting frequency shifts in the main vibration modes can give us some information about these interactions. The detailed chemical interactions occurring on the dust grain surfaces with organic molecules are of great interest, as they shed light on possible routes for life from extraterrestrial space to Earth, especially, adsorption of aminoacids, and ammonia-ices on silicate surfaces.
Beginning in the 1950s, and at an accelerating pace from the 1960s through the present, stable and radiogenic isotopic studies have added greatly to our understanding of the timing, conditions of formation, and post-formational alteration of clay minerals in soils, unconsolidated sediments, and sedimentary rocks. Clays neoformed in the weathering zone, in the sedimentary (epigenetic) environment, in the diagenetic environment, and in the hydrothermal environment carry oxygen and hydrogen isotopic signatures that relate to their conditions of formation. Those neoformed minerals which contain non-exchangeable K and Rb in many instances yield radiometric ages indicative of time of formation or alteration. Detrital clays may also carry $\overset{87}{\text{Sr}}/\overset{86}{\text{Sr}}$ ratios acquired in their source areas. Radiogenic and stable isotopic compositions of clays may thus be useful in establishing the provenance of those minerals in sediments. The isotopic compositions of clays are generally resistant to post-formational changes, absent chemical/mineralogical alteration. The magnitude of oxygen isotopic fractionations between a pair of minerals in equilibrium with one-another indicates the temperature at which the equilibrium was established. If formation of formation can be established independently of the oxygen isotopic data (e.g. from depth of burial and geothermal gradient), the isotopic composition of a clay can be used to infer the isotopic composition (and hence the source) of the mineral-forming fluid. Those latter studies may require geochronologic analyses to establish time of formation, from which depth of burial during clay mineral formation can be inferred.

In principle, intracrystalline isotopic fractionation between hydroxyl oxygen and structural bridging oxygen (e.g. Si—O—Si) in a clay can provide both temperature of formation and isotopic composition of the water from which the clay formed. Before this technique can be applied routinely, however, there remains need for additional work, refining analytical techniques and calibrating (as a function of temperature) the isotopic fractionation between the oxygens occupying different structural positions in the crystal.

Most studies of the formation and alteration history of clay minerals are enhanced by bringing to bear as many relevant techniques as possible. In particular, for most studies this means detailed analysis of geologic/geomorphologic setting, careful petrology and mineralogy, careful mineral separations followed by examination of mineralogy/crystallography of subfractions, and isotopic analyses of those well-characterized sub-fractions. For example, we have found (Giral-Kacmarcik et al., 1998) that in a laterite profile in Brazil, sub-fractions (separated by sieving) of kaolinite within the <2µm fraction of each sample had different oxygen isotopic compositions, and different fine-scale mineralogic/crystallographic characteristics. This indicated slightly different conditions of formation for each of those sub-fractions from a single <2µm fraction.
Shale formations are typically viewed as low-permeability seals in geologic carbon storage and have therefore received little attention with respect to acid gas interactions. Recently, utilization of captured CO2 for injection into fractured shale gas reservoirs to initiate secondary natural gas production is emerging as a parallel strategy with record US shale gas production. Early estimates indicate that between 10 and 30 gigatons of CO2 storage capacity may exist in the 24 shale gas plays included in current USGS assessments. However, storage of CO2 in clay-rich shale formations is fundamentally different from storage in more traditional reservoir rocks. Clay minerals have unique physical properties owing to their layered structure, small grain size, and consequently, large surface to volume ratio. For example, we recently reported the ability of CO2 to penetrate interlayer regions of swelling clays (montmorillonites) and expand the basal spacing. This mineral volume change was not observed with non-absorbing gases (He, N2) or with other clay minerals (kaolinite, chlorite, and mica). The diffusive nature of CO2 and processes controlling adsorption and desorption appear distinct for individual clay minerals.

Using specialized experimental techniques, clays were examined in situ while exposed to temperatures and pressures relevant to shale gas production and CO2 sequestration. Concentrations of adsorbed gases (CH4 and CO2) were obtained by monitoring the frequency changes on a quartz crystal microbalance. Structural changes and clay stability were measured with a pressurized X-ray diffraction technique in CO2 and CH4 atmospheres for comparison with non-absorbing gases (N2, He). In situ attenuated total reflectance infrared spectroscopy tracked clay hydration, gas adsorption, and water concentrations in the fluids during exposure to CO2 and CH4. Intercalation of CO2 appears dominant in some clay systems, whereas condensation of CO2 onto the clay surface prevails at supercritical conditions. Atomistic density functional simulations were employed to explain observed CO2 sorption or intercalation mechanisms.
CLAY MINERALS IN THE SAN ANDREAS FAULT: LESSONS LEARNED FROM ROCKS OF THE SAN ANDREAS FAULT OBSERVATORY AT DEPTH (SAFOD) DRILLHOLE

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Fault rocks in drill-cores from the SAFOD (San Andreas Fault Observatory at Depth) project in Parkfield, California contain a variety of newly formed clay minerals including smectite, illite-smectite and chlorite-smectite, as well as illite and chlorite. Using a range of analytical methods, we examine the influence of clay minerals on the mechanical behavior of the fault, namely X-ray diffractometry to analyze the bulk rock and clay mineralogy, electron microscopy (SEM and TEM) for element chemistry and microstructural analysis, ICP-OES for major element chemistry, 40Ar/39Ar dating for timing of illite growth, and X-ray texture goniometry for preferred orientation analysis. In this study of fault gouge and fractured mudrock, we describe the location and nature of smectitic clay minerals in the borehole, to assess the probable stability of smectitic phases at depth, the timing of clay growth, the fabric development during faulting, and the swelling behavior of smectite within the fault zone.

Samples from the fault zone show interconnected and pervasive networks of displacement surfaces that are coated with neoformed smectitic clay minerals. Geochemistry of major elements indicates element mobility occurred within the fault trace, attributable to the extensive circulation of hydrous fluids along fractures that were responsible for progressive dissolution and leaching of the wall rock during faulting. 40Ar/39Ar dating of the illicic mix-layered coatings demonstrate young crystallization and reveal an "older" fault strand (~8 Ma) at 3066 m measured depth and a "younger" fault strand (~4 Ma) at 3296 m measured depth. Today, the younger strand is the site of active creep behavior, reflecting continued activation/reactivation of clay-weakened zones. Fabric development, however, is low in the fault gouge at the mm-scale, showing little to no preferred orientation of clay minerals in the actively creeping section of the fault. Swelling of Mg-rich smectite in the fault gouge is repeatable and reversible, and able to occur at temperatures up to 95°C, comparable to the depths at which samples were collected. The localized concentration of chlorite-smectite minerals extends the role of smectitic clays to greater depths (down to ~10 km), with cataclasis and fluid infiltration creating nucleation sites for clay neomineralization. We conclude that ultrathin hydrous clay coatings on displacement surfaces play a key role in influencing weak fault and creep behavior along the San Andreas Fault at Parkfield and faults systems elsewhere.
INTELLECTUAL CLAY SCIENCE GENEALOGY OF PAUL A. SCHROEDER

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Paul A. Schroeder’s (past President of The Clay Minerals Society) intellectual clay science genealogy began in the 1970’s under the tutelage of Taylor H. Loop and Larry J. Doyle at New England College and the University of South Florida, respectively. Loop and Doyle were contemporaries of other great marine geologists (e.g., Orrin H. Pilkey*) who were associated with programs at Florida State and the University of Southern California, all inspired by Francis P. Shepard.

In the early 1980’s Paul took a position with Texaco Exploration and Production Services working under the direction of Harry M. Dahl. Dahl studied under Paul F. Kerr at Columbia University. It was at Texaco where Paul joined the CMS and also started working with his clay science colleague, Andrew R. Thomas (past CMS president). Robert A. Berner was Paul’s advisor at Yale University, where Karl K. Turekian and Robert C. Reynolds (Dartmouth College) also served as dissertation committee members. In 1991, Paul accepted a tenure track position as a clay mineralogist with the University of Georgia Department of Geology and collaborated with Vernon J. Hurst (CMS Pioneer in Clay Science). Paul currently continues to teach and conduct research in clay science at UGA promoting the intellectual ideologies of his scientific ancestors.

Links to learn more about people.

b http://en.wikipedia.org/wiki/Francis_Parker_Shepard
c http://www.minsocam.org/ammin/AM69/AM69_586.pdf
e http://www.geochemsoc.org/news/2013/03/18/karl-k-turekian-1927-2013
g http://www.gly.uga.edu/railsback/UGAGeoHistHurst.html
CARBON AND OXYGEN ISOTOPES IN PEDOGENIC GIBBSITE: AN EMERGING RESOURCE FOR UNDERSTANDING SOIL FORMING AND TRANSPORT PROCESSES

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The timing of crystallization and subsequent extent of mineral transport during soil formation are two factors that are often difficult to pinpoint in terrains dominated by moderate to severe chemical weathering. We suggest the complex interplay of factors responsible for soil mineralization such as changing respiration rate, parent mineral, biota, and climate, may be recorded by the stable and radiogenic isotopes trapped in the "carbonate" structure of pedogenic gibbsite and goethite. The exact mechanism for inclusion of carbon and oxygen into this carbonate component is poorly understood. Regardless, our observations of stable carbon and oxygen isotopes (and co-variation) in pedogenic gibbsite at various soil horizons in Cecil soils formed in the Southeast US Piedmont appears to reliably record the dynamics of soil CO₂ gas cycling. Dissolution and re-precipitation of gibbsite after incipient formation is suggested by the pattern of oxygen and carbon isotope compositions down profile, where at the top of the Bt horizon signatures are most like current atmosphere and deep in the C horizon signatures are most like the plants above. The gradient between the Bt and C is reflective of atmospheric CO₂ concentration / isotopic composition and the soil CO₂ concentration / isotopic composition at the time of mineralization. This suggests that carbonate component of pedogenic gibbsite may be useful for understanding soil forming conditions, which extends to proxying for paleo-PCO₂ estimates from paleosols (provided additional generations of recrystallization have not occurred).

Estimated exposure ages of the soil based on cosmogenic 10B and 26Al are useful for establishing the residence time of pedogenic minerals. Most soils are formed over time scales longer than natural climate change cycles and it is important to understand if the climate information is integrated and recorded in soil minerals. Resolution is needed to know if these isotopic signatures are representative of the most recent conditions or a combination of all past conditions. Carbonate occluded in pedogenic minerals offer the chance to determine both the age and environmental conditions of mineral formation and are therefore a powerful tool whose potential is only now beginning to be realized.
ALTERATION OF CLAYS IN ENGINEERED BARRIERS FOR NUCLEAR WASTE REPOSITORIES—WHAT ARE THE ISSUES?

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In most countries, geological disposal is the preferred option for final storage of high-level nuclear waste and spent nuclear fuel. The selected host rock and engineered barrier system will differ for the different national programs, but almost all programs foresee clay-based engineered barriers. For clay-based engineered barriers, bentonite and bentonite/sand mixtures are the favored option due to their inherently low hydraulic conductivity at full saturation. This ensures that diffusion of solutes such as nuclides will be the dominant mechanism for transport through the engineered barriers. Another advantageous property of bentonite is the build-up of swelling pressure in contact with water, ensuring the closure of unintentional gaps and openings. The predictability of the long-term behavior of bentonite (up to a million years) is key to the safety analysis and basically only untreated geological materials allow for such modeling.

The long time frame involved requires an in-depth understanding of possible alteration (in a very broad sense) processes affecting the bentonite:

a. Initially, when the repository is resaturated, strong hydraulic gradients will prevail and this may cause mechanical erosion of the bentonite in fractured host rock. Here, ion-exchange may be very important since the contact zone between the groundwater and the bentonite is small and the erosion properties of Ca- and Na-bentonite are very different.

b. The steep thermal gradient during early repository evolution when the near-field is undergoing resaturation may cause dissolution and re-precipitation of accessory minerals in the bentonite, resulting in some cementation of the bentonite matrix. In the long run, if the elevated temperatures persist, the smectite component in the bentonite may also undergo some crystallographic changes.

c. It is expected that bentonite will interact with repository components as well as with groundwater. Redox and chemical interactions with the metal waste canisters and cement-based reinforcements may also occur. The concentrations of cations in the local groundwater will determine the final composition of the exchanger in the bentonite. An intruding groundwater with a very low concentration of cations may also affect the mechanical stability of the bentonite.

All these alteration and transformation processes are safety-relevant as they may affect the hydro-mechanical properties of the bentonite. Therefore, it is important to have an in-depth understanding of expected processes in order to be able to quantify the extent of the alteration from a long-term perspective and to finally assess these alterations in the context of the safety analysis.
CLAY COMPOSITES AS BALLISTIC WITNESS MATERIALS: TIME, TEMPERATURE, AND HISTORY DEPENDENT MATERIAL PROPERTIES

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With the introduction of soft body armor in the 1960s methods for certifying armor systems were also developed. From several clay composites, foams, and gels, Roma Plastilina Clay #1 (RP1) was chosen and is currently used as the National Institutes of Justice ballistic witness material for back face deformation of soft body armor. Unfortunately, over the decades since RP1 was adopted, changes by the manufacturer to RP1 (brought about by pressure from other industries) have forced ballistics researchers to heat the composite to keep it within the specification developed in the 1960s. There is now a desire in the soft body armor testing community to replace the current material with new clay composites or materials which do not require thermal treatment prior to use. To support that effort a proper and complete characterization of the material properties of RP1 is needed.

Mechanical and thermal properties of RP1 were studied via small amplitude oscillatory shear (SAOS), large amplitude oscillatory shear (LAOS), uniaxial compression, and dynamic scanning calorimetry (DSC). Rheological characterization of RP1 via SAOS has confirmed antidegradative experience by users, the clay composite softens as it is “worked” (Figure 1a) and slowly stiffens as it rests (Figure 2a). Using small strains the mechanical properties can be observed without the measurement that strain is changing (Figure 1a, 0.07% strain). Higher strains result in time dependent mechanical properties (Figure 1a, 0.7% strain) and recovery of mechanical properties can also be observed by applying the small strain post “working” of the material (Figure 1b “Recovery”).

Upon heating the clay composite softens, prior “work” history is erased, and the composite undergoes a melting transition, however, recovery from heating is slow. Continuing mechanical characterizations into the LAOS or non-linear region, RP1 is a shear thinning material (modulus decreases with increasing strain) at all measured temperatures and transitions from a transient network to a viscous liquid when melted. The culmination of these experiments indicates a material with a time and work history dependent (thixotropic) non-linear mechanical response. Ideal replacement room-temperature ballistic witness materials should have a similar non-linear response to the heated RP1 without the time dependent material properties. In the interim understanding the time and temperature dependent properties will help guide RP1 users in developing procedures to mitigate the undesirable properties. The mechanical and thermal analysis and comparisons to “used” ballistic witness RP1 and proposed room-temperature clays will also be discussed.
Sodium bentonite clay comprised primarily of the mineral montmorillonite is the primary component in geosynthetic clay liners (GCLs). GCLs are thin (5-10 mm thick) factory-manufactured hydraulic barriers used in liners and covers for waste containment systems, including municipal solid waste (MSW) landfills. Replacement of the sodium cations (Na\(^+\)) in the exchange complex of bentonite by other cations in contacting liquids has been shown to affect swelling and hydraulic conductivity of the bentonite. Exchange reactions that cause a decrease in swell and an increase in hydraulic conductivity of the bentonite in GCLs can affect the performance of a waste containment facility adversely.

Ammonium (NH\(_4\)\(^+\)) in MSW leachate is known to replace Na\(^+\) in the exchange complex of montmorillonite, but the effect of NH\(_4\)\(^+\) in the exchange complex on the swelling and hydraulic conductivity of GCLs has not been studied extensively. This is important for GCLs used in bioreactor MSW landfills, which can have leachates with NH\(_4\)\(^+\) concentrations as high as 0.5 M (Barlaz et al. 2010).

The influence of ammonium on the hydraulic conductivity of GCLs for cases where complete or partial replacement of Na\(^+\) by NH\(_4\)\(^+\) occurs during permeation was explored in this study. Hydraulic conductivity tests were conducted on GCLs containing natural Na-bentonite with permeant solutions having NH\(_4\)\(^+\) concentrations of 0.005, 0.05, 0.1, and 1.0 M, with the latter simulating a worst-case scenario (Benson et al. 2007, Barlaz et al. 2010). Control tests were conducted using deionized (Di) water. Most of the tests were not in hydraulic or chemical equilibrium when this abstract was prepared. Thus, the findings represent a snapshot in time, and may not reflect the long-term equilibrium condition.

Hydraulic conductivity of the GCL is shown as a function of NH\(_4\)\(^+\) concentration in Fig. 1 for the tests conducted in this study. Hydraulic conductivities from tests set-up by Rauen (2007) of GCLs permeated with conventional and bioreactor MSW leachates are also shown in Fig. 1. For NH\(_4\)\(^+\) concentration < 0.05 M, the hydraulic conductivity is comparable to that obtained with Di water (~1.8×10
\(^{-11}\) m/s). The hydraulic conductivity increases slightly as the NH\(_4\)\(^+\) concentration approaches 0.1 M (4.7 times the hydraulic conductivity of Di water), and increases more than four orders of magnitude as the NH\(_4\)\(^+\) concentration increases from 0.1 to 1.0 M. The hydraulic conductivities obtained with actual MSW leachates are similar to those obtained by permeation with a NH\(_4\)\(^+\) solution (Fig. 1). Thus, GCLs with low hydraulic conductivity can be expected for many bioreactor leachates, but GCLs that are much more permeable may be realized for bioreactor leachates that have very high ammonia concentrations.

Fig. 1. Hydraulic conductivity vs. ammonium concentration for solutions prepared in this study and actual MSW leachates. Hydraulic conductivities obtained using Di water as the permeant solution are shown with solid lines.
The test conducted with 1.0 M NH$_4^+$ solution was continued for 50 pore volumes of flow. The influent liquid was then switched to DI water to determine if the hydraulic conductivity would return to the same hydraulic conductivity as obtained for a GCL with Na-bentonite that was permeated with DI water. After 18 PVF, the hydraulic conductivity of this GCL is 6 times greater (1.1x10$^{-10}$ m/s) than that of a GCL containing Na-bentonite (1.8x10$^{-11}$ m/s) and permeated with DI water (Fig. 1). Thus, replacement of Na$^+$ by NH$_4^+$ appears to cause a permeant change in the hydraulic conductivity of the bentonite.
Nitrogen is commonly identified as the major component of the Earth atmosphere and an important component of living organisms. The nitrogen content of rocks is much less widely known. The geochemical calculations of the nitrogen budget differ by wide margins, but they all agree that an amount of nitrogen comparable to atmospheric is fixed in the crust and that the majority of this nitrogen is fixed as ammonium in illite and micaceous minerals. The mechanism of supplying minerals with nitrogen is the diagenetic/metamorphic alteration of buried organic matter.

Details of this process have been studied using several collections of bentonites from around the world (Środoń, 2010) and a collection of shales from the Donbas coal basin (Ukraine: Środoń and Paukowksi, 2011), all representing a possibly broad range of diagenetic conditions. This study is mostly based on the bulk rock data, to avoid the question how representative for the bulk is the clay fraction of a rock, and to understand mass transfers within and between rocks. Quantitative mineral composition, %N, %Corg, %K2O and CEC were measured, and the nitrogen contents of the organic matter, of illite-smectite, and illite alone were calculated from these data, using the illite-smectite model of Środoń et al. (2009).

Bentonites are the simplest objects to study, as the detrital illite/micas and the organic matter do not complicate the pattern. The level of ammonium for potassium substitution in illite layers from bentonites ranges from a few up to 50%. The correlation of %N with % illite-smectite is low, and with % illite is high, which implies negligible contribution of exchangeable ammonium. Surprisingly, the content of N in illite layer (the parent of potassium substitution) is either decreasing or remains stable in the course of diagenesis. There is no source of N in bentonite layers, thus the bentonitic N records the migration of products of organic diagenesis within the basin.

In the Donbas shales the NH4+ for K+ substitution in illite ranges from 3 to 62%. The substitution is highest in the rocks with low amount of illite, which indicates that it is controlled by the supply of ammonium. 60-98% N is contained in the mineral fraction and the remaining parts in the organic matter. The mineral N is fixed in the authigenic illite and its concentration decreases during diagenesis, like in bentonites. This trend is reversed during anchimetamorphism when 1Md illite recrystallizes into 2M1, and gains additional N. In all but the most organic-rich shales, illite contains more nitrogen than could have been released from the organic matter present in these shales. These data imply that a big portion of the mineral N has been imported from outside the rock, what is consistent with the similar level of ammonium substitution in the organic-free bentonites.

Figure 1. Data for the Donbas shales demonstrate the supply control of the level of ammonium substitution in illite, most clear if only diagenetic 1Md illite is taken into account.

Modeling based on a realistic lithology of clastic sedimentary basin (relative volumes of coal, sandstone, and shale, plus illite content of the shale) indicates that the potential of N fixation by authigenic illite is often bigger that the release of N from the organic matter in such basin, and that a major vertical migration of ammonium is taking place. Such calculations can be used also in reverse: to evaluate the volume of source organic matter from the measurements of nitrogen fixed in shales. The modeling supports the dominant role of illite in the global cycling of nitrogen. It can be safely assumed that in common sedimentary environments almost all nitrogen released during organic diagenesis, and available as the ammonium cation, ends up fixed in illite.

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ABSTRACTS

CATION EXCHANGE CAPACITY WITH THE CU-TRIEN METHOD: SOURCES OF RANDOM AND SYSTEMATIC ERRORS IN THE DETERMINATION

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One of the increasingly used methods to determine the cation exchange capacity CEC is the exchange of the interlayer cations by Cu-Triethylene tetramine (Cu-Trien) following the procedure given by Meier & Kahr (1999). The advantage of this method is surely its simplicity, because the strongly coloured Cu-Trien complex can be quantified by a fast and precise photometric analysis. Precision and accuracy of the Cu-Trien method, however, has been recently discussed by Dohrmann et al. (2012), but observed differences even using the same (Cu-Trien) method still await explanations.

In this work we explored potential sources of errors of the Cu-Trien method in detail to elucidate the reasons. Own investigations, e.g., showed significant changes of the CEC with varying ratios of sample to Cu-Trien, although the CEC must not depend on sample weight. We found also that the first sample within a larger sample series deviated consistently from the following samples. Furthermore, reproducibility of sample series was poor, when repeated next day, despite of keeping all conditions constant (operator, sample, sample weight, Cu-Trien solution, pipette, time, ...).

We have identified various sources of errors: The temperature of the Cu-Trien solution varies the wetting behaviour of the pipette tips and thus changes the volume, when used twice or more often. A further source of error is the recommendation (originally made by L. Ammann, 2003) to add additional Cu-Trien to reach a nominal concentration of 100% Cu-Trien sensu strictu. This leads to substantial amounts of other ethylene amine molecules, which are not complexed with Cu²⁺. We could show that even pure Trien solution intercalates into smectites and blocks exchange sites. This effect of blocking the interlayer space is probably the largest source of error, rendering the exchange process a rather kinetic process, which depends then on rather subtle experimental details such as the fluid dynamics while mixing Cu-Trien with the solid.

Finally, we will present a modified version of the Cu-Trien method, which will provide better precision and accuracy, even for smectites with divalent interlayer cations.
THE LEGACY OF JOE L. WHITE, A FRIEND AND COLLEAGUE TO ALL HE MET

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Joe L. White served for most of his career as a professor in the Agronomy Department at Purdue University, West Lafayette, Indiana. He was one of a core group of faculty members at that time who promoted feelings of mutual respect, collegiality, and professionalism among faculty and students in the department. Students felt completely comfortable approaching him, as well as the other faculty members, because he, and they, treated them as peers, with a kindly interest that engendered warmth and understanding. He had a tendency to do his own research as much as possible during the night so that he did not tie up equipment being used by the students. When a student asked a question, he seemed to have an encyclopedic reservoir of information based on relevant literature citations. His many sabbatical leaves and travels throughout the world, and especially through Europe, also gave him an international reputation that attracted visitors from far and wide. He knew from memory where to go and how to find the many European research institutes, as well as the most efficient and economical ways of traveling.
Nitrate is linked to chronic human illness and to a variety of environmental problems, and continues to be a contaminant of concern in soils and natural waters. Improved methods for nitrate abatement, thus, are still needed. The purpose of this study was to expand upon previous studies which showed that redox-modified, iron-bearing smectite clay minerals can serve as nitrate reducers, and to measure the extent of structural Fe(II) reoxidation in the smectite as a consequence of nitrate reduction. In a recent study, we demonstrated that when the negative surface charge of smectite is made positive by adsorption of a polymeric organic cation (polydiallyldimethyl-ammonium chloride (poly-DADMAC)), the surface becomes attractive to anions, including nitrate. If the smectite is Fe-bearing, and the Fe has been previously reduced to Fe(II), then nitrate is reduced by redox interaction with the smectite. A similar reaction occurred when chitosan was used as the polymeric organic cation. The extent of structural Fe(II) reoxidation as a result of the redox interaction with nitrate was measured by chemical analysis and Mössbauer spectroscopy. The amount of nitrite (a reduction product from nitrate) found in solution failed to account for all of the Fe(II) oxidized, so other N reduction products may have also formed or perhaps nitrite was also present in the adsorbed phase. In this presentation further evidence regarding Fe(II) reoxidation will be presented and discussed.
Bentonite clay is planned to be used as a buffer material in high level radioactive waste repositories to protect the container of the waste from the surroundings. Montmorillonite is responsible for its sealing properties and any transformation of the montmorillonite to any non—swelling phase would negatively impact the repository performance. In Sweden, the waste is planned to be emplaced in a copper canister with an iron-insert for a combination of chemical resistance and mechanical strength. In addition to the iron in the canister, iron is also planned to be used for rock reinforcements and other constructions. It is known from the literature that metallic iron in several cases have caused mineral transformations of smectites. In 2006 the Alternative Buffer Material experiment started at Åspö Hard Rock Laboratory, Sweden, at 450 m depth. Two of each of the twelve different compacted clays (3 dm diameter discs) were placed in direct contact with each other, onto a heated iron cylinder (approx. 130 ºC). The first package (ABM1) was excavated in 2009, 2½ years after installation. In April 2013 the second package (ABM2) was excavated, 6½ years after the installation.

Powder X-ray diffraction data was collected using a Panalytical X’Pert Powder diffractometer using a Co-tube for X-rays. Complementary information about elemental composition was collected using a Panalytical Epsilon 3 XL X-ray fluorescence spectrophotometer (Rh-tube for X-rays; He gas). The analyzed samples are spatial profiles of the bentonite blocks, scramplings of the iron heater and also white and red precipitates from the iron heater or the bentonite. During the excavation visual observations indicated a strong interaction between the clay and the iron heater, seen as a dark discoloration of the iron-bentonite interface. The amount and/or type of corrosion on the iron heater were visually very different between the various types of bentonite. In several blocks centrosymmetrical precipitates such as anhydrite was found, and in one block a thick crust between the bentonite block and the iron heater was found (Fig. 1). This thick crust (Kungen #22) was correlated to a part of the package that had been somewhat warmer (approx 140-150 ºC), and within the crust halite was identified by XRD, hence boiling of the buffer may have occurred in this section causing salt enrichment.
In several scraping samples from the heater a mixture of corrosion products, bentonite and precipitates were found. Identified precipitates so far are calcite, aragonite, anhydrite and halite, and the corrosion products that have been identified are magnetite, hematite and goethite. In several cases at the iron-bentonite interface a new phase was found that seems to be a trioctahedral smectite (Fig. 2). The trioctahedral smectite show a reflection at about 1.55 Å compared to the 1.50 Å reflection found in dioctahedral smectite, and a 17 Å basal spacing when intercalated with ethylene glycol (Fig. 2). This trioctahedral phase was also seen in ABM1, however to a lower extent. There are also sporadic indications of other newly formed non-swelling phases with 7.6 Å and 10.0 Å reflections. So far 4 profiles have been analyzed, 11 white precipitates, 2 magnetic phases and 12 scrapings from the iron heater. More work is needed to sort out the differences between the clays caused by variations in their material composition, and the differences that are caused by variations in the experimental conditions. However, with a combination of data from ABM1 and ABM2 this seems rather achievable with time.

Figure 2. Powder X-ray diffraction data (Co K) of ABM2 Febex block 9—scraping of the iron heater: (i) Scraping on iron heater, (ii) magnetic part of scraping = magnetite, (iii) non-magnetic part of scraping (iv) non-magnetic part of scraping, with ethylene glycol showing 17 Å basal spacing (v) original Febex clay. Notice the difference in (v) and (iii) at 70-75 °2θ indicating a partial transformation from dioctahedral to trioctahedral smectite.
Silylation of layered double hydroxides (LDHs) has attracted much attention because silylated products exhibit properties suitable for many applications in materials science and environmental engineering. The covalent bond formed between silane and LDH surface enables a durable immobilization of the organic moieties, preventing their leaching into the surrounding solutions and improving the compatibility between LDHs and polymer matrix.

The main aim of this study is to investigate the influence of the number of hydrolysable groups in silanes on the structure and properties of the silylated products. Four silanes were used to investigate such an effect, i.e. trimethylchlorosilane (TMCS), dimethyldiethoxylsilane (DMDES), 3-aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS). The experiments were carried out in ethanol medium using water-rich LDHs as substrate via an induced hydrolysis silylation method (IHS).

Fourier transform infrared spectra (FTIR) clearly indicated new vibrations at around 1040 cm⁻¹ for APTES and TEOS modified products. These vibrations were ascribed to the concert bonding between silane and LDHs, which implied that APTES and TEOS could be grafted onto the surfaces of LDHs. For DMDES modified sample, only a weak vibration was observed at around 2960 cm⁻¹, corresponding to −CH₂ stretching of silane adsorbed on the LDHs surface. While for TMCS modified sample, not even −CH₂ could be observed, suggesting no concert bonding exists.

29Si MAS nuclear magnetic resonance spectra (29Si MAS NMR) displayed T (at -45−-75 ppm) and Q type (at -80−-75 ppm) signals for APTES and TEOS grafted samples, respectively. These signals indicated that tri- or quad- dentate silylation models were formed between silanes and LDHs. X-ray diffraction patterns (XRD) showed that the d003 values were not increased after silane modifications, which indicated that silanes were only present on the external surface and had little influence on the ordering of LDH sheets. The nitrogen adsorption tests displayed that all the samples had type IV isotherms with H₃ type hysteresis loop. The increase in value of BET surface area (S_BET) and total pore volumes (V_p) in all the silane modified samples partly contributed to the increase of S_BET and V_p.
Clathrate hydrates play a critical role in our nation's energy resources, energy security, and global climate change. Large quantities of untapped natural gas exist as hydrates in the arctic tundra and in seabeds where clay minerals compose a significant fraction of the sediments. Detrimentally, as seen in the Gulf oil disaster of 2010, gas hydrates can plug crude oil pipelines leading to flow assurance problems, considerable cost, and significant safety and environmental hazards. Additionally, greenhouse gas sequestration in hydrates could provide a partial solution to global climate change, especially if the hydrate formation rate could be enhanced by sediment surfaces, since methane is twenty times more effective than carbon dioxide in trapping heat.

Methane hydrates exist in nature as non-stoichiometric crystal structures formed at low temperatures and high pressures from ice-like water cages surrounding methane molecules. Large amounts of methane hydrates are known to exist in the arctic and within the shallow seafloor where the surrounding sediment plays a role in the stability of the hydrate (Hester and Brewer, Ann. Rev. Marine Sci., 2009). However, the recent discoveries in hydrate research are focused on homogeneous systems composed of simply water and methane (Walsh et al., Science, 2009). The smaller body of research investigating the kinetics and dynamics of heterogeneous systems has shown that the addition of a substrate affects the kinetics and thermodynamics of methane hydrate formation (Takahata et al., Mat. Trans., 2010).

To address the gap in fundamental knowledge regarding heterogeneous growth and stability of methane hydrates, we examine methane hydrate systems involving clay mineral surfaces that are common to many deposits (Boswell and Collett, Ener. Env. Sci., 2011). We used molecular simulations to evaluate the atomistic-level details of nucleation and structuring of methane hydrates on clay surfaces. Additionally, we explore how different surface properties, including the relative hydrophobicity and hydrophilicity, would enhance or destabilize the methane hydrates.

Clathrate hydrates play a critical role in our nation's energy resources, energy security, and global climate change. Large quantities of untapped natural gas exist as hydrates in the arctic tundra and in seabeds where clay minerals compose a significant fraction of the sediments. Detrimentally, as seen in the Gulf oil disaster of 2010, gas hydrates can plug crude oil pipelines leading to flow assurance problems, considerable cost, and significant safety and environmental hazards. Additionally, greenhouse gas sequestration in hydrates could provide a partial solution to global climate change, especially if the hydrate formation rate could be enhanced by sediment surfaces, since methane is twenty times more effective than carbon dioxide in trapping heat.

Methane hydrates exist in nature as non-stoichiometric crystal structures formed at low temperatures and high pressures from ice-like water cages surrounding methane molecules. Large amounts of methane hydrates are known to exist in the arctic and within the shallow seafloor where the surrounding sediment plays a role in the stability of the hydrate (Hester and Brewer, Ann. Rev. Marine Sci., 2009). However, the recent discoveries in hydrate research are focused on homogeneous systems composed of simply water and methane (Walsh et al., Science, 2009). The smaller body of research investigating the kinetics and dynamics of heterogeneous systems has shown that the addition of a substrate affects the kinetics and thermodynamics of methane hydrate formation (Takahata et al., Mat. Trans., 2010).

To address the gap in fundamental knowledge regarding heterogeneous growth and stability of methane hydrates, we examine methane hydrate systems involving clay mineral surfaces that are common to many deposits (Boswell and Collett, Ener. Env. Sci., 2011). We used molecular simulations to evaluate the atomistic-level details of nucleation and structuring of methane hydrates on clay surfaces. Additionally, we explore how different surface properties, including the relative hydrophobicity and hydrophilicity, would enhance or destabilize the methane hydrates.
The exchange of aqueous iron (Fe) atoms with solid phase Fe atoms has recently been demonstrated for many Fe (oxyhydr)oxide minerals. Whether this process is significant in environmentally complex systems, such as soils or sediments, however, remains unclear. Here, we demonstrate that in 28 days, approximately 14% of the Fe atoms in a natural soil from the Bisley Site in the Luquillo Critical Zone Observatory, Puerto Rico undergo iron atom exchange. The soil contained 1,039 ± 40 mmol kg\(^{-1}\) Fe with 182 ± 10 mmol kg\(^{-1}\) Fe (18% of total Fe) extractable by citrate-ascorbate (CA). X-ray diffraction (XRD) indicates the soil clay fraction is dominated by kaolinite (d-spacings of 7.21 Å and 3.34 Å) with well-crystallized goethite (4.16 Å) and a chlorite or vermiculite-like phase (14.17 Å) also detectable. Four broad populations of Fe were identified by Mössbauer spectroscopy including: Fe\(^{3+}\)-oxyhydroxides (80%), Fe\(^{3+}\) in clays or organic complexes (14%) and two populations of Fe\(^{2+}\) phases (6%). In batch sterile experiments, we introduced an aqueous \(^{57}\)Fe\(^{2+}\) spike to soil slurries under anoxic conditions and traced the isotopic composition of the aqueous phase and in 0.5 M and 7 M HCl extractions of the solid phase over 28 days. A period of rapid Fe atom exchange coincided with the initial sorption of Fe\(^{2+}\)(aq) over the first day and was followed by slower Fe atom exchange throughout the rest of the experiment. Mössbauer spectroscopy indicates that the \(^{57}\)Fe label re-crystallizes preferentially as Fe\(^{3+}\)-oxyhydroxides of very low crystallinity (i.e., short-range-order, SRO), suggesting these phases likely participate disproportionally in Fe atom exchange reactions with Fe\(^{2+}\)(aq) in natural soils. We conclude, soils exposed to anoxic conditions where significant Fe\(^{2+}\)(aq) is present are likely to exhibit Fe-atom fluidity in at least the SRO Fe-oxyhydroxide phases.
HYDRAULIC CONDUCTIVITY OF GEOSYNTHETIC CLAY LINERS TO LOW-LEVEL RADIOACTIVE WASTE LEACHATE

Kuo Tian*,1, Erin L. Hunter1, Jiannan Chen1, Craig H. Benson1, and James M. Tinjum1

1Department of Civil and Environmental Engineering, University of Wisconsin-Madison, Madison, WI, 53706 USA;
2Department of Engineering Professional Development, University of Wisconsin-Madison, Madison, WI 53706 USA
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Low-level radioactive waste (LLW) and mixed waste (MW) disposal facilities in the United States are required to function effectively for at least 1000 yr. Many of these disposal facilities employ multilayer barrier systems to control the flux of contaminants into the surrounding environment. Geosynthetic clay liners (GCLs) are common elements in barrier systems due to their low hydraulic conductivity (k) to water, which is typically < 10^-10 m/s. GCLs are thin prefabricated clay liners consisting of a layer of granular or powdered bentonite clay sandwiched between two geotextiles. In some cases, a geomembrane is laminated to the geotextiles too.

The swelling and hydraulic conductivity of bentonite are known to be sensitive to the chemical characteristics of the liquid that hydrates the bentonite as well as the permeant liquid. For some hydration conditions or permeant liquids, GCLs can be much more permeable than to deionized (DI) or tap water. Experiments were conducted in this study to evaluate how typical LLW leachates in facilities operated by the US Department of Energy’s (DOE) Office of Environmental Management affect the swelling of bentonite and the hydraulic conductivity of GCLs. Ion exchange during permeation was also evaluated.

Five commercially available GCLs were evaluated. Two of the GCLs contained conventional bentonite (labeled CS and GS) and the other three contained polymer-modified bentonite (labeled CR, GR, and CC). Two of the polymer-modified bentonites (labeled CC) consisted of polymer intercalated in the montmorillonite lamella using a specially developed process. The GCLs were hydrated and permeated with two synthetic leachates representative of leachates at DOE LLW disposal facilities. Control tests were also conducted with DI water. All of the hydraulic conductivity tests were conducted in flexible-wall permeameters. Chemical composition of the influent and effluent liquids was monitored during testing.

Characteristics of the synthetic leachates were identified through a review of leachate data compiled by DOE. The synthetic leachates used in the experiments were chemically identical, except one leachate was prepared without radionuclides (Non-radioactive Synthetic Leachate, NSL) and the other with radionuclides (Radioactive Synthetic Leachate, RSL).

Table 1. Chemical characteristics of the synthetic leachates.

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Radionuclide concentrations in RSL mimicked the highest concentrations observed at the DOE facilities to represent a worst-case scenario. Characteristics of the synthetic leachates are summarized in Table 1.

Hydraulic conductivity vs. time is shown in Fig. 1 for three of the GCLs permeated with RSL. The GCLs shown in Fig. 1 represent the three categories of polymer-modification used within the study. A gradual increase in hydraulic conductivity was observed for four of the five bentonites permeated with NSL or RSL. In contrast, one of the polymer-modified bentonites showed a rapid decrease in hydraulic conductivity initially. None of the tests are currently in hydraulic or chemical equilibrium at the time this abstract was prepared. Average hydraulic conductivities of four of the GCLs to NSL and RSL are shown in Fig. 2 for the most recent sampling times. At this point in the study, addition of radionuclides to the leachate has resulted in higher hydraulic conductivity for the polymer-modified GCLs. For all GCLs, permeation with RSL or NSL has resulted in hydraulic conductivities equal to or greater than the hydraulic conductivity to DI water.
Predicting the reliability of geologic carbon sequestration depends on understanding capillary and wetting interactions of supercritical (sc) CO₂ with reservoir and caprock minerals. However, relatively less information is currently available on capillary pressure (Pc) relations to brine saturation, especially for the imbibition (brine rewetting) process important at later stages of geologic sequestration. Given the limited availability of measurements of the Pc dependence on water saturation (Sw) with scCO₂ as the displacing fluid, large-scale models of CO₂ sequestration commonly rely on capillary scaling of nonreactive immiscible fluid pairs (air-water, or oil-water) to predict scCO₂–brine behavior in reservoirs. This common practice motivated us to conduct tests of capillary scaling predictions using homogeneous sands because their “standard” capillary properties are very well constrained. We measured drainage and imbibition processes on homogeneous quartz sand (~300 µm) with scCO₂ brine at pressures of 8.5 and 12.0 MPa (45 °C) and air-brine at 21 °C and 0.1 MPa. For this purpose, we employed a novel configuration of the scCO₂–brine reservoir with the sand sample chamber that allowed very fine Pc resolution while maintaining high total pressures. We found that drainage and imbibition at intermediate Sₚ levels shifted to P values that were from 30% to 90% lower than predicted based on accounting for differences in interfacial tensions. By augmenting interfacial tension-based predictions with differences in independently measured contact angles from different sources, more consistent scaled P(Sₚ) relations were obtained. However, these still did not converge onto universal drainage and imbibition curves. We also found that capillary-trapped volumes for scCO₂ measured at P = 0 were significantly greater than for air. Given that the experiments were all conducted on the same homogeneous sand, and that scCO₂–brine interfacial tensions are fairly well constrained, we conclude that the observed deviations from scaling predictions resulted from scCO₂–induced decreased wettability. Further studies are needed to better understand how wettability alteration by scCO₂ arises on different mineral surfaces, and how hydraulic behavior is affected by these alterations.
Non-crystalline hydrated silica phases, often termed “opaline phases,” occur in many industrial mineral deposits. Often they are misidentified as anhydrous crystalline silica phases such as cristobalite.

The usual classification of these phases is opal-A, opal-CT, and opal-C, proceeding from amorphous to states seemingly of some structural regularity. Research involving differential scanning calorimetry, thermal-XRD, and neutron diffraction show the situation to be much more complex. Opal-CT, for example, has characteristics not shared by either opal-A or opal-C. These findings further complicate quantification by questioning the appropriate calibration standard to use.
POROSITY AND GAS SHALE FORMATION DIAGENESIS

Tomasz Topór1*, Arkadiusz Derkowski1, and Douglas K. McCarty2

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Measuring porosity in shales is challenging because of the fine grained texture, the presence of extremely small pore size with complex pore structure within the matrix and organic matter, extremely low permeability, and the strong interaction of water with the clay mineral surface. Porosity measurements in shales and the other unconventional reservoirs (UCR) require a special approach to eliminate the significantly higher level of uncertainty.

In this study we use dual liquid porosimetry method (DLP) that is the modified water immersion porosity (WIP), to investigate over 100 core shale samples from 19 wells from Eastern Europe Silurian gas-shale plays. The samples represent the bottom of Silurian strata with a 50m target area from 1400m to 5700m. This sample set provides a unique opportunity to track the change in porosity from the same strata during diagenesis. The DLP method uses DI (deionized water) and kerosene as an immersing fluid to measure bulk density, grain density and total porosity. DI has strong affinity to clay mineral surface thus, it is believed to penetrate whole system of the pores, including the illite-smectite (I-S) expandable interlayer. Kerosene is a non-polar liquid and it is believed to act like a hydrocarbon inside the pore system, non-wetting the clay surfaces. The samples were characterized for whole rock quantitative mineral composition, along with cation exchange capacity, as a function of depth and a degree of organic matter maturation.

The preliminary results showed a wide range (2—36%) of the total porosity for samples saturated with DI (total porosity) and kerosene (effective porosity—a proxy for free gas), with the general trend of strong porosity reduction with depth. Bulk and grain density measured for both liquids are well correlated. Total porosity measured by DI, when kerosene porosity is subtracted is well correlated with the CEC of I-S and CBW estimated by thermogravimetric method, what is evidence that the ineffective porosity strongly depends on clay mineral content. Porosity measured by DI water, when CBW is subtracted, showed good correlation with porosity measured by kerosene. However, the variety of porosity, as well as TOC, within a ~50m interval suggests heterogeneity of mineral and organic matter within short intervals. The second order variability of the porosity depends on the type of organic matter dominating the sample.

Understanding the reason for strong heterogeneity among the samples and how diagenesis affects the ineffective/effective/mineral-organic porosity is a key to accurate evaluation of gas plays.
CLAY MINERALOGY AND DIAGENESIS OF DEVONIAN K-BENTONITES FROM WESTERN BLACK SEA REGION, TURKEY

Ozge Unluce1, Asuman Gunal Turkmenoglu*1, Omer Bozkaya2, M. Cemal Goncuoglu1, and I. Omer Yilmaz1

1Middle East Technical University, Department of Geological Engineering, Ankara, Turkey;
2Pamukkale University, Department of Geological Engineering, Denizli, Turkey

*asumant@metu.edu.tr

A set of thin K-bentonite beds interbedded with limestone-dolomitic limestone strata of Middle to Late Devonian—Lower Carboniferous Yılanlı Formation are exposed at quarries and along the roadcuts around Zonguldak and Bartın areas from the western Black Sea region of Turkey. The present study focuses on the clay mineralogy and origin of illites in these K-bentonites using data collected by optical microscopy, XRD, SEM-EDX and ICP-MS analysis.

Illite is the major phyllosilicate mineral which is occasionally associated with kaolinite and mixed-layer illite smectite, whereas quartz, feldspar, zircon, pyrite, calcite, dolomite and gypsum are the non-clay ones in K-bentonites. The crystal-chemical characteristics of illite (Kübler index-Ki, polytypes, d060) samples from two different locations at Yılanlı Burnu and Bartın areas, are identified as varying between 0.47-0.93 (average 0.69 D02q) and 0.63-1.05 (average 0.80 D02q), respectively. In addition to Ki data, the contents (maximum 5 %) of swelling component smectite and crystallite size values (10-20nm) of illites indicate that the K-bentonites are affected by high-grade diagentic conditions. Illite polytype ratios (2M1/(2M1+1Md %) are found to vary between 15-40% (average 25%) for the Yılanlı Burnu samples and 25-35% (average 30%) for those from the Bartın area. d060 values of the studied illites are 1.499-1.503 Å, averaging 1.499 Å, reflecting the octahedral Fe+Mg compositions are between 0.27-0.50 and indicate dioctahedral compositions close to ideal muscovite within muscovite-phengite interval.

The results obtained from the present investigation pointed out that K-bentonites evolved by high grade diagentic conditions, approximately 100-150°C, and formed from the products of volcanic eruptions having unknown source and distance during Middle-Late Devonian time.

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Upper crustal faults have traditionally been viewed in terms of brittle deformation, mostly involving processes such as fracturing and cataclasis. However, faults are not simple planar surfaces marking the contact between moving blocks. Instead, they are complex and evolving zones that often contain fault rock. There is growing evidence from recent observations on natural fault rocks that chemical and state transformations of clay play a key role in shallow faulting. For example, mudrocks from an actively creeping zone in the San Andreas Fault drillhole (~3.2 km depth) contain both illite-smectite (i-S) and chlorite-smectite (C-S) phases, based on microscopy and x-ray studies. Of particular significance is their occurrence as thin, nm-thick clay coatings on polished and striated fracture surfaces (Schleicher et al., 2010), similar in appearance to, but smaller than slickensided surfaces commonly found in exhumed brittle fault rocks. These clay precipitates on displacement surfaces promote creep and mechanically-weak fault behavior. Elsewhere, exhumed mountain belts, such as the Rocky Mountains, preserve clay-bearing fault gouge at major fault contacts containing neocrystallized illite (van der Pluijm et al., 2006). Clays in fault rock formed during enhanced circulation of aqueous fluids along evolving microfracture networks by low-temperature dissolution-precipitation reactions.

In addition to its potential for fluid fingerprinting, the process of clay growth allows the application of direct dating of faulting at low temperatures. Argon illite age analysis of drilled and exhumed illite-bearing fault rock constrains the absolute timing of faulting and regional sampling places constraints on rates of crustal deformation.

In summary, clays in faults rocks can preserve information on mineral and state transformations, fluids and mass transport, mechanical properties, and dates and rates of crustal deformation. This presentation will examine such aspects of clay mineralization in fault rocks, using new and recent examples from various settings, particularly focusing on clay characterization and the challenges of radiometric dating of detrital and authigenic illite crystallites.
 REPLACEMENT OF OLIVINE BY SERPENTINE IN THE QUEEN ALEXANDRA RANGE 93005 CARBONACEOUS CHONDRITE (CM2): REACTANT-PRODUCT COMPOSITIONAL RELATIONS, AND ISOVOLUMETRIC CONSTRAINTS ON REACTION STOICHIOMETRY AND ELEMENTAL MOBILITY DURING AQUEOUS ALTERATION

Michael A. Velbel1, Eric K. Tonui2, and Michael E. Zolensky3

1Department of Geological Sciences, Michigan State University, East Lansing, MI 48824, USA;
2Upstream Technology, BP America, Inc., Houston, TX 77079, USA;
3KT Astromaterials Research and Exploration Science, NASA Johnson Space Center, Houston, Texas 77058, USA

inosilicate pseudomorphic and alteromorphic replacement of olivine by serpentine produced both centripetal and counterclockwise serpentinization textures in several CM2 chondrites. The composition of this textural variety of serpentine is uniform in each previously studied meteorite, independent of the composition of olivine being replaced, and different between meteorites. Coarse olivines of widely varying compositions (Fosm) in Queen Alexandra Range (QUE) 93005 (CM2) are similarly replaced by compositionally uniform serpentine (Mg0.73±0.05Fe0.27±0.05)3Si2O5(OH)4. The narrow compositional range of serpentine replacing coarse olivine throughout each meteorite indicates that the aqueous solution from which the serpentine formed was compositionally uniform on scales at least as large as the meteorite. Isovolumetric textures and compositional observations constrain elemental redistribution from coarse olivine to serpentine and to surrounding phases during serpentinization. Regardless of olivine’s composition, isovolumetric replacement of coarse olivines by serpentine of the observed composition released more Mg and Si from olivine than was required to form the serpentine. Excess Mg and Si released by olivine destruction and not retained in serpentine were exported from the replaced volume.

Olivines with different Fa/Fo proportions contributed different amounts of Fe and Mg to the serpentine. Fayalitic olivines released more Fe than required to form the serpentine replacing them, so some of the Fe released from fayalitic olivine was exported from the replaced volumes. Forsteritic olivines released less Fe than required to form the serpentine replacing them, so some Fe was imported into the replaced volumes augmenting the small amount of Fe released from forsteritic olivine. In QUE 93005 Fs10 is the threshold composition between Fe-exporting and Fe-importing behavior in individual olivine-serpentine pairs, which released exactly the amount of Fe required for formation of the observed uniform composition. Compositions of serpentines sovoilumetrically replacing olivines, and threshold olivine compositions, in QUE 93005 differ from the corresponding values in the Nogoya (CM2) carbonaceous chondrite.

Solvent and solute species diffused through the serpentine between the olivine-serpentine interface and the aqueous solution outside the pseudomorphs/alteromorphs. In QUE 93005, some of the Fe released from fayalitic olivine in excess of the amount required to form serpentine reacted with S sourced from outside the pseudomorphs to form FeS decorating the margins of the pseudomorphs/alteromorphs of serpentine after fayalitic olivine. Such FeS-decorated outlines after fayalitic olivine do not occur in ALH 81002 or Nogoya, indicating different Fe and S mass transfer regimes in different CM2 chondrites. Mg, Fe, Si, and S in the aqueous solution, including the excess Mg and Si exported from all serpentines pseudomorphs/alteromorphs after olivine of any composition, were available to be incorporated into other phases spatially separate from the pseudomorphs/alteromorphs after olivine, including regularly interstratified serpentine-tochilinite. Serpentines that replaced coarse olivines in QUE 93005 and ALH 81002 are less magnesian than those in Nogoya, indicating that the Nogoya aqueous-alteration environment was more highly evolved toward Mg-rich solutions than the environment indicated by the composition of the serpentine in ALH 81002 and QUE 93005. This easily located and characterized phase assemblage may be potentially useful for characterizing classes of varying degrees of alteration in brecciated and heterogeneous CM chondrites.
John Hower was Professor of geology at Montana State University in the late 1950 and early 1960's where he began a very useful University career teaching and training students in basic research concerning mainly clay minerals. The impetus for this was the more or less recent discovery of a useful and reliable X-ray diffraction - diffractometer system which could be used to produce a large number of analyses of samples instead of the time consuming and less precise system of photographic film detection. At the time we had a new and fascinating method of multiple analysis. The field of clay mineralogy, dependent on microscopic identifications of very fine grained material became a new science. The old definition of a clay mineral, grains of less than 2 micrometers in diameter, was based upon the limit of optical identification. Below this limiting size the geological material was called clay, or "I don't know what it is" minerals. The X-ray diffractometer was the key to a new horizon, which of course John realized and used to great effect. A first step was to model the results of X-radiation and crystalline material using the clay mineral structures in order to interpret correctly the results obtained. This was done with Bob Reynolds and John spread the good word into the community.

John Hower came into his own, showing his intuition and rigor of scientific thought. As it turns out the scientific and commercial communities were ready for such research in that much of the "easy oil" had been found and explored and new resources needed to be investigated but they were often in deep water areas where drilling costs were greater than those on land and more precision was needed to find the existence of probable resources. Here diagenesis was the key in that much of the material investigated was in more or less recent basins where the diagenetic evolution would be the key to the presence of possible petroleum resources.

John gave his students the intellectual setting for the enterprise and encouraged us in the use of the new methods and materials. Of course not all of the research subjects were "oil oriented" but they stemmed from this area of application which gave us a valid position in the scientific community of the time. The most interesting aspect of his personality was this enthusiasm for scientific investigation. John was always fascinated with the way one obtained the results and the assemblage of the resulting data that could be used to understand the basis of the problem. He always insisted upon a good, solid reasoning based upon the data. He felt that the process of understanding the situation was the most exhilarating part of his scientific life. This of course he passed on to his students, as their number and scientific production attests. We had one diffractometer and were four or five to use it, so it worked 24/24 and we spent a lot of time at strange hours talking about our results and speculating about a number of things. John was always ready to talk, discuss and encourage us in our endeavors.

After John's initial work on glauconite, probably the diagenesis of clay minerals is the great achievement of his career. He certainly was an inspiration, guide and above all a very good friend to his students.

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Given John and Bob's initial professional experience with an oil company, the starting point for much of the early student work was the region of geological investigation dealing with sedimentary rocks and the effects of variable temperature and pressure on clay mineralogy. The geological realm of diagenesis was ripe for such work in that little was known at the time due to a lack of analytical methods to determine small changes in clay mineralogy in a series of samples. Here John Hower came into his own, showing his intuition and rigor of scientific thought. As it turns out the scientific and commercial communities were ready for such research in that much of the "easy oil" had been found and explored and new resources needed to be investigated but they were often in deep water areas where drilling costs were greater than those on land and more precision was needed to find the existence of probable resources. Here diagenesis was the key in that much of the material investigated was in more or less recent basins where the diagenetic evolution would be the key to the presence of possible petroleum resources.

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LONG-TERM BENTONITE HYDRAULIC CONDUCTIVITY EVOLUTION UNDER LOW HYDRAULIC GRADIENTS

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The application of Darcy’s law for the calculation of the coefficient of permeability requires that the velocity of the flow be proportional to the hydraulic gradient, that is to say, that the value of the coefficient obtained be independent of the hydraulic gradient applied during the determination. This means that the relationship between flow and hydraulic gradient is linear, and that this linear relationship crosses the origin. For different reasons, this condition may not be fulfilled, thus invalidating the use of Darcy’s expression. Furthermore, the values of bentonite permeability are frequently obtained under high hydraulic gradients, necessary to induce a measurable flow in such low permeability materials.

To clarify the effect of hydraulic gradient on the value of hydraulic conductivity, the hydraulic conductivity of a Spanish bentonite (the FEBEx clay) was measured under low hydraulic gradients (200 to 7500) applying low injection pressures (lower than 2.4 MPa). The bentonite was compacted at dry densities between 1.4 and 1.7 g/cm³. The diameter of the samples was 5.0 cm and their height 2.5 cm.

No evolution of the permeability with time (up to 2600 days) was observed, and no clear effect of the hydraulic gradient employed on the permeability value obtained was detected (Figure 1). In addition, the values obtained were in the order of those obtained for the same dry densities applying higher hydraulic gradients (of 15200 on average).

The permeability coefficient obtained was different if it was computed using the inflow or the outflow, being always lower in the latter case, due to the fact that, even after more than 2600 days of testing, the inflow continued to be...
higher than the outflow. The difference between both values seemed lower when the density of the bentonite was lower and decreased over time. The redistribution of water between macro and microstructure and the higher density of the water adsorbed on the bentonite interlayer could be the explanation for this observation.

The results are plotted in terms of flow as a function of hydraulic gradient in Figure 2, along with those results obtained applying higher hydraulic gradients for samples of the same dry density. The overall proportionality between flow and hydraulic gradient is clear. The dispersion found when hydraulic gradients lower than 2000 were applied could indicate that the critical gradient for this bentonite and this range of densities would be around this value. The critical gradient is the hydraulic gradient below which flow occurs but it is not Darcian. The possible threshold hydraulic gradient would be around 200 or 1400, depending on the dry density, since no measurable flows were obtained for hydraulic gradients below them. The threshold gradient seemed to depend not only on the density but also on the injection pressure.

This research was conducted in the framework of the FEBEX Projects (EC Contracts FI4W-CT95-006 and FIKW-CT-2000-00016), the NF-PRO Project (EC Contract FI6W-CT-2003-02389) and the PEB Project (FP7/2007-2011 Grant Agreement 249681), all of them related to the study of the engineered barrier system in underground nuclear waste disposal facilities.
Most of the upland soils of the Savannah River Site (SRS) are products of extensive weathering of mid-Tertiary coastal plain sediments, mostly micaceous sands. In the most mature of these soils, the only phyllosilicate minerals detectable by X-ray diffraction in the clay fraction are kaolinite and hydroxy-interlayered vermiculite (HIV). The HIV is thought to have formed by extensive weathering of muscovite, during which most of the original K was lost. Non-exchangeable K is associated with the HIV in an amount corresponding to a few percent by mass of the HIV. K-Ar measurements show that this K is in particles of late Paleozoic age, presumably fine remnants of muscovite within the highly weathered particles that are now mostly HIV. Non-exchangeable K associated with HIV in amounts corresponding to 1-2% by mass appears to be characteristic of the sandy coastal plain soils of the southeastern USA.

Sequential extractions have shown that most of the original K was leached away during pedogenesis. Only a few percent of the Cs and ~25% of the Rb now held by these soils are present as native constituents of the mica remnants. Sequential extractions have shown that very little (<5%) of the Cs and Rb occur on ordinary cation exchange sites or with non-silicate phases such as organic matter and iron oxides, which leaves interlayer wedge zones within particles that are now mostly HIV as the likely microenvironment where the Cs and Rb were selectively retained and are now held. In newly completed experiments under slightly acidic conditions approximating the natural soil environment, only about 12% of the natural Rb in each of three SRS soils mixed with added highly enriched 85Rb over 2.1 years. Thus, nearly 90% of the Rb in these soils is fixed against isotope exchange, and the amount of such fixed Rb is several times the amount of Rb expected to be native to the muscovite remnants.

Extraction of much of the fixed Rb by strong acid, at a temperature low enough that K and Ar are not extracted from the muscovite remnants, has confirmed the presence of fixed Rb elsewhere than in the muscovite. Slow extractions with weak acid show that this fixed Rb is more difficult to extract than the Cs. We infer that both Rb and Cs are held within slightly expanded di-trigonal cavities in the narrower parts of interlayer wedge zones that surround muscovite remnants and that the smaller Rb ions are more deeply entrenched toward the wedge apices (Figure 1). The Rb/K ratio in the SRS soils is sufficiently high that Rb ions may be the predominant species near the apices of interlayer wedges if the mica remnants are ~100 nm in diameter. Rb ions in slightly expanded cavities near the wedge apices should be held against ion exchange more strongly than K ions in these sites, and thus may have acted to stabilize the boundaries of the mica remnants and substantially limit further loss of K.

Figure 1. Conceptual view in cross-section of an interlayer wedge zone where HIV grades into mica. Kn denotes native K in mica, f denotes Rb and Cs ions that are effectively fixed in slightly expanded di-trigonal cavities, and ex denotes exchangeable ions. Modified from Wampler et al.9

Elevated Cs/K and Rb/K ratios indicate that Cs and to a lesser extent Rb were selectively retained in the SRS soils while most of the original K was leached away during pedogenesis. Only a few percent of the Cs and ~25% of the Rb now held by these soils are present as native constituents of the mica remnants. Sequential extractions have shown that very little (<5%) of the Cs and Rb occur on ordinary cation exchange sites or with non-silicate phases such as organic matter and iron oxides, which leaves interlayer wedge zones within particles that are now mostly HIV as the likely microenvironment where the Cs and Rb were selectively retained and are now held. In newly completed experiments under slightly acidic conditions approximating the natural soil environment, only about 12% of the natural Rb in each of three SRS soils mixed with added highly enriched 85Rb over 2.1 years. Thus, nearly 90% of the Rb in these soils is fixed against isotope exchange, and the amount of such fixed Rb is several times the amount of Rb expected to be native to the muscovite remnants.

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The structural characteristics of smectites are very important to understand the process of their formation and alteration as well as to optimize their technical application. X-ray powder diffraction is one of the most common methods used for analysis of structural properties. The Rietveld structure refinement from XRD powder patterns provides a possibility to obtain structural parameters from natural or impure samples, such as bentonites or clays. Unfortunately, almost all of smectites show turbostratic disorder. This type of structural defect leads to strongly asymmetric peak broadening and makes the use of conventional structural models impossible. Nevertheless, we try to use the Rietveld method to refine some important structural parameters of dioctahedral smectites, such as occupation of octahedral position (trans- or cis-vacant, iron content) and their proportions as well as the layer charge density from powder diffraction patterns. Thus, the project aimed to investigate what extent of structural information can be obtained from powder diffraction patterns of dioctahedral smectites. It intends to give the basis for a routine characterization of the smectites in mixtures, such as bentonites without chemical analysis of purified smectites fractions.

To overcome the problem of disorder, the structure of the smectites is described to be a turbostratically disordered stack by the single-layer approach (Ufer et al., 2004). A R0 mixed-layering of cis- and trans-vacant layers will be treated by a recursive calculation within the Rietveld method (Ufer et al., 2008). In order to avoid the problems of unknown species and positions of cations and amount of water in the interlayer, the patterns come from Cu-triethylenetetramine exchanged smectites (Kaufhold et al., 2011).

A series of dioctahedral smectites covering a broad range of composition and structure was chosen for testing the model. The smectites were purified and characterized by XRD, chemical and thermal analysis methods. Conventional laboratory XRD powder patterns were run for the Cu-triethylenetetramine exchanged samples. First results of the refinement from simulated diffraction data and the experimental data of the externally characterized smectites will be presented.
CONNECTIONS IN CLAY SCIENCE: OH WHAT A TANGLED WEB WE WEAVE!

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“Clays?! Who would want to take an entire class on clay minerals?” So began my thoughts of Clay Mineralogy class at Dartmouth College (1982). I knew not what I had done. Robert C. Reynolds, taught the class. He was kind, yet intimidating by the speed of his synapses. He loved talking basketball with his student Leo Lynch. He had just bought his first Kawasaki 1200cc, and broke a rib when it fell over on him. It was a stressful year; the year that John Hower died and Bob disappeared on his motorcycle for about three days, grieving. But on the day of class, we waited patiently and he stormed into the room, spoke for 50 minutes about the x-ray powder ring diffraction function with words flying out so fast that those in the front row had to duck from the spatter! Herman Roberson was a visiting scientist then, and showed great relief.

That year spawned several clay scientists. I was studying Economic Geology, looking for a litho-geochemical tool for finding sedimentary exhalative sulfides in black shales, which eventually led Bob to co-advise my thesis on ammonium illites. Michelle Hluchy (Alfred) was my classmate, and was advised by Bob for both M.S. and Ph.D. Michelle had worked with Rich April (Colgate) and later with Steve Altaner (Illinois). Patricia Maurice (Notre Dame) was also in our class and we worked together on writing NEWMOD 7, a class exercise that Bob led us through to show us how we could use computers to solve complex physical equations. Bob published his more sophisticated NEWMOD soon thereafter: Rod Parnell (NAU), worked with Ed Perry (UMass) and then with Bob for his Ph.D. Our families are close comrades in Arizona.

I landed at Louisiana State University in 1985, where I worked with Ray Ferrell, a student of Ralph Grim, and mentor of my work on ammonium illites in hydrocarbon basins. I introduced me to Dennis Eberl, (USGS) that year when we sampled the Walsen Dike bentonites. Denny and I have since collaborated on studies of antibacterial clays. It was not until I met Fred Longstaffe (Western Ontario) that I became convinced that stable isotopes of clays useful. He mentored my work on oxygen isotopes of clays, but it was not until my Ph.D. work on boron isotopes in illite that I realized the full circle of academic life... Bob Reynolds started his career studying B in illite; I wish we could compare notes.

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The Devonian-Mississippian Bakken Shale is arguably the most productive oil-shale in the United States, between 4.4 and 11.4 billion barrels of recoverable oil remaining (2013 USGS estimate). In addition, >6.7 trillion cubic feet of natural gas is technically recoverable. Unconventional stable isotopes may be useful in exploration of such unconventional oil-shales, to guide decisions regarding optimal resource recovery with minimal environmental impact.

Boron and lithium are found in elevated concentrations (100s ppm) in conventional oilfield brines, and appear to be released from kerogen along with hydrocarbons (HC). The isotopic composition of kerogen-derived B and Li is enriched in the light isotope relative to most minerals and waters in earth’s crust. Therefore, three samples of Bakken shale (lower member) representing immature (Ro=0.5), mature (Ro~1.0) and overmature (Ro=3.0) regions of the basin were studied for baseline data on the elemental abundance and isotopic exchange of these trace elements between kerogen and illite-smectite as the black shale matured thermally in this confined reservoir.

Using secondary ion mass spectrometry (SiMS), isotopic compositions of B and Li were measured on <2μm clay fractions, DCM extracted bitumen, and HF isolated kerogen from the Bakken shale. In addition, core samples were analyzed by NanoSiMS to map the distribution of nanopores (4-200 nm) that form in the mature kerogen as HC are generated and migration occurs. Variations in H/C and O/C in nanopores were explored, to identify ‘live-C’ (thermally matured, migrated HC) in the matrix of ‘dead-C’ (remnant kerogen).

Results for the <2μm clay fraction (organics removed) show a linear decrease in $^{11}\text{B}$ (+7 to −12 ‰) and $^{7}\text{Li}$ (+10 to −1‰) from immature to overmature shale (1s errors <1‰). The kerogen $^{11}\text{B}$ ranges from (−12 to −15‰) while $^{7}\text{Li}$ decreases (−6 to −18‰) with increasing thermal maturity. These trends suggest kerogen is the source of isotopically light B and Li that substitute in illite during diagenesis. Bitumen $^{11}\text{B}$ averages +3‰ and $^{7}\text{Li}$ averages +10‰, showing no change with kerogen thermal maturity.

Knowing isotope fractionation factors for B and Li between ilite and water and using the Ro values to estimate temperature, a calculation of the $^{11}\text{B}$ and $^{7}\text{Li}$ of water was made, assuming equilibrium. From this an estimate of isotope fractionations between the kerogen and water are calculated for B and Li as a function of temperature:

For B: $1000 \ln(a_{\text{ker-water}}) = −28(1000/K) + 39$; For Li: $1000 \ln(a_{\text{ker-water}}) = −8(1000/K) − 1$

There is a 30% range in B-isotope fractionation as B is released from kerogen over a temperature range of ~70–280°C, while Li-isotope fractionation changes by ~10‰. The large isotope fractionations over temperatures of HC generation make B and Li released from kerogen a viable tracer of mature HC related fluids. Elevated concentrations of light B and Li in shale nanopores may help to identify optimal targets for enhanced oil recovery.
SYNTHESIS AND CHARACTERIZATION OF CHABAZITE ANALOG FROM DELAMINATED META KAOLIN WITH HIGH CRYSTALLINITY AND LOW SI/AL RATIO

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Chabazite is a highly polarizing molecular sieve material. It is one of the most widely used natural zeolites because of its exceptional ion exchange and adsorption properties. Even in its impure natural state it can outperform synthetic zeolites for many applications. Even better forms of chabazite might emerge if uniform crystals could be grown in the laboratory. It would be especially interesting if this could be accomplished using natural reactants like clays without addition of templating or seeding agents. Here we report a template free, seedless chabazite synthesis. A chabazite analog was hydrothermally synthesized from delaminated metakaolin without addition of mineral chabazite as seeding agent and without a template. The as-synthesized chabazite samples were characterized by XRD (Figure 1), SEM (Figure 2), EDX, BET, TGA and DSC techniques. The results show that the as-synthesized chabazite samples display high crystallinity and a low Si/Al ratio of ~1.3. The morphology of the synthetic chabazite retained the platy morphology of the raw metakaolin. The synthesis compositions and crystallization conditions were optimized by systematic experiments.

Figure 1. Powder XRD patterns of: (a) metakaolin, and (b) synthetic chabazite analog.

Figure 2. SEM images of: (a) metakaolin, and (b) synthetic chabazite analog.
Natural sodalite rocks were mechanically sliced into membrane sheets with a thickness of about 1.5 mm. These membrane sheets were then characterized by XRD, SEM/EDX and TGA/DSC (Figure 1). Single gas hydrogen and CO$_2$ permeances through these membranes were experimentally evaluated at temperature range of 25 °C–500 °C. To the best of our knowledge this is the first time such measurements are recorded for natural sodalite membranes. Compared to the gas permeability data from various forms of supported synthetic sodalite membranes reported in the literature, relatively high hydrogen permeances of 7.01 $\times$ 10$^{-8}$ mol m$^{-2}$ s$^{-1}$Pa$^{-1}$ and ideal H$_2$/CO$_2$ selectivity of 12.7 were obtained at 500 °C through the natural sodalite rock membranes (Figure 2). The positive temperature dependence of gas permeances was observed indicating zeolitic activated diffusion through the natural sodalite membranes. Thermal analysis (TGA/DSC) of the natural sodalite showed distinctly different thermal behavior from that of the reported synthetic counterparts at high temperatures (above 300 °C). The corresponding experimental gas permeation results at high temperatures suggest partial crystal structure changes of natural sodalite due to high temperature cycle tests at ~500 °C. The observed ideal H$_2$/CO$_2$ selectivity is well above that predicted by Knudsen diffusion (4.7) at 500 °C, demonstrating the potential of using natural sodalite materials in high temperature gas separations. Further fundamental research of natural sodalite membranes and gas diffusion mechanism through them are needed to provide valuable insight into their potential applications in high temperature hydrogen separations.
The interfacial reactions between clay minerals and life materials such as amino acids, peptides, and DNA, were investigated based on the combination of spectroscopy methods and molecular simulation. Besides, a series of life materials/clay minerals composites were successfully prepared. The results of characterization and density functional theory showed that life material can be intercalated into the galleries of clay minerals. The limitation structure of “molecular container” in the galleries of layered double hydroxides can effectively protect the intercalated molecules from damage under extreme conditions such as heavy metal, ultraviolet, extremely pH and enzymatic destruction. This study provides theoretical and experimental evidence for the roles of clay minerals in the origin of life.
CRYSTAL STRUCTURES AND DOMAIN STRUCTURES OF FERRIHYDRITE: DIRECT OBSERVATION USING Z-CONTRAST IMAGING METHOD

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Ferrihydrite is a common Fe-oxy(hydroxide) nano-mineral with very reactive surfaces in modern sediments. It also occurs in ferritin, an Fe storage in human and other living organisms. Ferrihydrite is a common precursor of goethite and hematite in low-temperature geological environments, such as in banded iron formations. However, the structure of ferrihydrite is still under debate. Due to the nano-crystallinity, structural disordering of the ferrihydrite, and the uncertainty of whether or not ferrihydrite is single phase, previous studies from indirect measurements using both elastic scattering (diffraction, and nano-diffraction), and inelastic scattering of x-ray were not able to provide agreeable structure models. The issues such as number of structural phases, unit cell parameters, stoichiometry, ordering of Fe, and whether ferrihydrite has tetrahedrally-coordinated Fe are still controversial. With spherical aberration-corrected scanning transmission electron microscopy (STEM), we can obtain locations of Fe atoms and vacancies in ferrihydrite directly from high resolution Z-contrast images. Two polymorphs are confirmed: ferrihydrite-4H (~ 2/3) and ferrihydrite-2H (~1/3). Intergrowth of the two polymorphs can also occur with (001) as interface. The 4H polymorph has ABAC packing for oxygen atoms, and the 2H polymorph has ABAB packing. All Fe atoms occupy octahedral sites. Fe and vacancy ordering in ferrihydrite-4H phase results in locally doubled and tripled unit cells along a-b directions. Due to structural disordering between Fe and vacancies, ferrihydrite can be considered as a 2-D crystal with two strong (hk0) diffraction peaks. The calculated XRD pattern based on the new structural models fit observed and reported XRD patterns well. Stoichiometry of 6-line ferrihydrite is close to Fe(iii)$_{0.75}$$(O, OH)_2$ based on occupancy fitting, i.e., between Fe(OH)$_3$ and FeOOH, instead of between FeOOH and Fe$_2$O$_3$.
The results from electron diffraction, high-resolution transmission electron microscopy (HRTEM), and Z-contrast imaging indicate that there are periodic and nonperiodically interstratified structures in the Li-Al-chlorite (cookeite) — pyrophyllite series. The interstratified pyrophyllite / chlorite mineral (lunijianlaite) coexists with pyrophyllite (Al2Si4O10(OH)2), cookeite (LiAl4(Si3Al)O10(OH)8), corundum (Al2O3), and diaspore (AlO(OH)). The general stacking sequence of the interstratified structures is nonperiodic along the c-axis. Three polytypes (1-layer, 2-layer, and 1M d) of the 1:1 interstratified pyrophyllite / chlorite were identified based on selected-area electron diffraction (SAD) patterns and 1-dimensional HRTEM images. 2-dimensional HRTEM images show that neighboring chlorite and pyrophyllite layers are coherently bonded.

Z-contrast images directly show positions of atoms and stacking sequence of the 1:1 interstratified pyrophyllite / chlorite. The structure of the mixed-layer can be considered as a modified 2-layer cookeite structure (with Cc symmetry, Zheng and Bailey, 1997) by removing half of brucite-like layers (to form pyrophyllite layer). Z-contrast images also reveal polarity of the T-O-T layer of chlorite layer. Possible symmetry for the ordered 1:1 interstratified pyrophyllite / chlorite is C1.

The interstratified pyrophyllite / chlorite crystals crystallized from Al-rich hydrothermal solution which both chlorite and pyrophyllite can crystallize from. The nonperiodically interstratified chlorite/pyrophyllite is a non-equilibrium crystallization product, which is similar to the interstratified chlorite/biotite crystallized from hydrothermal solution at non-equilibrium state (Wang and Xu, 2006). The simplified reactions may be expressed as:

\[
\begin{align*}
4G^{4+} + 2A^{3+} + 12H_2O &= Al_2Si_4O_{10}(OH)_{2} + 22H^+ \\
3G^{4+} + 5.33A^{3+} + 18H_2O &= Al_{4.33}(Si_3Al)O_{10}(OH)_{8} + 28H^+
\end{align*}
\]
Figures and Captions: Left figure shows possible stacking structures between chlorite and pyrophyllite. The angle close to 90 degrees will be the most possible one for the 1:1 interstratified pyrophyllite / chlorite based on measured angle. Right figure is a Z-contrast image showing positions of Al and Si (bright spots). The neighboring T-O-T layers are related by 120 degrees rotation.
Interactions between clay minerals and microbes are ubiquitous in natural environments. It is reported that some bacteria may greatly influence the decomposition and transformation of clay minerals. For example, the illitization of nontronite took place in two weeks when catalyzed by a Shewanella strain under anoxic atmosphere at room temperature and pressure. However, the Fe-rich nontronite is not the most common type of smectite. Most natural smectite is montmorillonite bearing poor Fe. Up to now, few researches have been devoted to the interactions between Fe-poor smectite and bacteria under aerobic atmosphere. Therefore, we studied the effect of certain aerobic bacteria on the local structure transformation of montmorillonite.

Experiments were conducted under aerobic atmosphere at 35°C and 1 atm. The mineral samples were bentonite containing about 90% montmorillonite and 10% cristobalite, collected from Jianping District of Liaoning Province, China. The aerobic bacteria named Bacillus mucilaginosus 3027, kindly donated by Chinese Academy of Agricultural Science, was inoculated into suspension of sterilized bentonite powder and cultured for 20 days. The culture media contained 1.0 g/L of yeast extract, 5.0 g/L of sucrose, 0.5 g/L of MgSO4, 0.02 g/L of K2HPO4, 5 mg/L of FeCl3•6H2O and 10 mg/L of CaCl2. During this period, 1.0 mL solutions were extracted regularly for pH and Si concentration analysis. After the experiments, minerals were collected and characterized by FTIR, XANES, XRD and SEM. Abiotic controls with only sterilized bentonite were conducted simultaneously.

Initially, the pH of biotic solutions decreased, probably caused by acidic metabolites produced by bacteria during their growth and metabolism. Meanwhile, Si concentration in the solutions increased, suggesting the release of Si from the tetrahedral sheets of solid mineral. These might later trigger a local structure distortion in montmorillonite, as indicated by the FTIR spectrum. The local structure change was also implied by reduced symmetry of coordinate octahedral geometry, referred from the broadened edge crest in the Fe k-edge XANES. More importantly, newly formed quartz was detected in SR-XRD patterns, indicating phase transformation of montmorillonite after interacting with the bacteria. Furthermore, layer collapse and edge curling were observed by SEM. These morphological changes might be attributed to the diffusion of mineral structure transformation from local to a wider scale. The local structure change of montmorillonite represents an important initial stage of smectite transformation, and this aerobically microbe-mediated reaction might help explain Si release and mineral transformation in smectite bearing soils and sediments.
Tubular halloysite is a potential carrier for the loading of drug actives because of its significant reserves, unique mesoscopic (2-50 nm) or even macroscopic (>50 nm) lumen, and excellent biocompatibility. The active guests loaded on halloysite exhibited slow release under the diffusion limitation by the halloysite nanotube. Unfortunately, due to the weak interaction between halloysite and guest, the loading capacity of halloysite was relatively low. This disadvantage severely limits the application of halloysite as carrier in pharmaceutics. In this work, the performance of halloysite as carrier for ibuprofen (IBU) loading was studied. In particular, the effects of 3-aminopropyltriethoxysilane (APTES) modification and thermal pretreatment of halloysite on the loading and release of IBU were investigated. The purified halloysites were heated at 120°C and 400°C, and the products were labeled as Hal/120 and Hal/400, respectively. And the APTES-modified halloysite products were labeled as Hal/120-A and Hal/400-A. The loading of IBU was achieved by soaking method, and the IBU-loaded halloysite products were labeled as IBU-Hal/120, IBU-Hal/400, IBU-Hal/120-A, and IBU-Hal/400-A. The in vitro drug delivery assays were performed in phosphate buffer solution (pH=7.4).

IBU was mainly loaded into the lumen and partially on the external surface of halloysite. The order of IBU contents was as follows: IBU-Hal/400-A (14.8 wt %) > IBU-Hal/120-A (12.7 wt %) > IBU-Hal/400 (11.8 wt %) > IBU-Hal/120 (11.7 wt %). The IBU was initially anchored to the surface hydroxyl groups of halloysite by hydrogen bonding, followed by further bonding of IBU with the anchored IBU to form hydrogen-bonded aggregates. The APTES modification of halloysite promoted the loading of IBU by introducing a strong affinity through electrostatic attraction between the introduced aminopropyl groups of APTES and the carboxyl groups of IBU. Thermal treatment at 400°C did not destroy the tubular morphology or the crystal structure of halloysite and had little effect on IBU loading in unmodified halloysite. For the APTES-modified halloysite products, thermal treatment by reducing water content in halloysite restricted the grafting of APTES in the lumen space, and further increased IBU loading. All IBU-loaded halloysites exhibit a burst release of IBU with a following slow release. Owing to the strong electrostatic attraction in APTES-modified halloysites, the burst release was much more suppressed and the release rate was lower than that in unmodified ones. The in vitro release profiles of the IBU-loaded halloysites were well fitted with the modified Korsmeyer-Peppas model. The IBU release mechanism of the unmodified halloysites was Fickian diffusion, whereas it was non-Fickian diffusion for the modified ones. These mentioned findings are of meaning for broadening the use of halloysite as carrier for drugs and other active molecules in the pharmaceutical, pesticide, and coating industries.
One of the most efficient ways of disposal big volumes of low and middle active radioactive wastes is their injection in a liquid form to the deep permeable layers-reservoirs, constrained with low permeable clay layers of a big thickness. Liquid radioactive wastes (LRW) consist primarily of acids and alkaline. In the majority of cases the calculation of clay containing reservoir or isolating clay layers permeability and dynamics of the pollutant migration is based on the constant properties of migration media. Although many researches show that clays’ structure and properties may change dramatically after the acid and alkaline treatment. Obviously it will change the dynamics of the migration process of such wastes through the reservoir rocks and isolating layers. The present work aimed to reveal possible transformations of clay minerals under the accl and alkaline treatment for the further use in a wastes filtration and diffusion models.

Two consequent approaches were used to reveal such transformations. First of all sandstones from the liquid waste disposal reservoir layers were studied. Those samples were collected within and out of the influence zone of LRW. Obtained results showed the presence of a new-formed smectites, well-ordered and poorly ordered kaolinites as a possible result of the wastes solutions influence. Those minerals may appear as a result of the source clay minerals transformation provided by the additional material of a plagioclase and volcanic glass nature, or a synthesis on the source of plagioclases, carbonates and volcanic glass.

Samples composition and structure were primarily studied with the XRD, XRF, IR, TEM and SEM analyses. The XRD analysis combined with chemical analysis showed that samples primarily consist of quartz, feldspars with a small amount of clay minerals such as smectite, illite-smectite, kaolinite, illite, and vermiculite up to 10%. SEM analysis allowed us to find the difference in composition and morphology of clay minerals between the samples from the wastes’ influence and at a proximal distance from it.

Then, for the purpose of confirming one of the proposed mechanisms of clay mineral appearing, the following experiments were run. The fraction <0.1 mm was separated to decrease the amount of nonreactive quartz from the reservoir layer samples that weren’t exposed to LRW influence. These fractions then were treated with acid and alkaline solutions with a composition close to the real LRW but without unstable isotopes. Treatment was conducted in digesters at 150 °C for a time period from 8 hours to 2 weeks. Additionally the long-term experiments were run for a time period from 1 day to 2 months.

To confirm the possibility of clay minerals transformation in a way that was observed in real samples the following experiments were run. Ca-montmorillonite and two different kaolinites of good and poor degrees of order were used as objects. To provide an additional source of Al₂O₃, MgO and SiO a volcanic glass and aluminum oxide gels. The treatment was conducted with nitric and acetate acids and with sodium hydroxide solutions as a prevalent components of LRW under the same conditions described above.

One of the most efficient ways of disposal big volumes of low and middle active radioactive wastes is their injection in a liquid form to the deep permeable layers-reservoirs, constrained with low permeable clay layers of a big thickness. Liquid radioactive wastes (LRW) consist primarily of acids and alkaline. In the majority of cases the calculation of clay containing reservoir or isolating clay layers permeability and dynamics of the pollutant migration is based on the constant properties of migration media. Although many researches show that clays’ structure and properties may change dramatically after the acid and alkaline treatment. Obviously it will change the dynamics of the migration process of such wastes through the reservoir rocks and isolating layers. The present work aimed to reveal possible transformations of clay minerals under the accl and alkaline treatment for the further use in a wastes filtration and diffusion models.

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EFFECTS OF DESICCATION CYCLING AND CATION EXCHANGE ON HYDRAULIC CONDUCTIVITY OF GEOSYNTHETIC CLAY LINERS

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Geosynthetic clay liners (GCLs) consist of a thin layer of bentonite clay sandwiched between two geotextiles. Hydraulic conductivity of GCLs is largely governed by the extent of osmotic interlayer swelling of the bentonite during hydration and permeation, and depends strongly on the solution chemistry and its impact on composition of the cation exchange complex. If the bentonite in a GCL is hydrated insufficiently and if cation exchange has resulted in an exchange complex comprised predominantly of polyvalent cations, osmotic swelling is inhibited and the hydraulic conductivity of the GCL can be much higher than anticipated (Lin and Benson 2000; Benson and Meer 2009; Scalia and Benson 2010).

Laboratory experiments were performed to investigate the effects of wet-dry cycling and partial cation exchange on the hydraulic performance of two GCLs containing polymer-modified bentonite. One of the GCLs contained a dry mix of polymer and bentonite and the other a bentonite-polymer nanocomposite (BPN). GCL specimens were initially permeated for one month to simulate a wet spring scenario for a GCL in a landfill cover. Permeant solutions included deionized water (DI) used as a control, a dilute solution representing typical pore water chemistry encountered in cover soils used for containment facilities, and a dilute solution containing primarily divalent cations representing a worst-case pore water in cover soil (Scalia and Benson 2010).

Two desiccation techniques were used to assess the effects wet-dry cycling on the hydraulic conductivity of GCLs. The methods consisted of (i) ambient air-drying under an applied vertical stress simulating ~1 m of overlying cover soil, or (ii) an in-permeameter drying technique where gas of known humidity is circulated over the GCL (Fig. 1). Ambient air-drying requires removing the GCL from the permeameter after hydration, which causes a change in stress and can result in disturbance. The in-permeameter method precludes the need to move the GCL and eliminates the change in stress and the potential for disturbance. The ambient drying method employs rigid perforated PVC plates placed above and below the GCL to limit disturbance due to physical movement of the GCL. The in-permeameter drying technique employs direct control of relative humidity by employing the Automated Relative Humidity Control Apparatus. Gas of known humidity is circulated over the GCL (Fig. 1). Ambient air-drying requires removing the GCL from the permeameter after hydration, which causes a change in stress and can result in disturbance. The in-permeameter method precludes the need to move the GCL and eliminates the change in stress and the potential for disturbance. The ambient drying method employs rigid perforated PVC plates placed above and below the GCL to limit disturbance due to physical movement of the GCL. The in-permeameter drying technique employs direct control of relative humidity by employing the Automated Relative Humidity Control Apparatus.

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computer-proportioned mixing of vapor-saturated air and desiccated air in a closed environmental chamber. Air with a relative humidity of 25% was used in this study. Both drying methods were used to desiccate GCLs to gravimetric water contents near 15%. Rehydration was conducted in the permeameter concurrent with measurement of hydraulic conductivity.

GCLs are shown in Fig. 2 that were desiccated by (a) ambient air-drying and (b) the in-permeameter technique. Both approaches lead to uniform desiccation, as confirmed by water content measurements (ASTM D2216) obtained from samples spatially distributed across the GCL. Hydraulic conductivity testing of the specimens after wet-dry cycling is ongoing.
Swellings are common components of claystones, mudstones and shales, and are frequently present in the caprocks and faults that seal potential CO2 storage reservoirs in the shallow subsurface. Recent experiments have demonstrated that besides swelling due to water uptake, smectites can also swell by a few percent when exposed to supercritical CO2, provided that the hydration state of the smectite lies between the fully dehydrated state (basal d-spacing $d_{001}$ $\leq$ 10.0 Å) and the mono-layer or 1W hydration state ($d_{001}$ = 12.5 Å). This range of hydration states is widely believed to be relevant for the pressure-temperature conditions characteristic of potential CO2 storage reservoirs at depths of 1.5-3 km. However, since previous experiments on CO2-induced swelling have been done on unconfined samples, no data exist on the stress that develops when free swelling due to CO2 exposure is prevented by confinement of the sample under in-situ pressure, temperature and hydration conditions.

In this study, three series of 5 to 9 individual uniaxial compression experiments were performed in a 1-dimensional compaction die, i.e. under laterally confined conditions, using smectite samples prepared by pre-compacting fine montmorillonite powder (Wyoming Na-SWy-1) at an applied axial stress of ~60 MPa. We then reduced the axial stress to pre-selected values in the range 20-40 MPa and finally introduced supercritical CO2, maintaining the axial pressure ($P_{CO2}$) used was 10 MPa. The effective axial stress ($\sigma_i$) experienced by the samples at the instant that CO2 was introduced, due to purely mechanical effects of the CO2 pressure, fell in the range 9-26 MPa, thus simulating initial effective overburden stresses corresponding to burial depths of 0.5 to 2.5 km (depending on rock density and pore fluid pressure). The initial experimental conditions employed were therefore similar to in-situ reservoir and caprock conditions with a hydration state in the range from zero to 1 water layer.

Figure 1. Results of the present swelling stress experiments. Swelling stress is defined as the change in effective axial stress generated due to clay swelling after introduction of CO2 at 10 MPa pressure. a) Swelling stress versus initial effective stress $\sigma_i$ experienced by the sample at the instant of CO2 introduction. b) Swelling stress versus the final effective stress $\sigma_f$ experienced by the sample when equilibrium is reached.

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The experimental results for the three series of experiments are plotted in Figure 1. This shows the magnitude of the swelling stress measured versus the initial effective stress ($\sigma_i$—Figure 1a) and the final effective stress ($\sigma_f$) experienced by the samples (Figure 1b). The swelling stresses generated fall in the range 6 - 10 MPa. The results show that increasing the effective (overburden) stress does not prevent CO$_2$ uptake occurring but does reduce the swelling stress developed, presumably through a reduction in the amount of CO$_2$ taken up by the clay sample. In addition, focusing on Figure 1b which represents the final equilibrium state achieved in the experiments, the swelling stresses attained at 44°C in the presence of lab air and humidity (experiment series S1), and at 50°C in the presence of a fully water saturated pore space (experiment series S3), are generally higher than at 50°C in the presence of lab air and humidity (experiment series S2). Moreover, the S1 and S3 series exhibit a clear negative dependence of swelling stress on final effective stress while the S2 series shows less sensitivity to effective stress. This may reflect differences in hydration state between the samples under the respective conditions, or may result from changes in the chemical potential of the CO$_2$ with temperature and water activity.

The results imply that CO$_2$ penetration into smectite-bearing caprocks and faults in geological storage systems, under a given initial effective stress, will in general lead to an increase in effective normal stress components. This will in turn promote closure of fractures, thus enhancing sealing integrity. Further work is needed to evaluate the risk of swelling-induced damage effects and to determine the effects of temperature and the presence of liquid water on the hydration state of smectites under in-situ conditions.
INFLUENCE OF CATION EXCHANGE CAPACITY ON THE LAYER SPACING OF CATION-ANION ORGANO-MONTMORILLONITES

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With typical cationic and anionic surfactants cetyltrimethylammonium bromide (CTAB) and sodium dodecylsulfonate (SDS) as modifiers, natural Na-montmorillonites (Na-Mt), Ca-montmorillonites (Ca-Mt) and artificial Na-montmorillonites (A-Na-Mt) with different cation exchange capacity (CEC) were modified by solution intercalation method respectively. Then cation-anion organo-montmorillonites (O-Mt) were characterized by x-ray diffraction (XRD), the results show that the CEC of three type montmorillonites (Mt) and the influence mechanism were discussed. The results show that the CEC of three type Mt all have influence on the layer spacing of cation-anion organically modified Mt (see Figure 1). The smaller the CEC is, the easier it is to obtain the cation-anion OMt with bigger layer spacing (see Figure 1 O-Na-Mt-1, O-Ca-Mt-1 and O-A-Na-Mt-1). When CEC is greater than a certain value, the degree of layer spacing changes decreases. Among these Mt, the CEC of natural Na-Mt has the greatest influence on the layer spacing (see Figure 1 O-Na-Mt-1, d001=6.90nm), Ca-Mt comes second (O-Ca-Mt-1, d001=6.85nm) and the third is artificial Na-Mt (O-A-Na-Mt-1, d001=5.52nm). But the order degree of O-A-Na-Mt is the best. During the first 1.5 h, CTAB was added to three Ca-Mt (different CEC) and after 1.5 h, SDS was added. The resultant organo- montmorillonites (OMt) in different time were characterized by XRD. The relation curves that O-Ca-Mt layer spacing varies with time are obtained (see Figure 2). The result show : the rules that layer spacing varies with time are different in the three Ca-Mt. However, the layer spacing are basically the same after the reaction equilibrium (see Figure 2, t=1.5h). After adding SDS, the rules that layer spacing varies with time are same in the three Ca-Mt. However, the layer spacing are different after the reaction equilibrium (see Figure 2, t=3.0h) and the layer spacing are anticorrelated with CEC magnitude.

Fig.1 XRD patterns of modified different Mt by CTAB and SDS

Fig.2 Tendency chart of cation-anion OMt\(d_{001}\) as time changes from Mt with different CEC modified by cation-anion surfactants

Fig.3 Tendency chart of cation-anion OMt\(d_{001}\) as time changes from Mt with different CEC modified by cation-anion surfactants

ABSTRACTS

INFLUENCE OF CATION EXCHANGE CAPACITY ON THE LAYER SPACING OF CATION-ANION ORGANO-MONTMORILLONITES

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BIOLOGICAL OXIDATION OF IRON(II) IN MICROBIALLY REDUCED NONTRONITE COUPLED WITH NITRATE REDUCTION BY PSEUDOGULBENKIANIA SP. STRAIN 2002

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Nitrate contamination in aquifers is a serious worldwide environmental problem. Although much is known about nitrate degradation in these environments, especially via microbial pathways, a complete understanding of all degradation processes, especially in clay mineral-rich soils, is still poorly understood. The objective of this study was to study the coupled processes of microbial oxidation of Fe(II) in microbially reduced nontronite and nitrate reduction by Pseudogulbenkiania species strain 2002. Bio-oxidation experiments were conducted in bicarbonate-buffered medium under both growth and nongrowth conditions. The extents of Fe(II) oxidation and nitrate reduction were measured by wet chemical methods. X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM), and 57Fe-Mössbauer spectroscopy were used to observe mineralogical changes associated with Fe(III) reduction and Fe(II) oxidation in NAu-2. The bio-oxidation extent under growth and nongrowth conditions reached 67% and 57%, respectively. Over the same time period, nitrate was completely reduced under both conditions to nitrogen gas (N₂), via an intermediate product nitrite. Magnetite was a biogenic mineral product from nitrate–dependent Fe(II) oxidation, as evidenced by XRD data and TEM diffraction patterns. The results of this study highlight the importance of iron-bearing clay minerals in the global nitrogen cycle with potential applications in nitrate removal in soils.
A UNIQUE APPLICATION OF NATURALLY MIXED PALYGORSKITE AND MONTMORILLONITE (PALY-MONT) CLAY

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Palygorskite is a unique and very rare clay mineral. Palygorskite clay has found increasing applications but commercially acceptable quality palygorskite clay deposit is very limited worldwide. In reality, there are always some other minerals or impurities associated with palygorskite mineral in clay. A notable mixture with such other mineral is the natural mixture of palygorskite clay with montmorillonite clay. In the patent # 5008226, 1991, Dennis Taylor described this mixture as “Naturally occurring mixtures of calcium bentonite and attapulgite clay.” Although the term attapulgite is used, the term of palgyorskite clay is preferred per International Nomenclature Committee (p18, Murray 2007). In addition to the application described in the patent, other applications have been developed for the mixture. For simplicity, the term Paly-Mont is used here to refer to the naturally mixture of palygorskite and montmorillonite clay.

One of the valuable applications of Paly-Mont developed from commercial activity is its unique adsorption property of various mycotoxins. Paly-Mont is the combination of palygorskite with high absorption capacity and montmorillonite with high surface charge. Possibly because of this combined property, it has high adsorption rate, especially to mycotoxins with strong polarity such as aflatoxin. For the material with concentration of 200 ppb of aflatoxin, the adsorption of aflatoxin B1 with 0.1% processed Paly-Mont can reach 99%. With further treatment with organics, Paly-Mont shows good adsorption to weak polar mycotoxins such as zearalenone, in addition to the better adsorption of aflatoxins. The adsorption of zearalenone can be higher than 85% at the test condition of 0.1% Paly-Mont and 200 ppb of zearalenone.

For the same application, another very important feature of Paly-Mont is its selective adsorption between mycotoxins and nutrients, contributed by its unique structure. This is critical for its application in feeds. Commercially available mineral based mycotoxins binders, especially montmorillonite clay based binders have good adsorption of aflatoxins. But at same time they also adsorb nutrients effectively. The comparison of the basic structure of montmorillonite, palygorskite and Paly-Mont is shown in Figure 1. Montmorillonite has fish scale-like structure. After dispersion, Paly-Mont shows clearly base montmorillonite structure and the palygorskite needles above the base structure. It is this needle structure that may help to prevent the nutrients that may help to prevent the nutrients

Figure 1 Comparison of SEM photos and schematic micro structure of montmorillonite, palygorskite and Paly-Mont.
to be adsorbed easily because of polarity difference between mycotoxins and nutrients. Statistically, for water soluble type mycotoxins and nutrients, mycotoxins have strong polarity while nutrients have weak polarity. For not easily water soluble mycotoxins and nutrients, mycotoxins have weak polarity while nutrients are not-polar. The difference of polarity and the unique structure results in the selective adsorption of mycotoxins versus nutrients.

In summary, Paly-Mont is a naturally mixture of very rare palygorskite and montmorillonite and it has unique application properties in mycotoxins. After proper process, Paly-Mont has high adsorption capacity. More importantly, it has excellent selective adsorption property, contributed by its structure.
MOLECULAR SIMULATION STUDIES ON INTERLAYER STRUCTURES OF PRISTINE AND HDTMA+-INTERCALATED RECTORITE

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Rectorite is one member of mixed-layer clay minerals, consisting of illite layer and smectite layer in a regular order (ABAB...), therefore it provides us an ideal model to study illite-smectite mixed-layer clay minerals. Rectorite and organo-intercalated rectorite can be applied in many fields such as environmental and petroleum engineering. To shed light on interlayer properties of pristine and organo-rectorites, we have carried out systematic molecular simulation studies. First, we use grand canonical Monte Carlo (GCMC) and molecular dynamics methods to investigate the hydration of Na-rectorite in the comparison with Na-montmorillonite. The results of water adsorption curves, pressure and swelling free energy curves indicate that rectorite has the similar swelling property with montmorillonite. For both clay minerals, the free energy of the bilayer structure is lower than that of the monolayer. It shows that the bilayer hydrate is more stable than the monolayer. In addition, we find that the different distribution of sodium ions in rectorite: due to the difference of layer charges between illite layer and smectite layer, sodium ions prefer staying close to the surface of the illite layer, while sodium ions present symmetric distribution in the interlayer space of montmorillonite.

Second, we employ classical molecular dynamic simulations to study the microscopic interlayer properties of HDTMA+-intercalated rectorites with and without water at different HDTMA+ loading levels. According to our simulations, we find that as the loading level increases, monolayer, bilayer, transition and trilayer configurations of HDTMA+ occur in succession. The different layer charge characteristics between illite sheet and smectite sheet lead to special interlayer distributions of HDTMA+. Adsorption of water causes different influence on the mobilities of Na+ and HDTMA+ head groups, but it significantly decreases the mobility of alkyl chains. We also analyze the behavior of anions in the system exceeding 1 CEC HDTMA+ loading level.
The organic surfactant-modified clay minerals, or organoclays, have attracted much interest because of their wide applications in the environmental and material sciences. In the past half century, cation surfactant-modified montmorillonites may have been the most widely studied organoclays. The micro-structure and intercalation mechanism of cation surfactant-modified montmorillonites are already clear thanks to extensive studies in the past decades. The interlayer exchangeable cations of montmorillonite can be substituted easily by surfactant cations. Company with the swelling of lamellar structure, this intercalation process also modifies montmorillonite surface from hydrophilic to hydrophobic. The properties of the organo-montmorillonites depend largely on the species of the organic interlayer. For the different purpose, such as adsorbents for organic contaminants or inorganic contaminants, the cationic, anionic, nonionic, and amphoteric surfactants with various length and numbers of the alkyl chains have been used to modify the montmorillonite, and the resulting organo-montmorillonites show quite different structural characteristics and surface physical and chemical properties. Sulfobetaine (SB) is a zwitterionic surfactant containing long alkyl chain, positively charged trimethyl-ammonium and negatively charged sulfonate group at the whole pH range. More important thing is there are both positive and negative charges in single molecule at the same time, which may give the hybrids some unique property.

In this work, a series of zwitterionic surfactant-modified montmorillonites (ZSMMs) were synthesized using montmorillonite and three zwitterionic surfactants with different alkyl chain lengths at different concentrations (0.2–3.0 times of cation exchange capacity (CEC)). The structure and the intercalation mechanism of ZSMMs was discussed aided by the X-ray diffraction (XRD), Fourier transformed infrared spectra (FTIR), chemical elements analyses and thermo-gravimetric (TG) analyses. The XRD results revealed that zwitterionic surfactant could be intercalated into the interlayer space of montmorillonite and expand the basal spacing from 1.47 nm to 4.13 nm. The height of interlayer space increased with the surfactant loading levels. According to the chemical composition analysis results, the ratios of Ca/Si and Ca/Al kept unchanged after the surfactant came into the interlayer space of montmorillonites. The unchanged contents of Ca\textsuperscript{2+} indicated that there is no exchange reaction between the zwitterionic surfactant and the interlayer exchangeable cations. The new vibrations at 1095 and 1191 cm\textsuperscript{-1} in infrared spectra of ZSMMs may be the evidence of the new bonds between the Ca\textsuperscript{2+} and sulfonate. The positive end of SB could connect with the negative clay sheets through electrostatic attraction, just like the interaction between montmorillonite sheets and cation surfactant. The present study thus proved that the intercalation mechanism of ZSMMs is not an exchange reaction but a kind of combination reaction.
Organoclays synthesized by modifying smectites with small organic cations (e.g., TMA) can effectively uptake hydrophobic organic contaminants (HOCs) through a surface adsorption mechanism, and the siloxane surfaces of smectites have been considered as the primary adsorption sites for HOCs. Increasing the exposure of siloxane surface can enhance the adsorption capacity of organoclays. Therefore, organoclays synthesized with smectites of lower charge density always have better adsorption capacity, since fewer organic cations are needed to balance the smectite charges. One method to reduce the charge density of smectites is thermal treatment of smectite saturated with small cations (e.g., Li+, Ni2+). These small cations can irreversibly migrate into the smectites sheets to balance the negative charges, and thus the charge density of smectites can be reduced. With increasing heating temperature/time, more inorganic cations will migrate into the clay sheets and the resulting smectites will have smaller charge density. However, migration of the small cations is always accompanied by the collapse of interlayer spaces of smectites. Once the collapse of interlayer spaces reached a critical value, the adsorption capacity of the resulting organoclays then will decrease accordingly.

Here we introduce a novel method that can evidently reduce the collapse of interlayer spaces during the charge reduction of smectites. We start with the Li+ saturated montmorillonite. At first, part of the interlayer Li+ cations (e.g., 20% or 60%) were exchanged with TMA, and then the resulting samples were heated under high temperature (e.g., 200 °C) so that most of the Li+ can migrate into montmorillonite sheets. Finally, the remaining Li+ cations were further exchanged with TMA. Since the pre-exchanged TMA can serve as pillars within the interlayer spaces of montmorillonite, the collapse of interlayer space can be evidently reduced and the resulting organoclays have larger surface areas at low charge density region (Table 1). Adsorption experiments showed that the adsorption capacity of organoclays synthesized using both novel and traditional methods strongly depend on the surface areas, and the novel organoclay containing very low charges has the best adsorption capacity (Table 1).

### Table 1 basal spacing, surface area and sorption capacity of the organoclay

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d_0$ (nm)</th>
<th>$S$ (m²/g)</th>
<th>$Q$ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-23TMA-Mt</td>
<td>1.26</td>
<td>133.7</td>
<td>6.15</td>
</tr>
<tr>
<td>T-65TMA-Mt</td>
<td>1.38</td>
<td>216.5</td>
<td>10.3</td>
</tr>
<tr>
<td>M-25TMA-Mt</td>
<td>1.28</td>
<td>256.3</td>
<td>11.6</td>
</tr>
<tr>
<td>M-64TMA-Mt</td>
<td>1.39</td>
<td>216.3</td>
<td>9.22</td>
</tr>
</tbody>
</table>

*a: T- and M- denote the organoclays synthesized by traditional and new methods, respectively. The number indicates TMA loading amount (mmol/100g), which approximately equal to the CEC value of these samples.

*b: The initial nitrobenzene concentration is 100 mg/L.
EVERYTHING IS BIG
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College Station, Texas, USA

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Field trips
• Clay and lignite mining, processing, & reclamation (May 17)
• Local soil tour: genesis and mineralogy (May 21)

Workshop
• Surface modification of clays and nanocomposites (May 18)

Technical sessions
• Functional clay nanoparticles
• 2-D nanomaterials
• Qualitative and quantitative characterization of clay minerals and short-range ordered materials
• Structural characterization of lamellar materials
• Structural characterization of short-range ordered materials
• Spectroscopy of Clays
• Molecular simulation of clay minerals and reactions
• Clays in geological processes
• Clay mineralogy and geochemistry on Mars
• Clays and oil/gas production
• Clays in soils and sediments
• Clays and environments
• Clay interactions with radioactive waste and waste forms
• Interactions of clay minerals with microorganisms and biomolecules
• Clays, nanoparticles and health
• Asian Clay Minerals Group research progresses
• Teaching clay mineralogy
• General Session

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• Bruce Herbert, herbert@geo.tamu.edu
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Dates and deadlines
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