EVERYTHING IS BIG from Nanoparticles to Planets

51st Annual Meeting of the Clay Minerals Society

May 17-21, 2014
Texas A&M University, College Station, Texas, USA
EVERYTHING IS BIG from Nanoparticles to Planets

51st Annual Meeting of the Clay Minerals Society

May 17-21, 2014
Texas A&M University, College Station, Texas, USA
HRTEM image: A MnFe$_2$O$_4$ nanoparticle encapsulated in the inner channel of a halloysite nanotube. Image was supplied by Ao-Bo Zhang, et al. See more details in abstract “Facile preparation of MnFe$_2$O$_4$/halloysite nanotubular encapsulates with enhanced magnetic and electromagnetic performances” by Ao-Bo Zhang*, Ying Ye, and Xue-Gang Chen (Page 247)
TABLE OF CONTENTS

TABLE OF CONTENTS................................................................................................................. i
THE CLAY MINERALS SOCIETY............................................................................................... v
SOCIETY HISTORY ................................................................................................................ vi
SUSTAINING CONTRIBUTORS ........................................................................................... vii
AWARDS ................................................................................................................................. viii
EDITORS OF CLAYS AND CLAY MINERALS .................................................................. 10
PAST PRESIDENTS ................................................................................................................ xi
INTRODUCTION ....................................................................................................................... xii
TECHNICAL SESSIONS, ORGANIZERS, AND DESCRIPTIONS ........................................... xiii
BRYAN, COLLEGE STATION, AND TEXAS A&M UNIVERSITY ..................................... xviii
HISTORY OF BRYAN AND COLLEGE STATION ............................................................ xviii
BRYAN-COLLEGE STATION ATTRACTIONS OVERVIEW ........................................... xix
LOCATION OF CITY COLLEGE STATION, TEXAS, USA ............................................... xx
VENUE: MEMORIAL STUDENT CENTER (MSC), TEXAS A&M UNIVERSITY, COLLEGE STATION, TX.........................................................................................................................xxvi
BUS SCHEDULE FOR THE 51 ST ANNUAL MEETING OF CMS................................. xxix
DINING PLACES ON AND AROUND TAMU CAMPUS DURING CONFERENCE...... xxx
PROGRAM ..................................................................................................................................... 1
PROGRAM AT-A-GLANCE ..................................................................................................... 2
FRIDAY, MAY 16 ..................................................................................................................... 3
SATURDAY, MAY 17 .............................................................................................................. 3
SUNDAY, MAY 18 ................................................................................................................... 3
MORNING, MONDAY, MAY 19 ............................................................................................. 4
NOON, MONDAY, MAY 19 .................................................................................................... 6
AFTERNOON, MONDAY, MAY 19 ....................................................................................... 7
EVENING, MONDAY, MAY 19 ............................................................................................. 14
MORNING, TUESDAY, MAY 20 .......................................................................................... 15
NOON, TUESDAY, MAY 20 .................................................................................................. 17
AFTERNOON, TUESDAY, MAY 20 .................................................................................... 18
EVENING, TUESDAY, MAY 20 ........................................................................................... 22
MORNING, WEDNESDAY, MAY 21 ................................................................................... 23
51st Annual Meeting of CMS

Held on the Campus of Texas A&M University at College Station
May 17-21, 2014

ORGANIZING COMMITTEE
Youjun Deng, Texas A&M University, Chair
Gary Beall, Texas State University
Sam Feagley, Texas A&M University
Bruce Herbert, Texas A&M University
William Jaynes, Texas Tech University
Li Zhang, Graphic Design and Webmaster

Field Trips:
Sam Feagley, Texas A&M University
Bruce Herbert, Texas A&M University, College Station, TX.
Marty Irwin, Luminant Mining-Three Oaks, Elgin, TX
Cristine Morgan, Texas A&M University (Local soil tour), College Station, TX.
Charles Smith, BYK Additives Inc. (Southern Clay Products Inc.), Gonzales, TX.

Workshop:
Gary Beall, Texas State University, San Marcus, TX.
Clois E. Powell, Texas State University, San Marcus, TX.

Program and Abstracts Book:
William Jaynes, Texas Tech University, Lubbock, TX.
Copy Corner, College Station, TX.

Registration and Facilities:
Joani Groce, Texas A&M University, College Station, TX.
Kay Sanders, Texas A&M University, College Station, TX.
Stephen Senkel, Texas A&M University, College Station, TX.

Web Site and Publications Design:
Li Zhang, Texas A&M University, College Station, TX.
Vincent C. W. Chen, Texas A&M University, College Station, TX

Administrative Assitances:
Amanda H. Ray, Texas A&M University, College Station, TX.
Session Organizers and Chairs:

- Gary W. Beall, Texas State University
- Hyen-Goo Cho, Gyeongsang National University
- Georgios Chryssikos, National Hellenic Research Foundation
- Bethany Ehlmann, California Institute of Technology
- Bruce Herbert, Texas A&M University
- Qiaoyun Huang, Huazhong Agricultural University
- Deb P. Jaisi, University of Delaware
- Andrey Kalinichev, Laboratoire SUBATECH
- Jinwook Kim, Yonsei University
- Bruno Lanson, Université Poitiers
- Xiandong Liu, Nanjing University
- Sandra Carolina Londono, Arizona State University
- Douglas Ming, NASA Johnson Space Center
- Keith Morrison, Arizona State University
- Jim Neeway, Pacific Northwest National Laboratory
- Jae-Min OH, Yonsei University
- Michael Ploetze, ETH Zurich
- Manika Prasad, Colorado School of Mines
- Nik Qafoku, Pacific Northwest National Laboratory
- Craig Rasmussen, The University of Arizona
- Balwant Singh, The University of Sydney
- Paul A. Schroeder, University of Georgia
- Michal Skiba, Jagiellonian University
- Hung-Jue Sue, Texas A&M University
- Atsushi Takahara, Kyushu University
THE CLAY MINERALS SOCIETY

President: Michael A. Velbel, Michigan State University
Vice President: W. Crawford Elliott, Georgia State University
Secretary: Warren Huff, University of Cincinnati
Treasurer: J. Reed Glasmann, Willamette Geological Service
Vice-President Elect: Prakash Malla, Thiele Kaolin Company
Past President: Peter Komadel, Slovak Academy of Sciences
Editor-in-Chief: Joseph W. Stucki, University of Illinois

Council
Thru 2014 Jocelyne Brendlé Robert Gilkes Peter Ryan Tsutomu Sato
Thru 2015 Patricia Aparicio Alanah Fitch Michael Ploetze Balwant Singh
Thru 2016 Katja Emmerich Claire-Isabelle Fialips Michael Ploetze Martin Wells

Society Manager:
Mary Gray
The Clay Minerals Society
3635 Concorde Parkway, Suite 500
Chantilly, Virginia 20151-1125, USA
Phone: 703-652-9960
Fax: 703-652-9951
Email: cms@clays.org
SOCiETY HISTORY

The Clay Minerals Society began as the Clay Minerals Committee of the National Academy of Sciences—National Research Council in 1952, in response to the need for a formal way to hold national clay conferences. By 1962, the Clay Minerals Committee had become strong enough to stand on its own, and The Clay Minerals Society was incorporated. From 1952 to 1964, Proceedings of the annual conferences were published. The journal *Clays and Clay Minerals* was first published in 1964.

The primary purpose of The Clay Minerals Society is to stimulate research and to disseminate information relating to all aspects of clay science and technology. Through its conferences and publications, the Society offers individuals a means of following the many-sided growth of the clay sciences and of meeting fellow scientists with widely different backgrounds and interests.

The primary activities of The Clay Minerals Society consist of publication of the bimonthly journal *Clays and Clay Minerals*, organization of the annual conference, workshop, and field trip, student research grants, publication of a workshop lecture series, slide sets, and special publications, the providing of clays for research purposes through the Source Clays Repository, and publication of the society newsletter in the bimonthly *Elements*. Various committees within the Society deal also with such matters as regulatory issues, liaisons with other countries, and nomenclature.

Awards given by the Society include Distinguished Member, the George W. Brindley Lecture, the Pioneers in Clay Science Lecture, and the Marion L. and Chrystie M. Jackson Mid-Career Clay Scientist Award. Awards are also presented for student papers and posters at the annual conference. Student research grants totaling at least $10,000 per year are awarded.

The membership of The Clay Minerals Society is a diverse group because the study of clay touches upon so many fields. Members include clay mineralogists, crystallographers, physicists, chemists, geochemists, soil scientists, agronomists, ceramic scientists, civil engineers, petroleum geologists and engineers, and industrial scientists in fields involving products ranging from catalysts to cat litter. The Society has about 700 members, one half of whom represent countries outside the United States.

# Sustaining Contributors

## Sustaining Benefactors

<table>
<thead>
<tr>
<th>Wyo-Ben, Inc.</th>
<th>Thiele Kaolin Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chevron</td>
<td>M-I Swaco</td>
</tr>
<tr>
<td>Exxon</td>
<td>H.H. Murray &amp; Associates</td>
</tr>
<tr>
<td>The Sorptive Minerals Institute</td>
<td>IMERYS</td>
</tr>
</tbody>
</table>

## Patrons

<table>
<thead>
<tr>
<th>Richard W. Berry</th>
<th>Alanah Fitch</th>
</tr>
</thead>
<tbody>
<tr>
<td>David L. Bish</td>
<td>Will P. Gates</td>
</tr>
<tr>
<td>John D. Bloch</td>
<td>J. Reed Glassman</td>
</tr>
<tr>
<td>Carl J. Bowser</td>
<td>Stephen Guggenheim</td>
</tr>
<tr>
<td>Richard W. Brown</td>
<td>Necip Guven</td>
</tr>
<tr>
<td>Wen-An Chiou</td>
<td>Warren Huff</td>
</tr>
<tr>
<td>Michael L. Cummings</td>
<td>William D. Johns</td>
</tr>
<tr>
<td>Randall T. Cygan</td>
<td>Blair Jones</td>
</tr>
<tr>
<td>Joe B. Dixon</td>
<td>George H. Kacandes</td>
</tr>
<tr>
<td>Ray E. Ferrell, Jr.</td>
<td>Christian Bender Koch</td>
</tr>
</tbody>
</table>

## Individual Sustaining Members

<table>
<thead>
<tr>
<th>Richard W. Berry</th>
<th>Alanah Fitch</th>
</tr>
</thead>
<tbody>
<tr>
<td>David L. Bish</td>
<td>Will P. Gates</td>
</tr>
<tr>
<td>John D. Bloch</td>
<td>J. Reed Glassman</td>
</tr>
<tr>
<td>Carl J. Bowser</td>
<td>Stephen Guggenheim</td>
</tr>
<tr>
<td>Richard W. Brown</td>
<td>Necip Guven</td>
</tr>
<tr>
<td>Wen-An Chiou</td>
<td>Warren Huff</td>
</tr>
<tr>
<td>Michael L. Cummings</td>
<td>William D. Johns</td>
</tr>
<tr>
<td>Randall T. Cygan</td>
<td>Blair Jones</td>
</tr>
<tr>
<td>Joe B. Dixon</td>
<td>George H. Kacandes</td>
</tr>
<tr>
<td>Ray E. Ferrell, Jr.</td>
<td>Christian Bender Koch</td>
</tr>
</tbody>
</table>

## Funders of the Marilyn and Sturges W. Bailey Distinguished Member Award

Linda Bailey and David Bailey

## Funders of the Marion L. and Chrystie M. Jackson Mid-Career Clay Scientist Award

Marion L. and Chrystie M. Jackson
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  
1975 - William F. Bradley  
1975 - Joseph J. Fripiat  
1977 - Marion L. Jackson  
1979 - Toshio Sudo  
1980 – Haydn H. Murray  
1984 - C. Edmund Marshall  
1985 - Charles E. Weaver  
1988 - Max M. Mortland  
1989 - Robert C. Reynolds, Jr  
1990 - Joe L. White  
1990 - John Hower  
1991 - Joe B. Dixon  
1992 - Philip F. Low  
2006 - Frederick J. Wicks

**Bailey Distinguished Members**

1993 - Thomas J. Pinnavaia  
1995 - William D. Johns  
1996 - Victor A. Drits  
1997 - Udo Schwertmann  
1998 - Brij L. Sawhney  
2000 - Boris Zyvaygin  
2001 - Keith Norrish  
2002 - Gerhard Lagaly  
2004 - Benny K. G. Theng  
2005 - M. Jeff Wilson  
2008 - Norbert Clauer  
2009 - Joseph W. Stucki  
2010 – José M. Serratosa  
2011 – Sridhar Komarneni  
2012 – Akahiko Yamagishi  
2013- Stephen Guggenheim

MARION L. AND CHRYSTIE M. JACKSON MID-CAREER 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 Środoń  
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
2004 - Fred J. Longstaffe
2005 - Samuel J. Traina
2006 - J. Theo Kloprogge
2007 - Paul A. Schroeder
2003 - Peter Komadel

2008 - Hailiang Dong
2009 - Lynda B. Williams
2010 – Toshihiro Kogure
2011 – Douglas K. McCarty
2012 – Jeffrey E. Post
2013 – George E. Christidis
2014 – Will Gates

GEORGE BRINDLEY LECTURE AWARD

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

Brindley Lecturers

1984 – Walter D. Keller
1985 – José J. Fripiat
1986 – Ralph E. Grim
1987 – Sturges W. Bailey
1988 – Marion L. Jackson
1989 – William D. Johns
1990 – Alain Baronnet
1991 – Thomas J. Pinnavaia
1992 – Philip F. Low
1993 – Dennis D. Eberl
1995 – Gerhard Lagaly
1996 – Samuel M. Savin
1997 – Paul H. Nadeau
1998 – Bruce Velde
1999 – Richard Eggleton
2000 – Duane M. Moore
2001 – Robert Schoonheydt
2002 – David L. Bish
2003 – Alain Manceau
2005 – Maria F. Brigatti
2008 – Robert J. Gilkes
2009 – Michael F. Hochella, Jr.
2010 – Randy T. Cygan
2013 – Andrey Kalinichev

PIOENEER 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
<table>
<thead>
<tr>
<th>Year</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1995</td>
<td>Rustum Roy</td>
</tr>
<tr>
<td>1996</td>
<td>Max M. Mortland</td>
</tr>
<tr>
<td>1997</td>
<td>Koji Wada</td>
</tr>
<tr>
<td>1998</td>
<td>Robert C. Reynolds</td>
</tr>
<tr>
<td>1999</td>
<td>V. Colin Farmer</td>
</tr>
<tr>
<td>2000</td>
<td>William F. Moll</td>
</tr>
<tr>
<td>2001</td>
<td>Don Scafe</td>
</tr>
<tr>
<td>2002</td>
<td>Victor Drits</td>
</tr>
<tr>
<td>2003</td>
<td>Vernon J. Hurst</td>
</tr>
<tr>
<td>2004</td>
<td>Hideomi Kodama</td>
</tr>
<tr>
<td>2005</td>
<td>Jillian Banfield</td>
</tr>
<tr>
<td>2006</td>
<td>Jean-Maurice Cases</td>
</tr>
<tr>
<td>2007</td>
<td>Spencer G. Lucas</td>
</tr>
<tr>
<td>2008</td>
<td>Emilio Galan</td>
</tr>
<tr>
<td>2009</td>
<td>Hayden H. Murray</td>
</tr>
<tr>
<td>2011</td>
<td>Glenn A. Waychunas</td>
</tr>
<tr>
<td>2013</td>
<td>Thomas J. Pinnavaia</td>
</tr>
<tr>
<td>2014</td>
<td>Douglas W. Ming</td>
</tr>
</tbody>
</table>

CITATION OF SPECIAL RECOGNITION

1984 - Richards A. Rowland
1984 - Ada Swineford
1991 - Frederick A Mumpton
1994 - Kenneth M. Towe
1996 - Don Scafe
2003 - William D. Johns

EDITORS OF CLAYS AND CLAY MINERALS

1952 J. A. Pash and M. D. Turner
1953 Ada Swineford and Norman Plummer
1954 W. O. Milligan
1955 – 1961 Ada Swineford
1962 – 1964 William F. Bradley
1964 – 1969 Sturges 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
# PAST PRESIDENTS

Chair, Interdivisional Committee on Clay Minerals of the National Academy of Sciences – National Research Council

1952 – 1956  Ralph E. Grim  
1957 – 1959  Walter D. Keller  
1960 – 1962  A. F. Frederickson  
1963  Richards A. Rowland  

Presidents

<table>
<thead>
<tr>
<th>Year</th>
<th>President</th>
<th>Year</th>
<th>President</th>
</tr>
</thead>
</table>
INTRODUCTION

As the Clay Minerals Society (CMS) turns to a new page to embrace the inquiries, achievements, and services for the next 50 years, the organizing committee of the 51st annual meeting of CMS cordially invites and welcomes colleagues from diverse disciplines and industries around the world to attend this meeting at Texas A&M University, College Station, Texas, May 17-21, 2014. The theme of this year’s meeting is “Everything Is Big: From Nanoparticles To Planets”. Yes, clay science is big, not only in Texas but also in every other state and country. It is big to our industry, big to our environment, big to our energy, big to our research, and big to our student training.

The primary purpose of 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, the society offers individuals a means of following the multi-directional growth of the clay sciences and of meeting fellow scientists with widely different backgrounds and interests.

This year’s annual meeting will have sixteen technical sessions from May 19 to the morning of May 21, a one-day workshop on “Surface modification of clays and nanocomposites” on May 18, a one-day field trip on May 17 to clay and lignite mines to learn the mineralogy and geochemical processes in the mines, associated environmental problems, and mine reclamation operations. A half-day local soil tour will follow the meeting on May 21.

The CMS awards to be presented by the Society include the Marion L. and Chrystie M. Jackson Mid-Career Clay Scientist Award and the Pioneer in Clay Science Award. The winners of the 7th (2014) Reynolds Cup competition will be announced at the meeting. Awards will also be presented for student research and travel grants, student papers and posters.

Youjun Deng, Ph.D.
Chair, Local Organizing Committee
Associate Professor of Soil Clay Mineralogy

Local organizing committee:
Youjun Deng, Texas A&M University
Gary Beall, Texas State University
Sam Feagley, Texas A&M University
Bruce Herbert, Texas A&M University
William F. Jaynes, Texas Tech University
TECHNICAL SESSIONS, ORGANIZERS, AND DESCRIPTIONS

1. **Functional clay nanoparticles.** Atsushi Takahara\textsuperscript{1} and Hung-Jue Sue\textsuperscript{2} (\textsuperscript{1}Institute for Materials Chemistry and Engineering, Kyushu University CE11 Ito Campus, 744 Motooka Nishi-ku, 819-0395, Japan: takahara@cstf.kyushu-u.ac.jp; \textsuperscript{2}Polymer Technology Center, Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843-3123, USA: hjsue@tamu.edu)

Clay science and applications of clay minerals, such as montmorillonite, halloysite, imogolite, sepiolite, and others has received great attention from both academic and industrial points of view. Clay nanoparticles can be modified by several surface modification techniques in order to realize various functionalities. Appropriate modification of clay surfaces will enhance the dispersion of clay in various solvents and polymer matrices to realize desired functionalities. This symposium will focus on science and technology of clay particles for various scientific and engineering applications.

2. **2-D nanomaterials.** Gary W. Beall (Texas State University, San Marcus, Texas, USA: gb11@txstate.edu)

Since the awarding of the Nobel Prize in Physics in 2010 for the discovery of graphene the field of 2-D materials has become one of the most active research areas. In terms of the characteristics of graphene oxide and graphene they could easily be classified as clays. Many clay minerals when dispersed down to their primary particle size are very close to 2-D materials. This symposium will cover all 2-D materials including fundamental theory and practical applications.

3. **Qualitative and quantitative characterization of clay minerals and short-range ordered materials.** Michael Ploetze\textsuperscript{1} and Bruno Lanson\textsuperscript{2} (\textsuperscript{1}ETH Zurich, IGT, CH-8093 Zurich, Switzerland; ploetzel@ethz.ch; \textsuperscript{2}Université Poitiers-CNRS, F-86022 Poitiers, France; bruno.lanson@obs.ujf-grenoble.fr)

Because of effects on the physical and chemical properties of rocks, soils, clays, and industrial materials, knowledge of the types and relative amounts of the minerals present is essential. Quantitative phase analysis (QPA) represents, therefore, an important tool for characterization of mixed mineral phase systems; e.g. in mineral exploration and processing, in clay science, and material science to name a few. Whereas powder XRD is the method of choice for this task, further techniques exist, that deliver additional and unique information in mineral characterization. The current state of the art in QPA, approaches for improvement, and new methods particularly in characterization and modelling of layered minerals and disordered or amorphous clays will be covered in this session.

4. **Spectroscopy of clays.** Georgios Chryssikos (Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece: gdchryss@eie.gr)

Spectroscopy offers a powerful toolbox for the observation, classification, and identification of clay minerals, independent of (but in constant dialog with) XRD and other experimental techniques. Featured is the spectroscopist’s point of view on issues such as the structural variability within clay families in relationship to composition and properties, or the interactions between clays and small molecules (including, par excellence, H\textsubscript{2}O) and the use of the latter as structural proxies. Also considered are the practical challenges associated with high-throughput applications for geological mapping and exploration or process monitoring. Answers are sought from spectroscopy, but unexpected new questions are inevitable and very welcome.
5. **Molecular simulation of clay minerals and reactions.** Xiandong Liu¹ and Andrey Kalinichev² (¹School of Earth Sciences and Engineering, Nanjing University, Nanjing, China. Department of Chemistry, University of Cambridge, Cambridge, UK: xiangdongliu@gmail.com; ²Laboratoire SUBATECH - Ecole des Mines de Nantes 44307 Nantes, France: kalinich@subatech.in2p3.fr)

Molecular simulations have been widely applied in the study of clay minerals and related phases. These techniques have proven to be powerful tools for complementing experiments and field observations. As computer power and theoretical methods evolve, more and more properties and reactions at atomic and molecular levels can be explored, including mineralogy, (bio)geochemical behaviors, geological roles and material properties for environmental and engineering applications. The aim of this session is to highlight recent computational studies of clay minerals and related mineral phases, e.g. oxides, hydroxides, zeolites, advanced layered materials etc. The topics of interest include structures, dynamics, interfacial processes, chemical reactivity and material properties. The simulation techniques cover electronic structures methods, classical simulations, and coarse grained modeling. Multiple scale modeling studies of bulk or interface systems are encouraged.

6. **Clays in geological processes.** Michal Skiba (Department of Mineralogy, Petrology, and Geochemistry Institute of Geological Sciences, Jagiellonian University, ul. Oleandry 2a, 30-063 Kraków, Poland: michal.skiba@uj.edu.pl)

Clay minerals and phyllosilicates are found in igneous, metamorphic and sedimentary rocks. Clays are formed in a wide range of processes, such as magmatism, metamorphism, hydrothermal processes, weathering, sedimentation, and diagenesis. This session invites papers dealing with all aspects of clay and phyllosilicate geology. We are particularly interested in submissions related to the processes of clay mineral formation and transformation in different geological environments and the use of clay minerals and phyllosilicates in the dating and reconstruction of geological processes.

7. **Clay mineralogy and geochemistry on Mars.** Bethany Ehlmann¹ & Doug Ming² (¹California Institute of Technology, Pasadena, CA, USA: ehlmann@caltech.edu; ²NASA Johnson Space Center, Houston, Texas, USA: douglas.w.ming@nasa.gov.)

Orbital and landed missions have provided a wealth of datasets that have substantially improved our understanding of clay mineralogy and geochemistry on Mars. Infrared spectroscopic instruments on the Mars Global Surveyor, Mars Express, and Mars Reconnaissance Orbiter missions have identified and mapped clay minerals, carbonates, sulfates, chlorides and other phases in numerous discrete geologic units exposed at the surface. The Mars Exploration Rovers, Mars Phoenix Scout, and the Mars Science Laboratory (MSL) have encountered phyllosilicates, sulfates, carbonates, Fe-oxyhydroxides, perchlorates, and other minerals at several landing sites. Martian meteorites also provide the opportunity to probe the clay mineralogy and geochemistry of martian samples in terrestrial laboratories. This session will focus on the clay mineralogy and geochemistry of martian materials, including the latest datasets from the MSL Curiosity mission.

8. **Clays in soils and sediments.** Craig Rasmussen (Department of Soil, Water and Environmental Science, The University of Arizona, Tucson, Arizona, USA: crasmuss@calas.arizona.edu)

Soils and sediments serve as synthographs of environmental conditions and ecosystem processes. Understanding how clay minerals in soil and sediment interact with, control, and record ecosystem processes is fundamental to understanding soil and ecosystem function.
This session will explore the use of soil and sediment clay minerals to characterize ecosystem processes across nano- to landscape spatial scales, and over modern to Quaternary time scales. Topics may include coupling of molecular, isotopic, or imaging techniques for using soil clay mineral data as (i) proxy for environmental conditions and unraveling the coevolution of soil and ecosystem properties, (ii) understanding soil biogeochemical cycling in natural and managed systems, and (iii) quantifying mineral weathering and transformation processes.

9. **Clays and Environments.** Balwant Singh (Faculty of Agriculture and Environment, The University of Sydney, Australia: Balwant.Singh@sydney.edu.au)

Clay minerals have a long history for industrial and commercial uses; however, clay applications in environmental contexts have been recognized in the past few decades. This symposium invites papers covering a range of environmental applications of naturally occurring clay minerals, modified clay minerals, and synthesized nano-particles. We are particularly interested in submissions related to the application of clays - in organic and inorganic contaminant adsorption, for the delivery of particular compounds, in the protection of surface and ground waters, and the role of clays in soil carbon sequestration.

10. **Clays and oil/gas production.** Manika Prasad (OCLASH/Center for Rock Abuse, Petroleum Engineering Department, Colorado School of Mines, Golden CO 80401, USA: mprasad@mines.edu)

This session will be devoted to understanding the physical properties of clay minerals in the hydrocarbon world. There are numerous specific applications and problems arising from the presence of clay minerals. Such effects can include formation damage in the presence of swelling clays, proppant embeddment in clay layers, and porosity preservation and water retention. We invite papers on clay-organic interactions, clay swelling, clay stabilization, and clay effects on indirect measurements, such as resistivity, acoustics, and NMR.

11. **Clay interactions with radioactive waste and waste forms.** Nik Qafoku and Jim Neeway (Geosciences Group, Earth Systems Science Division, Pacific Northwest National Laboratory, Richland, WA 99352, USA: nik.qafoku@pnnl.gov, james.neeway@pnnl.gov)

Significant amounts of nuclear waste have been generated over the past decades from the production of energy from nuclear reactors and nuclear weapons production activities. This waste contains a variety of radionuclides and contaminants of concern and is stored in temporary waste containers or in permanent waste repositories, depending on the radionuclide, contaminants and stage of waste treatment. In some instances, the radioactive waste is immobilized in waste forms (i.e., solids with low solubility and low release rates for radionuclides and contaminants) and the disposal of this waste is set to be in an environment containing clays. The symposium will address different aspects of radioactive waste interactions with clay minerals. The clay minerals may be present as part of the natural repository environment or they may be used as engineered barriers to mitigate radionuclide release into the surrounding environment. The effects of variables, such as waste chemistry, waste form, radionuclide and contaminant concentrations, and types of clay minerals, on the transport and ultimate fate of radionuclides and contaminants in different environmental settings will be discussed.

12. **Interactions of clay minerals with microorganisms and biomolecules.** Qiaoyun Huang¹ and Deb P. Jaisi² (¹Dean, Faculty of Resources and Environment, Vice Director, State Key Laboratory of Agricultural Microbiology, Huazhong Agricultural University, Wuhan 430070, China: qyhuang@mail.hzau.edu.cn; ² University of Delaware, Newark, DE, USA: ...
Clay minerals, which have large surface areas and surface charges, are the major colloidal components in soils and sediments. The interactions between these fine particles and various microorganisms and biomolecules, such as enzymes and DNA have profound impacts on the structure, biological activity, and quality of soils and associated environments, and ultimately influence human health. Studies of the interactions have received increasing attention by scientists from different fields including soil science, plant nutrition, mineralogy, microbiology, chemistry, and environmental science. This session will discuss the latest research advances with respect to 1) Physical and chemical processes at interfaces between clay minerals and microorganisms; 2) Binding mechanisms of biomolecules with clay minerals and activities of bound biomolecules; 3) Interaction of clay minerals with microorganisms on the behavior and fate of nutrients and contaminants in various environments; 4) Microbial weathering of clay minerals and biomineralization; and 5) Interactions of clay minerals with biomolecules and microorganisms on soil structure and stability.

13. **Clays, nanoparticles and health.** Sandra Carolina Londono & Keith Morrison (School of Earth & Space Physical Sciences, Arizona State University Tempe, Arizona, USA: slondonl@asu.edu, & kdmorri3@asu.edu. )
The study of clays and health represents an emerging research field that encompasses a range of scientific disciplines. Additionally, clays are environmentally important for their impact on element reactivity, mobility, toxicity and effects on public health. The advancement of new technologies and methodologies for evaluating these nanometric minerals has enhanced our study of their interactions with biological systems. This session invites studies on how clays can be utilized as unique resources to impact human and environmental health, considering both the benefits and the detrimental effects.

14. **Asian Clay Minerals Group research progress.** Jinwook Kim¹, Hyen-Goo Cho² and Jae-Min OH³ (¹Department of Earth System Sciences, Yonsei University, Seoul, Korea: jinwook@yonsei.ac.kr; ²Department of Earth and Environmental Science, Gyeongsang National University, JinJu, Korea: hacho@gnu.ac.kr; and ³Dept. Chemistry and Medical Chemistry, Yonsei University, Wonju, Korea: jaemin.oh@yonsei.ac.kr) The Asian Clay Research Group was organized through the Nagoya and Seoul meetings in 2010 and 2012. The purpose of this session is to present current research progress of the Asian Clay Research Group. This session will bring active Asian clay scientists together and promote scientific communication with the Clay Minerals Society. The topics are clay and clay materials in natural environments as well as industrial applications. Clays undergo biotic and abiotic reactions in natural environments that impact a number of geological and environmental processes, such as sediment diagenesis, colloid transport, the mobility and the ultimate fate of organic and inorganic contaminants, integrity of waste repositories, and stability of the ocean floor. Furthermore, the science and technologies of industrial clays, including exploration and clay resource development, particle engineering from macro to nano, chemical and physical modification, industrial application, sustainable resource development and bio-medical applications are currently investigated. We would like to invite presentations that include, but are not limited to, clay interactions with environmental contaminants in soils and sediments, clays and energy, microscopic characterization of clay mineral reactions, soil clays and clay chemistry, clays in medicine, and industrial clays.
15. Teaching clay mineralogy. Paul A. Schroeder (Department of Geology, University of Georgia 210 Field Street, Athens, GA 30602-2501 USA: schroe@uga.edu)
Teaching clay science embraces the challenge of including students from many disciplines. Classes are often comprised of geologists, chemists, soil scientists, material scientists, and ecologists. The rapid growth of nano-composite engineering and mineral health science is creating even more diversity in the clay classroom. This session seeks contributions that demonstrate class activities or field experiences that can be shared with the clay science community. The purpose is to help expand teacher repertoires in a multidisciplinary field. Students (current and past) are also encouraged to participate to reflect their perspectives on past pedagogy or present projects experienced in a class.

16. General session. Bruce Herbert (Department of Geology and Geophysics, Texas A&M University, College Station, TX: herbert@geo.tamu.edu)
This session will include all presentations not coming under one of the specific session categories previously listed.
HISTORY OF BRYAN AND COLLEGE STATION

BRYAN- Bryan was established in 1859 in honor of William Joel Bryan, nephew of Texas pioneer Stephen F. Austin. Bryan has been the agricultural and commercial center of the rich Brazos River Valley farmlands since 1867, when the H&TC Railroad initiated train service through the town. Within a few years, Bryan was linked by rail to major agricultural markets across the country.

COLLEGE STATION- College Station became a city in 1938, although it was “born” in 1876 with the Agricultural and Mechanical College of Texas, which became known as Texas A&M. College Station, named as a railway stop by the Postal Service in 1877, flourished in the 1960’s when the college opened its doors to women and became Texas A&M University. From its humble beginning with fewer than 50 students, Texas A&M has grown to become one of the nation’s largest universities, with a student body totaling about 50,000 and with internationally acclaimed research programs. Its 1,800-member Corps of Cadets is the nation’s largest uniformed student organization other than at the service academies.

Today, Bryan and College Station form a delightful community to live in and to visit. Aggieland is a destination with a unique blend of cultural opportunities and warm hospitality.
BRYAN-COLLEGE STATION ATTRACTIONS OVERVIEW

Bryan-College Station is a favorite vacation destination for family fun, romantic escapes, sports events, and traveling professionals. Conveniently located within driving distance of 80% of Texas’ population, Bryan-College Station is an ideal location for your next get-away.

New hotels and bed and breakfasts are opening all the time, which makes it easy to find excellent accommodations with amenities to fit your needs and budget.

Discover a region that is so diverse you can wander through the scenic campus of Texas A&M University, go shopping and dining Downtown, take a winery tour, go to a museum and more, all in one day! With two cities offering the best attractions in Texas, there is so much for visitors to explore, experience, and enjoy.

Bryan-College Station has a wide selection of museums. Whether your interests range from wildlife, the military, or politics, Bryan-College Station showcases a variety of vibrant and charming museums. In fact, the George Bush Presidential Library and Museum is one of the top 30 attractions in Texas!

Downtown Bryan is bursting with history, live entertainment and attractions. Visitors to Downtown can enjoy plays, concerts, strolling through art galleries, attending a festival or having drinks with friends at a restaurant or wine bar.

If you are the type of traveler who likes to tickle your taste buds with local products, Bryan-College Station is the place to visit. We are home to the fastest growing award-winning winery and resort in Texas, Messina Hof Winery & Resort. Here guests can enjoy a tour of the winery, wine tasting and events year-round. Come during harvest season, April – August, and pick and stomp your own grapes. In addition to producing wine, we also have locally produced chocolate, cheese, beef and a pecan farm.

The fun doesn’t stop there! Tee off at one of Bryan-College Station’s challenging golf courses. Visit Kyle Field and the Bonfire Memorial on the Texas A&M University campus. Enjoy a delicious meal at one of our local eateries.

Bryan-College Station is also a great choice for events. It can be the beautiful backdrop for a wedding, a place to team build or the gathering for this year’s family reunion. Bryan-College Station offers first-class state of the art venues ranging in economical to deluxe. Whatever the occasion Bryan-College Station is sure to have a facility that will make your next big event successful.

Bryan-College Station is probably best known for its history and traditions. With all the amenities of a big city, yet the atmosphere and hospitality of a small town, make each visit to Bryan-College Station unique. Here “Howdy is more than just a greeting; it’s a genuine spirit no one forgets.
LOCATION OF CITY COLLEGE STATION, TEXAS, USA
Bryan-College Station Accommodations

- Approximately 3,400 rooms available over 30+ properties
- Affordable rates
- Variety of hotel properties from Hilton, Marriott, Starwood and IHG.
- All properties are within a 5 mile radius of Northgate

1. Aggie Land Knights Inn
2. America's Best Value Inn
3. Best Western Acre
4. Comfort Suites Aggieland
5. Comfort Inn & Suites
6. Country Inn & Suites
7. Courtyard Marriott
8. Days Inn
9. EZ Travel Inn
10. Executive Inn & Suites
11. Fairfield Inn
12. Four Points
13. Hampton Inn
14. Hampton Inn & Suites
15. Hawhorn Suites
16. Hilton
17. Hilton Garden Inn
18. Holiday Inn & Suites
19. Holiday Inn Express
20. Homewood Suites
21. Howard Johnson Express
22. Hyatt Place Hotel
23. La Quinta
24. LaSalle Hotel
25. Manor House Inn
26. Motel 6
27. Quality Inn and Suites
28. Quality Suites
29. Ramada Inn BCS
30. Residence Inn
31. Super 8
32. Town Place Suites
33. University Inn
34. Value Place
35. Villa at Messina Hof
36. Vineyard Court
<table>
<thead>
<tr>
<th></th>
<th>Restaurant Name</th>
<th>Address</th>
<th>Phone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Freebirds World Burrito</td>
<td>700 Earl Rudder Fwy, College Station, TX</td>
<td>(979) 695-0151</td>
</tr>
<tr>
<td>2</td>
<td>Cheddars</td>
<td>1701 University Drive East, College Station, TX</td>
<td>(979) 260-1701</td>
</tr>
<tr>
<td>3</td>
<td>Nukes</td>
<td>1613 University Drive, College Station, TX</td>
<td>(979) 268-3300</td>
</tr>
<tr>
<td>4</td>
<td>Fish Daddy's Grill House</td>
<td>1611 University Drive East, College Station, TX</td>
<td>(979) 260-1611</td>
</tr>
<tr>
<td>5</td>
<td>Texas Roadhouse</td>
<td>1601 University Drive East, College Station, TX</td>
<td>(979) 268-0558</td>
</tr>
<tr>
<td>6</td>
<td>Wings n More</td>
<td>1511 University Dr. E, College Station, TX</td>
<td>(979) 691-2100</td>
</tr>
<tr>
<td>7</td>
<td>Chipotle</td>
<td>1505 University Drive East, College Station, TX</td>
<td>(979) 260-4824</td>
</tr>
<tr>
<td>8</td>
<td>Panera</td>
<td>1407 University Dr. East, College Station, TX</td>
<td>(979) 268-1013</td>
</tr>
<tr>
<td>9</td>
<td>Red Lobster</td>
<td>1200 University Drive East, College Station, TX</td>
<td>(979) 260-3709</td>
</tr>
<tr>
<td>10</td>
<td>McAlister's Deli</td>
<td>1006 University Dr. East, College Station, TX</td>
<td>(979) 846-6000</td>
</tr>
<tr>
<td>11</td>
<td>Grub Burger Bar</td>
<td>980 University Drive East, College Station, TX</td>
<td>(979) 268-1041</td>
</tr>
<tr>
<td>12</td>
<td>Pei Wei</td>
<td>980A University Drive East, College Station, TX</td>
<td>(979) 260-1209</td>
</tr>
<tr>
<td>13</td>
<td>Buffalo Wild Wings</td>
<td>903 University Drive East, College Station, TX</td>
<td>(979) 691-8453</td>
</tr>
<tr>
<td>14</td>
<td>Abuelos Mexican Food Embassy</td>
<td>840 University Drive East, College Station, TX</td>
<td>(979) 260-3400</td>
</tr>
<tr>
<td>15</td>
<td>Boston's Gourmet Pizza</td>
<td>820 University Drive, College Station, TX</td>
<td>(979) 864-8667</td>
</tr>
<tr>
<td>16</td>
<td>Boneheads</td>
<td>800 University Dr. East, College Station, TX</td>
<td>(979) 587-6868</td>
</tr>
<tr>
<td>17</td>
<td>Atami Steak and Sushi</td>
<td>800 University Drive East, College Station, TX</td>
<td>(979) 268-8883</td>
</tr>
<tr>
<td>18</td>
<td>Blue Baker</td>
<td>800 University Drive East, College Station, TX</td>
<td>(979) 268-3096</td>
</tr>
<tr>
<td>19</td>
<td>Veritas Wine &amp; Bistro</td>
<td>830 University Dr. East, College Station, TX</td>
<td>(979) 268-3251</td>
</tr>
<tr>
<td>20</td>
<td>Rosa's Café</td>
<td>710 University Drive East, College Station, TX</td>
<td>(979) 691-8501</td>
</tr>
<tr>
<td>21</td>
<td>Genghis Grill Mongolian Stir-fry</td>
<td>700 University Drive, College Station, TX</td>
<td>(979) 260-6800</td>
</tr>
<tr>
<td>22</td>
<td>The Republic Steakhouse</td>
<td>701 University Drive East, College Station, TX</td>
<td>(979) 260-4120</td>
</tr>
<tr>
<td>23</td>
<td>Golden Corral – Buffet and Grill</td>
<td>700 University Drive East, College Station, TX</td>
<td>(979) 846-8667</td>
</tr>
<tr>
<td>24</td>
<td>Fox and Hound</td>
<td>505 University Drive East, College Station, TX</td>
<td>(979) 846-0211</td>
</tr>
<tr>
<td>25</td>
<td>Jimmy Johns</td>
<td>200 University Dr. East, College Station, TX</td>
<td>(979) 695-9200</td>
</tr>
<tr>
<td>26</td>
<td>Pizza Hut</td>
<td>102 University Dr. East, College Station, TX</td>
<td>(979) 696-2512</td>
</tr>
<tr>
<td>27</td>
<td>Fuego Tortilla Grill</td>
<td>108 Poplar St, College Station, TX</td>
<td>(979) 703-1804</td>
</tr>
</tbody>
</table>
51st Annual Meeting of CMS

Everything is big: From nanoparticles to planets
VENUE: MEMORIAL STUDENT CENTER (MSC), TEXAS A&M UNIVERSITY, COLLEGE STATION, TX
MEMORIAL STUDENT CENTER (MSC) FLOOR PLANS
DINING PLACES ON AND AROUND TAMU CAMPUS DURING CONFERENCE
Everything is big: From nanoparticles to planets

Program
51st Annual Meeting of CMS

PROGRAM AT-A-GLANCE

<table>
<thead>
<tr>
<th>Time</th>
<th>Saturday May 17</th>
<th>Sunday May 18</th>
<th>Monday May 19</th>
<th>Tuesday May 20</th>
<th>Wednesday May 21</th>
</tr>
</thead>
<tbody>
<tr>
<td>7:30</td>
<td>Field Trip: Clay and lithium mining, processing, reclamation (Leave at the bus stop in front of MSC* at 7:30 am sharp, lunch served)</td>
<td>Workshop: Surface modification of clays and nanocomposites (MSC* 2406A)</td>
<td>Registration (MSC* 2300B)</td>
<td>Welcome ceremony, Jackson Award lecture (MSC 2300A)</td>
<td>Plenary session, Pioneer lecture (MSC 2300A)</td>
</tr>
<tr>
<td>8:00</td>
<td></td>
<td></td>
<td></td>
<td>Coffee break (MSC 2300B)</td>
<td></td>
</tr>
<tr>
<td>8:20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9:00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11:00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11:30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12:00</td>
<td>Council Meeting (MSC* 2402)</td>
<td>Sustaining members' luncheon (invitation only, MSC 2401)</td>
<td>Lunch on your own</td>
<td>Past presidents' luncheon (invitation only, MSC 2401)</td>
<td>Local soil tour (13:30 to 17:00) (Leave at the bus stop in front of MSC* at 13:30 sharp)</td>
</tr>
<tr>
<td>12:30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13:00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13:30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14:00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14:30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15:00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15:20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16:00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16:30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17:00</td>
<td>Opening Reception (MSC 2300B)</td>
<td>CMS business meeting (MSC 2300A)</td>
<td>New member, Student Reception (MSC 2300B)</td>
<td>Conference Banquet (MSC 2400)</td>
<td>CCM Editorial board dinner (invitation only) (MSC 2401)</td>
</tr>
<tr>
<td>17:30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19:00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19:30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20:00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21:00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*MSC: Memorial Student Center at Texas A&M University.

Session key:
1. Functional clay nanoparticles
2. 2-D nanomaterials
3. Qualitative and quantitative characterization of clay minerals and short-range ordered materials
4. Spectroscopy of clays
5. Molecular simulations of clays and related phases: properties and reactions
6. Clays in geological processes
7. Clay mineralogy and geochemistry on Mars
8. Clays in soils and sediments
9. Clays and Environments
10. Clays and oil/gas production
11. Clay interactions with radioactive waste and waste forms
12. Interactions of clay minerals with microorganisms and biomolecules
13. Clays, nanoparticles and health
14. Asian Clay Minerals Group research progress
15. Teaching clay mineralogy
16. General session
FRIDAY, MAY 16
18:00-21:00 Executive Committee Meeting. (Heep Center, 440, on TAMU west campus)

SATURDAY, MAY 17
7:30-17:30 Field trip: Clay and lignite mining, processing, and reclamation. Leave at the bus stop in front of MSC\textsuperscript{1} at 7:30 sharp. Return to MSC. Lunch served.
8:00-17:00 CMS Council meeting. MSC 2402

SUNDAY, MAY 18
8:00-17:00 Workshop: Surface modification of clays and nanocomposites. MSC 2406A
13:20-19:00 Registration, MSC 2300B
18:00-20:00 Opening reception, MSC 2300B

\textsuperscript{1} MSC: Memorial Student Center.
MORNING, MONDAY, MAY 19

7:30-8:20  Registration, MSC 2300B

WELCOME CEREMONY/ PLENARY SESSION
Room: MSC 2300A

8:20-8:30  INTRODUCTORY REMARKS AND ANNOUNCEMENTS, Youjun Deng, Chair of organizing committee.

8:30-8:55  WELCOME REMARKS AND INTRODUCTION OF TAMU SYSTEM
1. David D. Baltensperger, Head of Department of Soil and Crop Sciences, TAMU; President of Crop Science Society of America.
2. Alan Sams, Executive Associate Dean, College of Agriculture and Life Sciences, TAMU
3. Craig L. Nessler, Director of Texas A&M AgriLife Research
4. Larry Boleman, Special Assistant to the President and Associate Vice Chancellor

8:55-9:05  CMS PRESIDENTIAL REMARKS, Michael Velbel, 2013-2014 CMS President

Peter Komadel, Institute of Inorganic Chemistry, Slovak Academy of Sciences


10:00-10:20  Coffee break, MSC 2300B

TECHNICAL SESSIONS

Session 1a. Functional clay nanoparticles
Organizers/chairs: Atsushi Takahara and Hung-Jue Sue
Room: MSC 2300A

10:20-11:00  DESIGN AND CHARACTERIZATION OF HYBRID MATERIALS FROM NATURAL INORGANIC NANOTUBE “HALLOYSITE”. Atsushi Takahara*, Wei Ma, Hui Wu, Di Tao, and Weng-On Yah

11:00-11:20  INTERLAYER IN-SITU REACTION PREPARATION METHOD OF NANOSTRUCTURED TIO2/MONTMORILLONITE MATERIALS. Hongjuan Sun*, Tongjiang Peng, Hailiang Dong, and Chaojian Gu

11:20-11:40  EFFECT OF THE CLAY TYPE ON THE PROPERTIES OF REINFORCED-
Session 11a. Clay interactions with radioactive waste and waste forms
Organizers/chairs: Nik Qafoku and Jim Neeway
Room: MSC 2406A
10:20-11:00 WATER AND ION DIFFUSION IN THE OSMOTIC HYDRATE OF NASMECTITE. Ian C. Bourg*, Ruth Tinnacher, Michael Holmboe, Christophe Tournassat, and Jim Davis
11:00-11:20 INTERACTION BETWEEN BENTONITE AND VARIOUS METALS MIMICKING SPENT NUCLEAR WASTE PACKAGES AT ELEVATED TEMPERATURES AND PRESSURES. Michael C. Cheshire*, Florie A. Caporuscio, and Carlos Jove-Colon
11:40-12:00 ADSORPTION OF MONOVALENT AND DIVALENT CATIONS AT THE CLAY – WATER INTERFACE INVESTIGATED BY MOLECULAR COMPUTER SIMULATIONS. Narasimhan Loganathan*, Brice F. Ngouana Wakou, and Andrey G. Kalinichev

Session 5a. Molecular simulation of clay minerals and reactions
Organizers/chairs: Xiandong Liu and Andrey Kalinichev
Room: MSC 2406B
10:20-11:00 CHALLENGES FOR FORCE FIELDS OF CLAY MINERALS AND NEW KAOLINITE PARAMETERS. Hendrik Heinz*, Valentina Erastova, and H. Christopher Greenwell
11:00-11:20 HYDRATION STUDY OF PALYGORSKITE AND SEPIOLITE USING MOLECULAR SIMULATION. Jinhong Zhou, Xiancai Lu*
11:20-11:40 MOLECULAR DYNAMICS SIMULATIONS OF CATION ADSORPTION AT MICA-WATER INTERFACES. Ian C. Bourg, Christophe Tournassat
11:40-12:00 MOLECULAR SIMULATIONS OF WATER-METHANE AND WATER-CARBON DIOXIDE FLUIDS BETWEEN NA-MONTMORILLONITE CLAY SURFACES. Qi Rao, Yuan Xiang, and Yongsheng Leng*
NOON, MONDAY, MAY 19

12:00-13:20  Lunch on your own; Sustaining members’ luncheon (invitation only, MSC 2401)
AFTERNOON, MONDAY, MAY 19

Session 1b. Functional clay nanoparticles

Organizers/chairs: Atsushi Takahara and Hung-Jue Sue

Room: MSC 2300A

13:20-14:00 SURFACE FUNCTIONALIZED ZIRCONIUM PHOSPHATES: A UNIQUE CLASS OF FUNCTIONAL MATERIALS. Abraham Clearfield*

14:00-14:20 TAILORING THE THIRD DIMENSION IN LAYERED MATERIALS. Jingfang Yu, Lichen Xiang, Benjamin R. Martin, Jingjing Liu, Abraham Clearfield, Zhiping Luo, and Luyi Sun*

14:20-14:40 EFFECT OF SURFACE MODIFIER AND ASPECT RATIO ON RHEOLOGY OF MODEL NANOCERAMIC PARTICLES IN EPOXY. Kevin L. White*, Peng Li, Spencer Hawkins,

14:40-15:00

15:00-15:20 Coffee break, MSC 2300B

15:20-17:00 Authors present at poster session. Posters will be displayed until noon, Wednesday, May 21, 2014

Session 11b. Clay interactions with radioactive waste and waste forms

Organizers/chairs: Nik Qafoku and Jim Neeway

Room: MSC 2406A


13:40-14:00 EFFECT OF CALLOVO-OXFOR DIAN CLAY ROCK ON THE DISSOLUTION RATE OF THE SON68 SIMULATED NUCLEAR WASTE GLASS. James Neeway*

14:00-14:20 TECHNETIUM INTERACTIONS WITH HUMIC SUBSTANCES. Nathalie A. Wall*

14:20-15:00 URANIUM(VI) AND NEPTUNIUM(V) RETENTION BY CLAY MINERALS AND NATURAL CLAY ROCK–INFLUENCE OF CLAY ORGANICS, TEMPERATURE AND PORE WATER SALINITY. Katja Schmeide*, Claudia Joseph, and Katharina Fritsch

15:00-15:20 Coffee break, MSC 2300B

15:20-17:00 Authors present at poster session. Posters will be displayed until noon, Wednesday, May 21, 2014
Session 5b. Molecular simulation of clay minerals and reactions

Organizers/chairs: Xiandong Liu and Andrey Kalinichev

Room: MSC 2406B

13:20-14:00  MOLECULAR SIMULATION OF THE INITIAL STAGE OF SILICATE GROWTH. Thuat T. Trinh, A. Pavlova, Rutger A. van Santen, and Evert Jan Meijer

14:00-14:20  YTTRIUM ADSORPTION ON SOLVATED EDGE SURFACES OF KAOLINITE: INSIGHTS FROM FIRST PRINCIPLE MOLECULAR DYNAMICS. Lei Li*, Xiandong Liu, Xiancai Lu, and Rucheng Wang

14:20-15:00  THE STRUCTURE, DYNAMICS AND FUNCTION OF SYNTHETIC AND BIOLOGICAL POLYMERS AT THE CLAY MINERAL SURFACE FROM MOLECULAR DYNAMICS SIMULATION. Jacob B. Swadling, James L. Suter, Derek Groen, David W. Wright, and Peter V. Coveney*

15:00-15:20  Coffee break, MSC 2300B

15:20-17:00  Authors present at poster session. Posters will be displayed until noon, Wednesday, May 21, 2014
POSTER SESSION

Room: MSC 2300B.

Set up: by 12 pm on Monday, May 19, 2014. Push pins will be supplied.

Presenting time: Authors present at poster session 15:20-17:00

Display time: Posters will be displayed until Wednesday noon, May 21, 2014.

Session 1. Functional clay nanoparticles

Organizers/chairs: Atsushi Takahara and Hung-Jue Sue

1. ELECTROSPUN POLYACRYLONITRILE MAT CONTAINING SYNTHETIC NA-MONTMORILLONITE OR ORDERED MESOPOROUS SILICA PARTICLES: PREPARATION AND CHARACTERIZATION. Sliman Al Muhamed, Nabyl Khenoussy, Magali Bonne, Laurence Schacher, Jocelyne Brendlé*, Dominique Adolphe, and Bénédicte Lebeau

2. EFFICIENCY AND MECHANISM OF HEAVY METALS SORPTION ON GRAFTED KAOLINITES OF DIFFERENT STRUCTURAL ORDER. Anna Koteja*, Jakub Matusik

3. ULTRA-STRONG EPOXY NANOCOMPOSITES CONTAINING SELF-ASSEMBLED SYNTHETIC CLAY IN SMECTIC ORDER. Peng Li*, Kevin L. White, Chienhong Lin, Anastasia Muliana, Riichi Nishimura, and Hung-Jue Sue

4. FERRIC CHLORIDE TREATMENT ON HALLOYSITE NANOTUBES. Shu-Ting Liu*, Ao-Bo Zhang, Xue-Gang Chen, and Ying Ye

5. MECHANICAL AND GAS BARRIER PROPERTIES OF RUBBER/KAOLIN NANOCOMPOSITES. Qinfu Liu*, Yinmin Zhang, and Hongfei Cheng

6. HALLOYSITE CLAY NANOTUBES USED FOR FABRICATION OF SUPERAMPHIPHOBIC SURFACES. Wei Ma*, Atsushi Takahara

Session 3. Qualitative and quantitative characterization of clay minerals and short-range ordered materials.

Organizers/chairs: Michael Ploetze and Bruno Lanson

7. PyXRD: CAN WE IMPROVE AUTOMATIC PARAMETER REFINEMENT FOR FULL-PROFILE X-RAY DIFFRACTION FITTING OF DISORDERED LAYERED STRUCTURES USING A MULTI-SPECIMEN APPROACH? M. Dumon*, E. Van Ranst

8. CHARACTERIZATION AND QUANTIFICATION OF WATER IN SMECTITES WITH NUCLEAR MAGNETIC RESONNANCE AND SMALL ANGLE X-RAY SCATTERING. Eric Kohler*, Marc Fleury, Françoise Nornant, Serge Gautier, Jalel M’Hamdi, and Loic Barré

Session 4. Spectroscopy of clays.

Organizer/chair: Georgios Chryssikos
9. SYSTEMATICS OF BENTONITE BY NEAR-INFRARED SPECTROSCOPY. Aglaia Deligianni\textsuperscript{1}, Vassilis Gionis*, and Georgios D. Chryssikos.


Session 5. Molecular simulation of clay minerals and reactions. 

Organizers/Chairs: Xiandong Liu and Andrey Kalinichev.

11. STRUCTURE AND DYNAMICS OF UO\textsubscript{2}\textsuperscript{2+} SORPTION ON KAOLINITE SURFACES: AN ATTEMPT TO IMPROVE UNDERSTANDING OF THE \textsuperscript{230}Th/\textsuperscript{234}U DATING ACCURACY USING COMPUTATIONAL MOLECULAR MODELING TECHNIQUES. Helena Hercman, Jacek Pawlak, and Andrey G. Kalinichev*.


Organizers/chairs: Michal Skiba and Manika Prasad.


Session 7. Clay mineralogy and geochemistry on Mars.

Organizers: Bethany Ehlmann & Doug Ming.


17. X-RAY DIFFRACTION STUDIES OF FE-SAPONITE UNDER LOW HUMIDITY CONDITIONS: IMPLICATIONS FOR PHYLOSILICATES IN YELLOWKNIFE BAY, GALE CRATER, MARS. Cherie N. Achilles*, David...
L. Bish


19. ALTERATION OF AMORPHOUS AND CRYSTALLINE PHASES, FORMATION OF CLAY MINERALS IN GEOLOGICAL SUCCESSIONS, A PROJECT PRESENTATION. Henning Dypvik*, Helge Hellevang, and Stephanie Werner

20. ALTERATION OF BASALTIC GLASS TO Mg/Fe-SMECTITE UNDER ACIDIC CONDITIONS: A POTENTIAL SMECTITE FORMATION MECHANISM ON MARS. Tanya Peretyazhko*, Brad Sutter, and Douglas W. Ming


Organizers/chairs: Craig Rasmussen and Balwant Singh

21. CLAY MINERALOGY OF AN ALLUVIAL AQUIFER, RIFLE, COLORADO. W. Crawford Elliott*, David Lim, Rebecca Pickering, Laura K. Zaunbrecher, Kenneth H. Williams, and Philip E. Long

22. EGYPTIAN “BENTONITIC CLAYS”: MINERALOGY, CEC, AND ORIGIN. Ray Ferrell*, Mohamed Agha, and George Hart

23. AEOLIAN AND AUTHIGENIC CLAY MINERALS IN THE BROWN PEDOSEDIMENTARY SEQUENCE OF PALEOLITHIC SITE, KOREA. Gi Young Jeong*


25. ASSESSMENT OF KAOLINITES ORDER-DISORDER FOR SOILS AND SEDIMENTS FROM DOCE RIVER BASIN, MINAS GERAIS–BRAZIL. Anderson A. Pacheco*, Mauricio P.F. Fontes, Juan S. Lezama-Pacheco, and Scott Fendorf

26. WEATHERING OF GLAUVONITE IN A LUVISOL PROFILE FROM GORA PULAWSKA, POLAND. Michał Skiba*, Katarzyna Maj-Szeliga, Wojciech Szymański, and Artur Błachowski

27. DISTINGUISHING BETWEEN PORE-FILLING AND PARTITIONING OF NEUTRAL ORGANICS CONTAMINANT SORPTION ON GEOSORBENTS. Kamol Das*, Cliff T. Johnston

28. A PHOSPHATE ADSORBENT FROM HETEROCOAGULATION OF MONTMORILLONITE AND LAYERED DOUBLE HYDROXIDE. Fangqun Gan*, Xiaoshuai Hang, Hongting Zhao, Jianmin Zhou, and Yijie Ma

Session 11. Clay interactions with radioactive waste and waste forms.
Organizers/chairs: Nik Qafoku and Jim Neeway

29 ALTERATION OF CLAY MINERALS DUE TO INFLUENCE OF ACID AND ALKALINE SOLUTIONS ACCOMPANY RADIOACTIVE WASTE IN THE DEEP GEOLOGICAL LAYERS. Victoria V. Krupskaya*, Sergey V. Zakusin, Anatoliy P. Zhukhlistov, Andrey A. Zubkov

30. OVERVIEW OF GAPS IN HIGH-LEVEL NUCLEAR WASTE FORM/CLAY INTERACTIONS. James Neeway*

Session 12. Interactions of clay minerals with microorganisms and biomolecules

Organizers/chairs: Qiaoyun Huang and Deb Jaisi

31. INTERFERENCE OF MAJOR ORGANIC COMPOUNDS IN FERMENTATION SOLUTION ON AFLATOXIN B₁ ADSORPTION BY SMECTITES. Sabrina S Alaın*, Youjun Deng

32. SPATIAL VERSUS SPECTRAL RESOLUTION: MAPPING HOT SPRING CLAYS USING METER SCALE SATELLITE DATA AND GROUND TRUTH MINERALOGY. Laura E. Fackrell*, Paul A. Schroeder

Session 13. Clays, nanoparticles and health.

Organizers/chairs: Sandra Carolina Londono & Keith Morrison

33. SYNERGETIC BENEFITS OF NIXTAMALIZATION AND CLAY ADSORBENTS IN DETOXIFICATION OF AFLATOXIN. Stacy Arteaga, Ana L. Barrientos Velázquez*, and Youjun Deng

34. ASSESSING AND MODIFYING CHINA BENTONITES FOR AFLATOXIN DETOXIFICATION. Fangqun Gan*, Yijie Ma, Qiaoyun Huang, and Youjun Deng

35. SMECTITE CRYSTAL STRUCTURAL AND SURFACE FACTORS IN DETERMINING THE BINDING EFFICACY FOR ZEARALENONE. Chun-Chun Hsu, Youjun Deng

36. INTERCALATION OF PHYTOCHEMICAL FROM JABORANDI LEAVES INTO SYNTHETIC BEIDELLITE CLAYS. Vanessa Yumi Sakai*, Leiz Maria Costa Véras, Maria Adelaide Guimarães, Filipe Camargo Dalmatti Alves Lima, José Roberto de Souza de Almeida Leite, Helena Maria Petrilli, Jocelyne Miehé-Brendlé, and Vera Regina Leopoldo Constantino

37. AFLATOXIN SORPTION ON VOLCANIC ASH DERIVED SOILS. Maria Guadalupe Tenorio Arvide*, Yolanda P. Silva Uribe, Youjun Deng, Ricardo Munguía P., and Miguel A. Valera P.

38. AFLATOXIN B₁ REMOVAL ON BENTONITE INTERCALATED BY SURFACTANTS. Ya T. Chan*, Yu-Min Tzou


Organizer(s): Jinwook Kim, Hyen-Goo Cho and Jae-Min Oh

39. GAS BARRIER PROPERTIES OF NATURAL RUBBER/MECHANOCHEMICAL TREATMENT COAL BEARING
STRATA KAOLINITE NANOCOMPOSITES PREPARED BY MELT BLENDING. Hongfei Cheng*, Qinfu Liu

40. DESORPTION OF PHOSPHATE FROM KAOLINITE KGa-1b. Hyen Goo Cho*, Soon-Oh Kim

41. SYNTHESIS AND CHARACTERIZATION OF IRON/MANGANESE OXIDE COMPOSITE AND ITS SORPTION CAPACITY FOR HEAVY METALS AND PHOSPHATE FROM AQUEOUS SOLUTION. Chul-Min Chon, Seung-Bum Roh, Soh-joung Yoon*, In-Hyun Nam, Hocheol Song, and Jae-Gon Kim

42. SIZE AND SURFACE CHARGE DEPENDENT BLUE GREEN ALGAE FLOCCULATION OF ANIONIC CLAYS. In-Taek Hong*, Tae-Hyun Kim, and Jae-Min Oh

43. CLAY MINERALS IN ASIAN AIR. Gi Young Jeong*

44. ANIONIC CLAYS AS POTENTIAL NANO CARRIERS FOR COMBINATION CHEMOTHERAPY. Tae-il Kim, Gyeong Jin Lee, Tae-Hyun Kim, and Jae-Min Oh*

45. PRELIMINARY RESULTS OF THE MICROBE-MINERAL INTERACTION IN ACIDOHYPER THERMAL ENVIRONMENTS, YELLOWSTONE NATIONAL PARK. Tae-hee Koo*, Gill Geesey, and Jin-wook Kim

46. INFLUENCE OF ANIONIC SURFACE MODIFIER ON THERMAL STABILITY AND MECHANICAL STRENGTH OF POLYPROPYLENE/LAYERED DOUBLE HYDROXIDE NANO COMPOSITES. Jae-Hun Yang*, Wei Zhang, Joung-Yoon Choi, and Jin-Ho Choy

47. WELL-ORDERED POROUS TITANIA-PILLARED CLAYS FROM MODIFIED LAYERED SILICATES. Jae-Hun Yang*, Huiyan Piao, and Jin-Ho Choy

Session 15. Teaching clay mineralogy.

Organizer/Chair: Paul A. Schroeder

48. IMACS: AN INTERNATIONAL MASTER PROGRAMME ENTIRELY DEVOTED TO CLAY MINERALS. S. Petit*, P. Patrier Mas, G. Christidis, F. Rocha, C. Detellier, and A. Mexias

Session 16. General session.

Organizer/Chair: Bruce Herbert

49. GEOCHEMICAL CONTROLS FOR THE PRESERVATION OF HUMAN REMAINS AND MUMMIES: SOR JUANA INES DE LA CRUZ, LA REINA ROJA, AND PEPITA. Javiera Cervini-Silva*, Lourdes Muñoz, Arturo Romano-Pacheco, Elizabeth Mejía-Pérez Campos, Ximena Chávez-Baldes, Eduardo Palacios, Paz del Angel, Ascención Montoya, Eduardo Ramos, and Fanny López

50. CLAY SWELLING IN ANHYDRITIC CLAYSTONE. Timothy P. Wangler*, Amir R. Shahab, and Robert J. Flatt
EVENING, MONDAY, MAY 19

18:00-19:00  New member and student reception (invitation only), MSC 2300B
19:00-21:00  CCM editorial board dinner (invitation only, MSC 2401)
MORNING, TUESDAY, MAY 20

7:30-8:20 Registration, MSC 2300B

PLENARY SESSION
Room: MSC 2300A

8:20-9:05 ANIONIC CLAY-BIOMOLECULAR INTERACTION SELF-ASSEMBLIES: MULTIFUNCTIONAL NANO-BIO HYBRID MATERIALS FOR GENE AND DRUG DELIVERY. Jin-Ho Choy*


9:15–10:00 CLAYS AND CLAY MINERALS ON MARS: INDICATORS FOR AQUEOUS PROCESSES AND HABITABLE ENVIRONMENTS. (PIONEER IN CLAY SCIENCE LECTURE). Douglas W. Ming*

10:00-10:20 Coffee break, MSC 2300B

TECHNICAL SESSIONS

Session 7a. Clay mineralogy and geochemistry on Mars
Organizers/chairs: Bethany Ehlmann & Doug Ming
Room: MSC 2300A

10:20-10:50 MARTIAN SMECTITES AND RELATED MATERIALS IN THE NAHLITE MARTIAN METEORITES. Allan H. Treiman*, John C. Bridges

10:50-11:10 COMPOSITION OF CLAY MINERALS ON MARS FROM ORBITING INFRARED SPECTROSCOPY: KEY MINERALS AND KEY QUESTIONS. Bethany L. Ehlmann*


11:30-12:00 SMECTITES ON THE RIM OF ENDEAVOUR CRATER MARS AS INFERRED FROM MARS RECONNAISSANCE ORBITER CRISM HYPER SPECTRAL IMAGES AND OPPORTUNITY ROVER OBSERVATIONS. Raymond E. Arvidson*
Session 1c. Functional clay nanoparticles
Organizers/chairs: Atsushi Takahara and Hung-Jue Sue
Room: MSC 2406A

10:20-10:40 FACILE PREPARATION OF MnFe₂O₄/HALLOYSITE NANOTUBULAR ENCAPSULATES WITH ENHANCED MAGNETIC AND ELECTROMAGNETIC PERFORMANCES. Ao-Bo Zhang*, Ying Ye, and Xue-Gang Chen

10:40-11:00 INTERCALATION OF MACROSCOPIC VERMICULITE PARTICLES INTO NANOPARTICLES WITH ANIONIC SURFACTANTS. Sevim İşçi*, Yavuz İşçi, Huaming Yang*, Peiwei Hu

11:00-11:20 ROD-LIKE KAOLINITE COATED WITH METAL OXIDES: MICROSTRUCTURE AND FUNCTIONS. Huaming Yang*, Peiwei Hu


11:40-12:00 CLAY-ASSISTED DISPERSION OF NANOPARTICLES IN POLYMER MATRICES. D. Sun*, X. Zhang, C.C. Chu, W.N. Everett, and H.-J. Sue

Session 14a. Asian Clay Minerals Group research progress
Organizers/chairs: Jinwook Kim, Hyen-Goo Cho and Jae-Min Oh
Room: MSC 2406B

10:20-10:40 TRANSFORMATION OF ZINC/GALLIUM-LAYERED DOUBLE HYDROXIDE TO GALLIUM ZINC OXYNITRIDE VIA UREA PYROLYSIS. Jae-Hun Yang*, Yirong Pei, and Jin-Ho Choy

10:40-11:00 IMPROVEMENT OF METHYLENE BLUE ADSORPTION TEST METHODS FOR BENTONITE. Youko Miyoshi*, Yu Horiuchi, and Tetsuichi Takagi

11:00-11:20 EUROPIUM(III)-PHENANTHRONE INTERCALATED HECTORITE/ POLYPROPYLENE NANOCOMPOSITE FILM WITH BIFUNCTIONAL PHOTOLUMINESCENT AND SUPERHYDROPHOBIC PROPERTIES. Hyun Jung*, Aran Kim


11:40-12:00 ONE-POT SYNTHESIS OF HETERO-ION DOPED GRAPHENE BY USING ELECTRON-BEAM IRRADIATION. Myunggool Kang*, Dong Heon Lee, Jeong Hoon Yang, Mi Ru Jo, Yong-Mook Kang, and Hyun Jung
NOON, TUESDAY, MAY 20

12:00-13:20  Lunch on your own
AFTERNOON, TUESDAY, MAY 20

Session 7b. Clay mineralogy and geochemistry on Mars
Organizers/chairs: Bethany Ehlmann & Doug Ming
Room: MSC 2300A


14:20-14:40  SULFATE FORMATION FROM ACID-WEATHERED PHYLLOSILICATES: IMPLICATIONS FOR THE AQUEOUS HISTORY OF MARS. Patricia I. Craig*, Doug W. Ming, and Elizabeth B. Rampe


15:00-15:20  Coffee break, MSC 2300B

Session 14b. Asian Clay Minerals Group research progress
Organizers/chairs: Jinwook Kim, Hyen-Goo Cho and Jae-Min Oh
Room: MSC 2406B

13:20-13:40  INTERACTION BETWEEN ANIONIC CLAYS AND BLOOD COMPONENTS. Jae-Min Oh*, Hyoung-Mi Kim

13:40-14:00  FORMATION OF CLAY MINERALS IN DEEP SUBSEA FLOOR SEDIMENT, SOUTH PACIFIC GYRE: IODP EXPEDITION 329. Kiho Yang*, Kogure Toshihiro, Bryce Hoppie, Robert Harris, Hionsuck Baik, IODP Expedition 329
51st Annual Meeting of CMS
Program

Everything is big: From nanoparticles to planets

<table>
<thead>
<tr>
<th>Time</th>
<th>Session Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:00-14:20</td>
<td>STRUCTURES OF SERPENTINE-CHLORITE MIXED-LAYER MINERALS FROM HYDROTHERMAL SYSTEMS. Sayako Inoué*, Toshihiro Kogure</td>
</tr>
<tr>
<td>14:20-14:40</td>
<td>AVATAR DNA@CLAY NANOSHELL HYBRID SYSTEM. Dae-Hwan Park*, Jin-Ho Choy</td>
</tr>
<tr>
<td>14:40-15:00</td>
<td>DRIFT SPECTROSCOPIC ANALYSIS OF &lt;2μM CLAY SIZE FRACTION IN ARGILLACEOUS SOURCE ROCKS. Yingli Li*, Jingong Cai</td>
</tr>
<tr>
<td>15:00-15:20</td>
<td>Coffee break, MSC 2300B</td>
</tr>
</tbody>
</table>

**Session 13. Clays, nanoparticles and health**
Organizers/chairs: Sandra Carolina Londono & Keith Morrison

Room: MSC 2406A

<table>
<thead>
<tr>
<th>Time</th>
<th>Session Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>13:20-13:40</td>
<td>CHROMIUM IN THE CENTRAL OKLAHOMA AQUIFER: DIAGENETIC IRON REDISTRIBUTIONS PROVIDE WINDOWS INTO THE RELATIVE ROLES OF CLAYS, IRON OXIDES, AND CARBONATES. Shelbie A. Bartlett, Jeffrey P. Westrop, Andrew L. Swindle, and Andrew S. Elwood Madden*</td>
</tr>
<tr>
<td>13:40-14:00</td>
<td>THE DEVELOPMENT OF NOVEL ANTIBACTERIAL POLYMER-CLAY COMPOSITE SYSTEMS. Ashley R Hamilton*, Matthew Roberts, Gillian A Hutcheon, and Elsie E Gaskell</td>
</tr>
<tr>
<td>14:00-14:20</td>
<td>ANTI-INFLAMMATORY AND ANTI-OXIDANT ACTIVITY, AND CYTOXICITY OF HALLOYLITE SURFACES. Javiera Cervini-Silva*, Antonio Nieto-Camacho, Eduardo Palacios, Ascención Montoya, Virginia Gómez-Vidales, and María Teresa Ramírez-Apán.</td>
</tr>
<tr>
<td>14:20-14:40</td>
<td>THE ANTIBACTERIAL ACTIVITY OF MINERALS PROVIDES NEW INSIGHTS ON METAL TOXICITY. Keith D. Morrison*, Lynda B. Williams</td>
</tr>
<tr>
<td>14:40-15:00</td>
<td>TRANSMISSION ELECTRON MICROSCOPY IN ANTIBACTERIAL CLAY INVESTIGATIONS. Sandra C. Londono*, Lynda B. Williams</td>
</tr>
<tr>
<td>15:00-15:20</td>
<td>Coffee break, MSC 2300B</td>
</tr>
</tbody>
</table>

**Session 3. Qualitative and quantitative characterization of clay minerals and short-range ordered materials**
Organizers/chairs: Michael Ploetze and Bruno Lanson

Room: MSC 2300A

<table>
<thead>
<tr>
<th>Time</th>
<th>Session Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>15:40-16:00</td>
<td>ELECTRON MICROSCOPY STUDIES OF CLAYS AND CLAY-BASED</td>
</tr>
</tbody>
</table>
COMPOSITES. Oren Regev*, Jaime C. Grunlan

16:00-16:20 RECOGNITION OF SODIUM CARBONATE ACTIVATED BENTONITES. S. Kaufhold*, K. Emmerich*, R. Dohrmann, A. Steudel, and K. Ufer

16:20-16:40 MINERALOGICAL ANALYSIS OF MUDSTONE AND CLAYSTONE SAMPLES BY MINERAL MAPPING: HOW ACCURATE CAN THAT BE? Claire I. Fialips*, Jean-Paul Laurent, Bernard Labeyrie, Benoit Lasserre, François Umbhauer, and David Haberlah

16:40-17:00 RESULTS OF THE SEVENTH REYNOLDS CUP CONTEST IN QUANTITATIVE MINERAL ANALYSIS. M. Ploetze*

Sessions 12. Interactions of clay minerals with microorganisms and biomolecules / 13b. Clays, nanoparticles and health

Organizers/chairs: Qiaoyun Huang and Deb Jaisi; Sandra Carolina Londono & Keith Morrison

Room: MSC 2406A

15:20-15:40 SORPTION-DESORPTION OF CARBOXYLIC AND AMINO ACIDS ON PURE CLAY MINERALS. Sabina Yeasmin*, Balwant Singh, Rai Kookana, Mark Farrell, Donald Sparks, and Cliff T. Johnston

15:40-16:00 RECOVERY OF SOIL MICROBIAL POPULATIONS, FUNCTION, AND COMMUNITY COMPOSITION FOLLOWING RECLAMATION OF A LIGNITE SURFACE MINE. Justin Ng, Terry Gentry*, Frank Hons, and Jizhong Zhou

16:00-16:20 MICROBIAL COMMUNITY DYNAMICS AND ARSENIC CHEMISTRY OF IRON-OXIDE RICH ROOT-PLAQUE IN RICE RHIZOSPHERE UNDER WATER MANAGEMENT PRACTICES. Anil Somenahally*, Wengui Yan, Richard Loeppert, and Terry Gentry

16:20-16:40 MICROBIAL CYCLING OF PHOSPHATE AT THE MINERAL-WATER INTERFACE. Deb P Jaisi*

16:40-17:00 INCREASED AFLATOXIN AND FUMONISIN ADSORPTION TO FEED ADDITIVES BY REDUCING THE ADSORPTION OF SOLUBLE FEED COMPOUNDS. William Jaynes*, Richard Zartman

17:00-17:20 ADSORPTION AND INTERACTION OF CIPROFLOXACIN AND PROBE COMPOUNDS WITH PALYGORSKITE. Po-Hsiang Chang*, Wei-Teh Jiang, Zhaohui Li, Qing-feng Wu, Jiin-Shuh Jean, Guo-Cheng Lv, and Chung-Yih Kuo
Session 5c. Molecular simulation of clay minerals and reactions

Organizers/chairs: Xiandong Liu and Andrey Kalinichev

Room: MSC 2406B


15:40-16:00 MOLECULAR MODELING OF THE EFFECT OF 40Ar RECOIL IN ILLITE PARTICLES ON THE K-Ar ISOTOPE DATING OF THEIR HOST ROCKS. Marek Szczerba*, Arkadiusz Derkowski, Andrey Kalinichev, and Jan Średoń

16:00-16:20 MOLECULAR INVESTIGATION OF CO₂ ADSORPTION AND SWELLING STRAIN IN NA-EXCHANGED WYOMING MONTMORILLONITE. Paul Spiering, Rick Wentinck, Andreas Busch, Johannes G.E.M. Fraaije, and Tim J. Tambach*

16:20-16:40 MOLECULAR MODELING STUDY THE ADSORPTION OF FULLERENE ON CLAY MINERAL SURFACE. Runliang Zhu*, Qing Zhou, Jianxi Zhu, and Hongping He

16:40-17:00 HYDRATION AND MOBILITY OF INTERLAYER IONS OF (NAX, CAY)-MONTMORILLONITE: A MOLECULAR DYNAMICS STUDY. Lihu Zhang*, Xiancai Lu, Xiandong Liu, Kan Yang, Huiqun Zhou, and Rucheng Wang
EVENING, TUESDAY, MAY 20

17:00-18:00 CMS business meeting (MSC 2300A). Everyone is invited.
18:30-19:30 Conference banquet (MSC 2400)
19:30-20:15 Featured presentation (MSC2400): The BIGGEST collection of NASA extraterrestrial samples: Texas of course. Mary Sue Bell. JACOBS@NASA Johnson Space Center.
20:15-21:00 Awards, future conference announcements, & CMS traditions (MSC 2400).
MORNING, WEDNESDAY, MAY 21

Session 4. Spectroscopy of clays
Organizers/chairs: Georgios Chryssikos
Room: MSC 2404

8:00-8:40 CONTRIBUTION OF IR SPECTROSCOPY TO CLAY MINERALS STUDIES. S. Petit*

8:40-9:00 SPECTRAL TRENDS IN AQUEOUSLY ALTERED CM/CI METEORITES. M. M. McAdam*, J. M. Sunshine, K. T. Howard, and T. M. McCoy

9:00-9:20 A FORGOTTEN BAND–INFRARED SIGNATURE OF THE INTERLAYER WATER IN SMECTITES. Artur Kuligiewicz*, Marek Szczerba, Arkadiusz Derkowski, Vassilis Gionis, and Georgios D. Chryssikos

9:20-9:40 NEAREST NEIGHBOR DISTRIBUTIONS IN SMECTITES. Will P. Gates*, John D. Cashion

9:40-10:00 HOW DOES METHYLENE BLUE INTERACT WITH THE SURFACE OF KAOLINITE? Cliff T. Johnston*, Robert A. Schoonheydt

10:00-10:20 Coffee break, MSC 2300B

Session 16. General session
Organizers/chairs: Bruce Herbert
Room: MSC 2406A

8:00-8:20 FINE-GRAINED REGULARLY INTERSTRATIFIED SERPENTINE-TOCHILINITE INTERGROWTH IN THE MIGHEI-TYPE CARBONACEOUS CHONDRITE QUEEN ALEXANDRA RANGE 93005: IMPLICATIONS FOR EXTENT OF PARENT-BODY AQUEOUS ALTERATION. Michael A. Velbel

8:20-8:40 LONG-TERM LABORATORY EXPERIMENTS OF ARTIFICIAL WEATHERING TO EXAMINE HYDRATION PROPERTIES OF MONTMORILLONITE. Slávka Andrejkovičová, Martin Pentrák, Jana Madejová, and Peter Komadel*

8:40-9:00 SPATIAL VARIATION OF ZINC SPECIES IN PEAT SOILS: AN X-RAY ABSORPTION STUDY. Soh-joung Yoon*, Carmen Enid Martinez

9:00-9:20 ADSORPTION OF OLIVE OIL ON CLAY MINERALS AND NANOCOMPOSITES. Giora Rytwo*, Roy Lavi, Yelena Konovalova, and Roee Gutman


9:40-10:00 PHOSPHOROUS-FILLED NANOBRICK WALL MULTILAYER THIN FILM
ELIMINATES POLYURETHANE MELT DRIPPING AND REDUCES HEAT RELEASE ASSOCIATED WITH FIRE. Amanda A. Cain, Craig R. Nolen, Yu-Chin Li, Rick Davis, and Jaime C. Grunlan*

10:00-10:20 Coffee break, MSC 2300B


Organizers/chairs: Michal Skiba and Manika Prasad

Room: MSC 2406B

8:00-8:20 K-BENTONITES IN THE UPPER ORDOVICIAN OF THE SIBERIAN PLATFORM. W.D. Huff*, A.V. Dronov

8:20-8:40 MINERALOGICAL CHARACTERIZATION OF TEXAS BENTONITES IN THE MANNING FORMATION OF JACKSON GROUP. Ana L. Barrientos Velázquez*, Thomas E. Yancey, Charles Smith, and Youjun Deng

8:40-9:00 DIAGENESIS AND ANCHIMETAMORPHISM OF THE MESO-NEOPROTEROZOIC AND THE LOWER PALEozoic ALONG PROFILE YANGJIAPING IN NORTH HUNAN PROVINCE, CHINA. Hejing Wang*, Jian Zhou, Ling Wang, Zhao Zhou, and Lei Yuan

9:00-9:20 ROLE OF CLAYS IN BITUMEN EXTRACTION FROM ATHABASCA OIL SANDS: FROM A RHEOLOGICAL PERSPECTIVE. Brad Komishke*, Louxiang Wang, and Kenleigh Pasay

9:20-9:40 NONTRONITE AND SI-SUBSTITUTED IRON OXIDE FORMATION IN AN EEMIAN INTERGLACIAL LAKE IN DENMARK. Christian Bender Koch*, Takeshi Kasama

9:40-10:00 EFFECT OF CLAYS ON ORGANIC MATTERS OCCURRENCE IN ARGILLACEOUS SOURCE ROCKS. Xiaojun Zhu*, Jingong Cai

10:00-10:20 Coffee break, MSC 2300B

Session 2. 2-D nanomaterials

Organizers/chairs: Gary W. Beall

Room: MSC 2404

10:20-10:40 CYANIDE-BRIDGED TRANSITION METAL NANOSHEETS AS PRECURSORS FOR PLATINUM-NICKEL BIMETALLIC CATALYSTS. Tyler L. Nash*, Gary W. Beall

10:40-11:00 CHARACTERIZATION OF HUMIC ACID DERIVED FUNCTIONALIZED GRAPHENE AND MECHANICAL EVALUATION OF ITS POLYURETHANE BASED COMPOSITES. Brandon G. Henderson*, Gary W. Beall
11:00-11:20  A NOVEL 2-D MATERIAL FOR HIGH EFFICIENCY, REDUCED FOULING, REVERSE OSMOSIS DESALINATION COMPOSITE MEMBRANES. Marcus Goss*, Gary W. Beall


Session 15. Teaching clay mineralogy
Organizers/chairs: Paul A. Schroeder
Room: MSC 2406A

10:20-10:40  LOOKING TO THE FUTURE TO PRESERVE THE PAST: THE CLAY MINERALS SOCIETY AND THE USE OF SOCIAL MEDIA TO INCREASE COMMUNICATION AND VISIBILITY. Shane K. Butler*

10:40-11:00  TEACHING CLAY SCIENCE IN A PROJECT-ORIENTED FORMAT. Warren D. Huff*

11:00-11:20  TEACHING CLAY MINERALOGY IN AN UNDERGRADUATE GEOCHEMISTRY CLASS. Pat Harris*

11:20-11:40  THE PERSON WHO INTRODUCED ME TO CLAYS SYNTHESIS AND INFRARED SPECTROSCOPY. S. Petit*

11:40-12:00  STUDENT LEARNING FROM THE REYNOLDS CUP COMPETITION. Paul A. Schroeder*

12:00-12:20  FUNGI AND THEIR USEFUL ROLE IN SOILS. Joe B. Dixon*, Muhammad Wasim, Ana L. Barrientos Velázquez, and Youjun Deng

Sessions 8. Clays in soils and sediments and 9. Clays and Environments
Organizers/chairs: Craig Rasmussen and Balwant Singh
Room: MSC 2406B

10:20-10:40  MINERAL DIVERSITY IN SOUTH WESTERN AMAZON SOILS, BRAZIL. Elaine Almeida Delarmelinda*, Valdomiro Severino de Souza Junior, Paulo Guilherme Salvador Wadt, and Youjun Deng

10:40-11:00  CLAY NANOHYBRIDS: REASSESSING THE ROLE OF DEHYDROINDIGO IN THE INDIGO/PALYGORSKITE SYSTEM. Nathália D. Bernardino*, Vera R. L. Constantino, and Dalva L. A. de Faria

11:00-11:20  IDENTIFICATION AND QUANTIFICATION OF HEMATITE AND GOETHITE IN SEDIMENTS AND PALEOCLIMATE IMPLICATION. Junfeng Ji*

11:20-11:40  ADSORPTION OF 2-NAPHTHOL AND COPPER BY CATIONIC AND ZWITTERIONIC SURFACTANTS MODIFIED MONTMORILLONITE: A
COMPARATIVE STUDY. Lingya Ma*, Jianxi Zhu, Hongping He, Runliang Zhu, and Qi Tao

11:40-12:00 AL\textsubscript{13}-PILLARED MONTMORILLONITE MODIFIED BY INTERCALATION OF CATIONIC AND ZWITTERIONIC SURFACTANTS. Jianxi Zhu*, Lingya Ma, Jingming Wei, Runliang Zhu, and Hongping He

12:00-12:20 MINERALOGICAL TRANSFORMATION AND TRANSPORT INSIDE ACID MINE TAILINGS AND IN NEARBY RIVER SEDIMENTS IN ZIMAPAN, MEXICO. Luke Morgan*, Youjun Deng
NOON, WEDNESDAY, MAY 21

12:00-13:20 Lunch on your own; Past presidents’ luncheon (invitation only, MSC 2401)

AFTERNOON, WEDNESDAY, MAY 21

13:30-17:00 Local Soil Tour, leave at the bus stop in front of MSC at 13:30
WITHDRAWALS

- DRUG DELIVERY SYSTEM BASED ON THE INORGANIC LAYERED DOUBLE HYDROXIDE MATERIAL. Vanessa R. R. Cunha*, Philippe A. D. Petersen, Helena M. Pettrilli, and Vera R. L. Constantino
- POSSIBLE ROLE OF CLAY MINERALS IN PHOTOCATALYST. Makoto Ogawa*
Everything is big: From nanoparticles to planets
**X-RAY DIFFRACTION STUDIES OF FE-SAPONITE UNDER LOW HUMIDITY CONDITIONS: IMPLICATIONS FOR PHYLLOSILICATES IN YELLOWKNIFE BAY, GALE CRATER, MARS**

Cherie N. Achilles¹, David L. Bish¹

¹Department of Geological Sciences, Indiana University, Bloomington, IN 47405, USA.

The Mars Science Laboratory (MSL) rover, Curiosity, is using a comprehensive scientific payload to explore the geologic environment and characterize the past habitability of Gale Crater. The CheMin X-ray diffraction (XRD) and X-ray fluorescence (XRF) instrument is providing a mineralogical assessment of the composition of rocks and soils. To date, CheMin has analyzed three samples: Rocknest, a soil (loose, unconsolidated material) from an aeolian sand shadow, and two mudstones, John Klein and Cumberland, from an ancient lacustrine environment. XRD patterns of the mudstone drill samples revealed two broad diffraction peaks centered at 10 Å and 13.2 Å, characteristic of phyllosilicate minerals. The 10 Å peak likely corresponds to a collapsed 2:1 trioctahedral smectite but the identity of the 13.2 Å peak remains speculative. Several hypotheses have been proposed, including a hydrated smectite containing interlayer cations with high hydration energies, such as Mg$^{2+}$ or Ca$^{2+}$, and a smectite with incipient chloritization. Although each can produce a broad low-angle peak in an XRD pattern, more research is needed to differentiate between these two suggestions under low humidity and temperature conditions. This study focused on the behavior of a natural and cation-exchanged Fe-saponite from Griffith Park, CA, at low relative humidities (RH).

Preliminary findings reveal that the natural Fe-saponite did not collapse to 10 Å after 22 hrs at 0% RH. This sample is therefore not a good analog for the 10 Å peak in the martian mudstone. These data suggest that the Fe-saponite has a low layer charge, likely due to octahedral Fe$^{3+}$, thereby allowing partial hydration of the smectite’s interlayer cations even at low RH. A low-charge Fe-saponite coupled with an interlayer dominated by cations with high hydration energies poses a conceivable explanation for the 13.2 Å peak in the CheMin XRD patterns. To explore this theory, the natural Fe-saponite was cation exchanged with K, Na, Ca, and Mg using 1 M chloride solutions. XRD data were measured for each sample at 0% RH and ~0-95% RH (Fig. 1). Focusing on the high hydration energy cations, Mg$^{2+}$ and Ca$^{2+}$, low-angle XRD data were measured at 2.8 and 3.3% RH, respectively, and also after 24-hours at ~0% RH. The Mg-exchanged sample had a 001 reflection of 13.7 Å, which collapsed to 12.75 Å at 0% RH. The Ca-exchanged sample showed two distinct basal peaks at 3.3% RH, signifying the presence of two intermediate phases (Fig. 2). ClayStrat modeling of these data indicated that the dominant phase (~80%) consists of a 1-H$_2$O-layer trioctahedral smectite, whereas the minor phase is an interstratified 2-H$_2$O (55%) and 1-H$_2$O (45%) trioctahedral smectite (Yuan 2010). At 0% RH, these two peaks coalesced to a single basal peak at 12.2 Å, a 1-H$_2$O layer phase (Fig. 2).

These data indicate that although the high hydration energy cations facilitated an increase in basal spacing at low RH, this Fe-saponite also is not a good analog for the 13.2 Å peak in CheMin diffraction patterns. Future studies will characterize this and other saponites under low-temperature and low-RH conditions to assess the combined effects of these two factors on smectite basal spacing. As Curiosity continues to traverse to the phyllosilicate-rich regions of...
Gale Crater, characterizing the stability of smectites under martian conditions is essential to identifying and understanding the clay minerals encountered by MSL.

**Figure 1.** Basal peak position as a function of % RH for K-, Na-, Mg-, and Ca-exchanged Fe-saponite, measured from 0-95% RH (dark) and 95-0% RH (light).

**Figure 2.** Basal reflection for the Ca-exchanged Fe-saponite at 3.3% RH. The dominant peak at 12.76 Å is consistent with a 1-H$_2$O layer trioctahedral smectite and the 14.52 Å peak is an interstratified 2-H$_2$O (55%) and 1-H$_2$O (45%) trioctahedral smectite.
SPECIFIC SURFACE AREA OF CLAYEY SOILS BY ETHYLENE GLYCOL MONOETHYL ETHER AND WATER VAPOR SORPTION METHODS

Idil Deniz Akin¹*, William J. Likos¹

¹Department of Civil and Environmental Engineering, University of Wisconsin-Madison, Madison, WI 53706-1691, USA: iakin@wisc.edu

Soils with high montmorillonite content swell significantly when exposed to water, and cause costly hazards to engineering infrastructure, especially to lightly loaded structures, pavements, and earthworks. Classification of expansive soils is a required component of geotechnical and structural design necessary to improve the long-term performance of the structure. The current methods to classify swelling soils are based primarily on manually-determined indices like the Atterberg limits, which are only indirectly related to clay mineralogy and clay structure.

The long-term goal of this research is to explore an alternative way to classify clays and to modernize geotechnical soil classification methods based on their surface properties. Clay surface properties like specific surface area (SSA) and cation exchange capacity (CEC) are indicative of the clay mineralogy. For expansive clays, interactions of the clay surface with water molecules influence behavior. Consequently, water vapor sorption methods will be used to determine the clay surface properties.

As an initial step for this overall goal, SSA values obtained by BET Theory are determined from water vapor sorption behavior at low relative humidity (RH) values, and compared with values obtained using the standard Ethylene Glycol Monoethyl Ether (EGME) Method. The study includes testing 20 natural soils, five different mixtures of end-member Georgia kaolinite and Wyoming bentonite, and Mg²⁺, Ca²⁺, Na⁺, K⁺, and Li⁺-saturated forms of the bentonite. Procedures are discussed for both of the methods. For the EGME Method, the effect of cup sizes on SSA calculation and equilibrium time was tested. For the Water Vapor Sorption Method, the effects of oven drying, and using the wetting or drying path on SSA calculation were tested. The two methods give very similar results for low SSA values (SSA < 100 m²/g), whereas the EGME Method gives higher values at higher SSA. Overall, the Water Vapor Sorption Method gives 0.55 times smaller SSA values than the EGME Method. This difference is attributed to the complicated sorption behavior of water molecules on clay surfaces. The assumptions of the BET Theory do not hold for the water vapor sorption behavior of clay surfaces. Thus, new isotherm equations should be investigated to model this specific behavior.
Figure 2: Comparison of SSA values obtained by the Water Vapor Sorption and the EGME Method. (For Water Vapor Sorption Method, the desorption data of the air-dried samples between 0.1 RH-0.3 RH were used in the BET Equation, for EGME Method, small cups having 50 mm inner diameter were used)
INTERFERENCE OF MAJOR ORGANIC COMPOUNDS IN FERMENTATION SOLUTION ON AFLATOXIN B₁ ADSORPTION BY SMECTITES

Sabrina S Alam*, Youjun Deng

Department of Soil and Crop Sciences, Texas A&M University, 370 Olsen Blvd, College Station, TX, USA: ssalam@neo.tamu.edu

Due to stringent regulations on aflatoxins and increasing demand on biofuel production, it is reasonable to direct aflatoxin contaminated corn into the biofuel industry. An up to three-fold enrichment of the mycotoxins in distiller’s grains, the co-product of ethanol from fermentation, is a great concern to both the ethanol and animal production industries. It is desirable to have the mycotoxins decomposed or inactivated during the fermentation process. More than three decades of smectite-aflatoxin interaction studies have shown that smectites were capable of binding aflatoxins and will likely play critical role in aflatoxin detoxification. The objectives of this study were to evaluate the efficiency of smectites in adsorbing aflatoxins in corn fermentation solution, and to identify the interfering compounds in aflatoxin adsorption.

The clay fraction of a Mississippi bentonite (3MS) was separated from the bulk clay and saturated with Ca. Its aflatoxin adsorption capacity in the presence of 20% (v/v) ethanol and 10% (w/v) glucose, the upper limits of the two major water soluble compounds in fermentation solutions, was measured with batch adsorption experiment. The adsorption isotherms of spiked aflatoxin in a real fermentation solution and in its dilute (1:2) by the smectite were also collected. To investigate the effect of ethanol, sugar, and other compounds in the fermentation solutions on the bonding between aflatoxin and smectite, aflatoxin was loaded onto smectite in water, 20% (v/v) ethanol, 10% (w/v) glucose, and real fermentation solutions. Excess compounds on the complexes were removed by water washing. The aflatoxin adsorption capacity (Qₘₐₓ) of a smectite 3MS was still as high as 0.53 and 0.56 mol/kg in the glucose and ethanol solutions, respectively. The aflatoxin adsorption isotherms of 3MS in the original and diluted fermentation solutions suggested that both the adsorption capacity and affinity (kₐ) were much lower (Qₘₐₓ=0.44 mol/kg, kₐ= 0.0238) in the real fermentation solutions than those in water, glucose, and ethanol solutions (Fig. 1). Moreover, the curve could not be fitted well with the Langmuir model. The FTIR analyses of the smectite-aflatoxin complexes saturated in original fermentation solution indicated that no remarkable changes in the FTIR bands of smectite-aflatoxin complexes in the presence of ethanol or glucose compared with the complex formed in water. The in-phase C=O stretching vibration band 1727 cm⁻¹ (at ~0% humidity) of aflatoxinB1 revealed the irreversible bonding of aflatoxinB1 in the interlayer of smectites (Fig. 2). The strong bands at 1490 to ~1700 cm⁻¹ on the FTIR spectrum of smectite reacted with fermentation solution indicated one or more compounds from the fermentation were adsorbed onto the smectite and could not be washed off by water. These compounds competed with aflatoxin B1 in the fermentation solutions and remained on the smectite. Despite the strong interference of these unidentified compounds, aflatoxin presence on smectite could be confirmed by the weak IR bands at 1205 and 1583 cm⁻¹. The interfering compounds will be identified and strategies would be developed to minimize their interference on aflatoxin adsorption by the clays in fermentation solution.
Fig 1: Aflatoxin B1 adsorption capacity of 3MS in diluted distiller’s wet cake solution

Fig. 2. FTIR spectra of smectite-AfB1 complexes formed in fermentation solution (FS), water, 20% (v/v) ethanol and 10% (w/v) glucose solutions
LONG-TERM LABORATORY EXPERIMENTS OF ARTIFICIAL WEATHERING TO EXAMINE HYDRATION PROPERTIES OF MONTMORILLONITE

Slávka Andrejkovičová1,2, Martin Pentrák1,3, Jana Madejová1, and Peter Komadel*1

1Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, SK-845 36, Slovakia: peter.komadel@savba.sk; 2Geosciences Department, Geobiotec Research Unit, University of Aveiro, 3810-193 Aveiro, Portugal; 3Department of Natural Resources and Environmental Sciences, University of Illinois at Urbana-Champaign, Urbana, IL 61801-4798, USA.

Bentonites are important in the environmental applications, being used in combination with geosynthetics to form geosynthetic clay liners (GCLs) and used as hydraulic barriers for the landfill constructions. Exchangeable cations substantially affect geotechnical properties of bentonites, including the swelling and permeability coefficients.

The long-term experiments were devoted to investigation of cation exchange reactions on hydration properties of Na-bentonite S130, (Envigeo Banská Bystrica, Slovakia), a commercial material containing less than 45 µm fraction of Na-bentonite with prevailing montmorillonite and muscovite, kaolinite, and quartz as the most abundant accessory minerals. Feldspars and other SiO2 phases including volcanic glass were also present. The cation exchange capacity of 83 mmol/100g for S130 was lower than expected. Clay samples were kept in basins containing 500 g of S130.

Each year of the experiments was split into four trimesters to simulate natural conditions during the seasons in Slovakia. The winter trimester typically consists of cycles with freezing.
and thawing conditions and at the winter period start 2 L of DI water and 12.5 mM solutions of K\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) were added to the samples. The other basins were soaked with 2 000 ml of water or 0.0125 mol.dm\(^{-3}\) solutions of K\(^+\), Ca\(^{2+}\), or Mg\(^{2+}\). The second and fourth trimester simulate spring and autumn, which are typically of mild temperatures with irregular wetting and drying periods, simulated here by drying at room temperature. Higher summer temperatures were simulated by more intense drying of the samples under the IR lamps. Hydration properties of the samples included water adsorption by Enslin test, free swelling, and determination of the total specific surface area by the ethylene glycol monoethyl ether (EGME) retention.

Further information on water content and swelling of the samples was obtained from infrared (IR) spectroscopy in the middle and near IR regions and from the X-ray diffraction patterns, respectively. Insufficient space is available here for detailed analysis of the results obtained. The positive conclusion is that some samples treated mainly with water kept their Enslin test values after the complex set of treatments above the required value 400 cm\(^3\).g\(^{-1}\). However, substantial replacement of Na\(^+\) with other cations can be detrimental. Fig. 1 shows substantial changes in the XRD traces of the K\(^+\) - form of S130 upon the wetting and drying treatments. The swelling ability of this material was removed with the number of cycles. Further evidence on changes of the samples obtained by other methods will be discussed as well.
NANOPHASE CARBONATES ON MARS: IMPLICATIONS FOR CARBONATE FORMATION AND HABITABILITY


1Jacobs, NASA Johnson Space Center, Houston, TX  77058, USA: doug.archer@nasa.gov; 2Barrios Technology–Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX 77058; 3NASA Johnson Space Center, Houston, TX  77058, USA.

Despite having an atmosphere composed primarily of CO2 and evidence for abundant water in the past, carbonate minerals have only been discovered in small amounts in martian dust [1], in outcrops of very limited extent [2, 3], in soils in the Northern Plains (the landing site of the 2007 Phoenix Mars Scout Mission) [4] and may have recently been detected in aeolian material and drilled and powdered sedimentary rock in Gale Crater (the Mars Science Laboratory [MSL] landing site) [5]. Thermal analysis of martian soils by instruments on Phoenix and MSL has demonstrated a release of CO2 at temperatures as low as 250-300 °C, much lower than the traditional decomposition temperatures of calcium or magnesium carbonates. Thermal decomposition temperature can depend on a number of factors such as instrument pressure and ramp rate, and sample particle size [6]. However, if the CO2 released at low temperatures is from carbonates, small particle size is the only effect that could have such a large impact on decomposition temperature, implying the presence of extremely fine-grained (i.e., “nanophase” or clay-sized) carbonates.

We hypothesize that this lower temperature release is the signature of small particle-sized (clay-sized) carbonates formed by the weathering of primary minerals in dust or soils through interactions with atmospheric water and carbon dioxide and that this process may persist under current martian conditions. Preliminary work has shown that clay-sized carbonate grains can decompose at much lower temperatures than previously thought. The first work took carbonate, decomposed it to CaO, then flowed CO2 over these samples held at temperatures >100 °C to reform carbonates. Thermal analysis confirmed that carbonates were indeed formed and transmission electron microscopy was used to determine crystal sized were on the order of 10 nm. The next step used minerals such as diopside and wollastonite that were sealed in a glass tube with a CO2 and H2O source. After reacting these materials for a number of hours, thermal analysis demonstrated the formations of carbonates that decomposed at temperatures as low as 500 °C [7].

Further work is underway to carry out the weathering process under more Mars-like conditions (low pressure and low temperature) to determine if the carbonate decomposition temperature can be shifted to even lower temperatures, consistent with what has been detected by thermal analysis instruments on Mars.


---

**Figure 3.** Evolved Gas Analysis (EGA) data, m/z 44 (CO₂) in particular, for samples analyzed on Mars and in terrestrial labs. The laboratory sample of a Winchester magnesite with particle size <150 µm, analyzed under conditions similar to the martian samples, has a peak decomposition temperature of ~600 °C. Martian samples of an aeolian material, a drilled mudstone, and soil from the martian Northern Plains have peak decomposition temperatures of 250 to 550 °C (the northern plains sample has a second peak >1000 °C not shown in this plot). The lower decomposition temperatures of martian samples could be due to the presence of nanophase carbonates, formed at low temperatures from the interaction of CO₂ and water vapor in the martian atmosphere with surface materials.
SYNERGETIC BENEFITS OF NIXTAMALIZATION AND CLAY ADSORBENTS IN DETOXIFICATION OF AFLATOXIN

Stacy Arteaga, Ana L. Barrientos Velázquez*, and Youjun Deng

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

Aflatoxin contamination can occur in a wide variety of grains when high humidity and high temperatures favor the growth of fungi Aspergillus flavus and Aspergillus parasiticus. Aflatoxins represent the highest toxicity to animals and humans. To reduce the aflatoxin exposure, the maximum level of aflatoxin in corn in food is regulated as 20 ppb by FDA. The risk for aflatoxicosis increases with the consumption of contaminated grains. In Mexico, corn tortillas represent an important portion of the daily diet. Nixtamalization, boiling and soaking corn in lime water, had been used to process corn since ancient cultures. Some researchers have shown that nixtamalization can decrease the concentration of aflatoxins by 20 to 46 %, or even to 90% in the final dough. Other detoxification techniques such as adding clay adsorbents, especially montmorillonite-rich bentonites, have demonstrated high efficacy in inactivating the toxicity of aflatoxin by adsorption. The main objective of this study was to evaluate the synergetic effects of clay adsorbents and nixtamalization in aflatoxin detoxification.

A Ca-bentonite with high montmorillonite content and high adsorption capacity for aflatoxin (up to 0.8 mol/kg) was used. To simulate the nixtamalization, a 8 ppm aflatoxin solution was prepared in saturated lime water (1.5 g/L of Ca(OH)2). The adsorption efficacy of the clay for aflatoxin in lime water was measured after adjusting the pH to different values to mimic the various pH conditions in digesting systems.

The UV spectra and HPLC chromatographs showed that Afb1 was converted to more polar and water soluble form at pH12 in the lime water. The alkaline pH caused Afb1 molecules to open their lactone ring structures and therefore, become negatively charged and more solubilized in water. Due to the change in chemical structure and conversion of the nonionic species to an anionic species, the mycotoxin molecules were repelled by the negatively charged montmorillonite. The adsorption of this new structure by the clay decreased to minimal (less than 0.1 mol/kg) at pH 12.

When the pH of aflatoxin-lime water was reduced with HCl to 10, 7, 6, 4, 3 and 2, the UV-spectra of the solutions showed that at low pH 4-2, a typical pH value in stomach, the initial Afb1 structure was recovered. At neutral pH both the nonionic Afb1 and the ring-opened structures existed. At pH 2, the lactone-ring-opened form converted completely back to Afb1. Single point adsorption tests at the different pH’s suggested that aflatoxin adsorbed by the clays increased from ~0.07 mol/kg at pH 12 to ~0.29 at pH 4 and 2 (figure 1).
Figure 1. Aflatoxin adsorption at different pH values.

The preliminary results indicated that nixtamalization process removed aflatoxin by increasing aflatoxin’s solubility through the ring-opening reaction. The high pH of the nixtamalization solution would decrease smectites’ adsorption for aflatoxin. Regeneration of original AfB1 structure at low pH similar to stomach condition could restore its toxicity but this form could be adsorbed by smectite at those pH conditions. The synergetic benefits of nixtamalization and clay adsorbent in aflatoxin detoxification should be further explored.
SMECTITES ON THE RIM OF ENDEAVOUR CRATER MARS AS INFERRED FROM MARS RECONNAISSANCE ORBITER CRISM HYPERSPECTRAL IMAGES AND OPPORTUNITY ROVER OBSERVATIONS

Raymond E. Arvidson*

Department of Earth and Planetary Sciences, McDonnell Center for the Space Sciences, Washington University in Saint Louis, Saint Louis, MO 63130, USA: arvidson@wunder.wustl.edu.

The Opportunity Mars Exploration Rover has been exploring the plains of Meridiani since the rover landed in January 2004. A key scientific result was the discovery and characterization of late Noachian to Hesperian age sulfate-rich sandstones, subsequently named the Burns formation, that dominate the outcrops on the plains (Squyres and Knoll, 2005). These materials were deposited when neutral, reducing groundwater emerged onto shallow lakes and encountered an oxidizing atmosphere (Hurowitz et al., 2010). Ferrous ions were converted to ferric ions, releasing hydrogen, and depositing sulfates and iron oxides under highly acidic and oxidizing conditions. Reworking of the playa deposits by wind and water, with later cementation by rising groundwater, produced the sulfate-rich sandstones that dominate the Burns formation.

A second key scientific result was a consequence of combined use of Mars Reconnaissance Orbiter CRISM hyperspectral imaging data (0.4 to 4.0 µm) to identify and map smectite outcrops on the rim of the ~22 km wide Noachian age Endeavour crater, with subsequent detailed characterization of the outcrops by Opportunity (Arvidson et al., 2014). Endeavour was partially eroded by fluvial processes during the Noachian Era before being largely covered by Burns formation materials. Only higher crater rim segments stand above the surrounding plains. Opportunity arrived at the Cape York rim segment in August 2011 and has been exploring and characterizing these ancient rim materials on Cape York and Murray Ridge since arrival, with an emphasis on localities where CRISM data showed the presence of smectite-bearing outcrops.

As Opportunity was conducting initial investigations on Cape York of the Shoemaker formation breccias deposited during the Endeavour impact event, CRISM observations were commanded using a new mode in which data were acquired in an along-track oversampled (ATO) manner. The ATO data allowed processing of hyperspectral image cubes to ~5 m/pixel along track. This is a much higher spatial resolution as compared to the normal 18 m/pixel spatial resolution. The ATO data allowed detection and mapping of a small (~30 to 40 m long) ferric smectite exposure on the eastern side of Cape York, in an area subsequently named Matijevic Hill (Arvidson et al., 2014). Opportunity was driven to this location and found evidence for finely layered strata that are older than the Shoemaker formation breccias, i.e., predate the Endeavour impact event. The strata, subsequently named the Matijevic formation, exhibit dark veneers whose outcrop distribution matches the CRISM-based localities for the ferric smectite detections. Compositional data derived from Opportunity’s Alpha Particle X-Ray Spectrometer (APXS) observations showed that the veneers are basaltic materials with enhanced levels of soluble elements such as Zn, S, Cl, Br. Isochemical alteration in mildly acidic, slightly salty water to produce ferrous smectites, with later oxidation to ferric smectite, is the preferred model for formation of the dark veneers. Oxidizing conditions subsequent to formation are also indicated by the presence of small iron oxide rich concretions distributed throughout the rocks.
and interpreted to be generated by later movement of oxidizing groundwater through the outcrops. Opportunity observations also showed the presence of box-work like fractures that cut through the deposits. An extensive measurement campaign on one of the fractures, including grinding into the subsurface using the Rock Abrasion Tool, with subsequent APXS and Microscopic Imager observations, showed a composition moving to Al-rich smectite as the surface coatings and rinds were removed. Lack of iron oxides, coupled with the presence of Al-rich smectite, demonstrate that significant leaching under mildly acidic and reducing conditions altered the basaltic rocks within the fracture zone. This is interpreted to be due to more extensive fluid flow through the permeable fracture zone as compared to flow associated with formation of iron smectite in the veneers.

After completing observations on Cape York, Opportunity was directed to the Murray Ridge rim segment, located ~2.5 km to the south of Cape York. CRISM ATO data showed spectral evidence for a minor amount of Al-rich smectite on the eastern side of Murray Ridge, in an outcrop subsequently named Moreton Island. Opportunity-based observations showed extensive areal exposure of Shoemaker formation materials dominated by a bright, fine-grained matrix with embedded dark rock clasts. The outcrop has slightly higher Fe/Si, Mn/Si, and Ca/Si ratios as compared to the Shoemaker formation materials exposed on Cape York. Unfortunately, the need to drive Opportunity to Cook Haven (located ~30 m south) to have the solar panels tilted northward for the southern winter precluded grinding into the matrix to remove coatings and rinds, i.e., repeating the grinding and measuring campaign conducted on the boxwork fracture on Cape York. The Al-rich smectite signature from CRISM observations for Moreton Island is interpreted to be due to a slight amount of aqueous alteration of the fine-grained and likely glassy matrix that dominates the outcrops.

After the winter campaign in Cook Haven, focusing on a detailed examination of an extensive stratigraphic exposure of Shoemaker formation materials, Opportunity will be directed ~600 m to the south, where CRISM ATO data indicate the presence of Al-rich smectite exposed along ~100 m long outcrop. The rover will then be directed even further south, where normal 18 m/pixel CRISM data have been used to identify and map a mix of Fe and Mg smectites on a rim segment called Cape Tribulation (Wray et al., 2009). ATO data show that these exposures are associated with outcrops on walls of a deep valley that cuts across Cape Tribulation. The walls expose extensive outcrop and will likely allow characterization of both Shoemaker formation breccias and older rocks, perhaps similar to the Matijevic formation found on Cape York. The evolving model for the environmental evolution of Mars begins with relatively warm, wet conditions with active fluvial processes and both surface and groundwater that were mildly acidic to neutral in pH and reducing to mildly oxidizing. These conditions shifted to high oxidizing surface conditions that led to formation of extensive sulfate and iron oxide strata. Mars then went into an extensive period that continues until present with very cold and dry conditions in which surface and near-surface water (as opposed to vapor and ice) rarely occurs.

MINERALOGICAL CHARACTERIZATION OF TEXAS BENTONITES IN THE MANNING FORMATION OF JACKSON GROUP

Ana L. Barrientos Velázquez¹, Thomas E. Yancy², Charles Smith³, and Youjun Deng¹

¹Soil & Crop Sciences Department, Texas A&M University, College Station, TX, 77840-2474, USA: *anabarrientos@tamu.edu
²Department of Geology & Geophysics, Texas A&M University, College Station, TX, 77843-3115, USA;
³BYK Additives, Gonzales, TX, 78629, USA.

Bentonite deposits in Texas occur in the Eocene Yegua and Jackson groups that extend across the southeast part of the state. Due to the importance of mineralogy in selecting clay processing procedures, their commercial applications, and as an indicator of the diagenetic processes, it is important to understand the origin, age, deposition environment, transport history, and mineral transformations that occurred in the bentonite deposits. Debates on the origin and the geochemical processes affecting the deposits remain unsettled. The objective of this study is to delineate the geological and geochemical processes affecting east-central Texas bentonites, based on reported and new mineralogical data.

Bentonite and partially altered volcanic ash samples were collected from six locations: 1) a white ash layer from the Somerville Lake spillway in Washington County, dated at 34.4 million years by Ar-Ar dating, 2) brown and yellow clays at the Miller pit, 3) white and blue clays at the Helms, Clark-Kennard, Magdalene Johnson, and Dubose pits, 4) white grey clay at the HW Johnson pit, 5) a partially altered white volcanic ash at Smiley outcrop, and 6) a white clayey volcanic ash at Sickenious pit in Karnes County. These bentonite and ash samples were characterized with X-ray diffraction, Fourier transformation infrared spectroscopy, and scanning and transmission electron microscopy.

Stratification with different mineralogy occurs in the Miller, Helms and HW Johnson pits, suggesting either different depositional environments or different diagenesis caused by local hydrology. In the Helms deposit, partially altered volcanic ash layer is sandwiched between a thin (10 to 30 cm) upper white bentonite layer and a thick (1.5 m) lower white bentonite layer. There are textural differences in the volcanic ash that divide it into upper and lower layers. In the
Helms deposit, large masses of manganese oxides occur in the lower bentonite as well as red, orange, and black coatings along the margins of bentonite blocks.

The Dubose, Kennard, Clark, and Magdalene Johnson deposits occur within the same deposit. Blue bentonites occur in lower parts of the unit whereas white bentonites occur at higher levels. The HWJ deposit contains a blue layer of bentonite sandwiched between two white bentonites, with the blue layer inclined toward the Northeast. Black manganese oxide coatings were observed at the top of the upper white bentonite layer.

The major mineralogical differences are in the sand and silt composition. The color difference between white and blue clays is due to the presence of pyrite in the blue samples. The volcanic ashes are rhyolitic and had similar chemical composition. The presence of opal-cristobalite is the main difference in the clay fraction of the central deposits, which indicates a poor drainage system when the bentonite formed. In the Helms deposit, opal-cristobalite is concentrated in the bentonite layer but is absent in the upper ash. Halloysite occurs in the upper volcanic ash but not in the lower ash layer, suggesting an environment with insufficient Mg to form smectites. Similar trend is observed in the Clark deposit where the difference between soft and hard clays correlates to the amount of opal.

The mudstone and brown clay in the Miller deposit were similar in their mineralogy. Compared with bentonites from other deposits, the bentonites in the Miller pit contain more quartz, feldspar, mica, and kaolinite due to mixing with outside sediment. The yellow clay sample has the highest clay content. In the HW Johnson pit the upper white clay layer was dominantly smectite and opal-cristobalite with minor amounts of quartz and feldspar. The middle blue layer composition is similar to the upper white bentonite but pyrite was also present. Opal-cristobalite occurs in the lower white clay layer, but clinoptilolite is present in the silt fraction. These mineralogy differences in the same bentonite pit suggest local hydrology-controlled variation in diagenesis.

The FTIR analysis of the clay fractions showed differences in the structural cation composition. The clays from the central deposits (Helms, Clark-Kennard, Magdalene Johnson, and Dubose) had $\text{Al}^{3+}$ as the dominant octahedral cation with some $\text{Mg}^{2+}$ substitutions only, while the Miller and HWJ clays also contained octahedral Fe substitutions.

The mineralogy differences in the deposits and among the strata of the same deposit suggested that local hydrology control on genesis 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 overlaying and underneath materials.
CHROMIUM IN THE CENTRAL OKLAHOMA AQUIFER: DIAGENETIC IRON REDISTRIBUTIONS PROVIDE WINDOWS INTO THE RELATIVE ROLES OF CLAYS, IRON OXIDES, AND CARBONATES

Shelbie A. Bartlett¹, Jeffrey P. Westrop¹, Andrew L. Swindle¹, and Andrew S. Elwood Madden¹*

¹School of Geology and Geophysics, University of Oklahoma, Norman, OK 73019, USA: amadden@ou.edu

Water supply for growing populations in cities and towns across central Oklahoma relies increasingly on groundwater to supplement limited surface water resources. Unfortunately for water supply managers, groundwater in the Central Oklahoma Aquifer (COA) frequently contains natural levels of arsenic, chromium, and uranium that exceed guidelines for public safety. In the oxygenated, low-organic COA system, previous work demonstrated that water-rock interactions primarily control the distribution of these elements. Ongoing efforts to understand the cycling of trace elements between minerals and groundwater will provide guidance to protect and expand the public water supply.

Conceptual models for understanding chromium distribution in the COA have lagged behind those for arsenic, despite toxic hexavalent chromium levels higher than any other U.S. city tested in a national survey. To determine the vertical distribution of chromium and gain insight into mineral-water interactions influencing Cr fate, we selected samples from the Norman Arsenic Test Hole Core (USGS/EPA) at 50 different depths for bulk chemistry, BET surface area, X-ray diffraction, and microscopic analyses. Our initial results suggested that while arsenic was associated primarily with nanoscale iron oxides, chromium correlated more closely with the distribution of clay minerals. To further clarify the relative roles of clays and iron oxides in Cr distribution, we selected additional core samples with cm-scale bleached zones from diagenetic iron mobilizations, from which petrographic thin sections were prepared for optical microscopy and electron microprobe analyses. Additionally, we selected three sub-samples to compare the surface area, chemistry, and mineralogy of adjacent bleached and red areas (six sub-samples in total). These areas had the same lithology and bulk mineralogy, but bleaching indicated differences in the distribution of iron oxides and potentially clays.

The two bleached and red samples from the shallowest depths had systematic differences in surface area, clay mineralogy, and chromium extracted by 6M HCl. For two of the samples, bleaching led to a 31-35% reduction in specific surface area. SEM imaging of red and bleached samples revealed no significant differences in microtexture, although some nanoscale clusters and needles may be responsible for the coloration in the red samples. Chromium extracted with 6M HCl for 24 hours at 60 degrees C was 48% and 21% lower in bleached samples as measured by Atomic Absorption Spectrophotometry, suggesting the iron mobilization caused coincident enrichment of chromium. The clay fraction mineralogy for the red and bleached both contained abundant kaolinite, quartz, and illite, and mixed-layer illite-smectite and chlorite-smectite. Based on profile modeling with MDI ClaySim, the chlorite layers in chlorite-smectite were extremely iron rich in both red and bleached areas, but bleached areas exhibited a slightly greater proportion of expandable layers.
The third sample was from the deepest water supply zone in the aquifer, where groundwater chromium concentrations were highest. The mineralogy was similar to samples from shallower depths, except dolomite was present in both the bulk and clay fractions of red and bleached areas. HCl-extracted Cr was slightly higher in the deep red than the shallower samples. On the other hand the bleached area from the deep sample contained approximately one order of magnitude greater HCl-extractable chromium, despite a lower extractable iron content. While this suggests the carbonate distribution may be important for total chromium, bulk carbonate by XRD throughout the core does not correlate with bulk chromium. Further work with core samples and thin sections will explore the relationships between iron mobilization during diagenesis and mineral-water interactions that control chromium cycling in the COA.
CLAY NANOHYBRIDS: REASSESSING THE ROLE OF DEHYDROINDIGO IN THE INDIGO/PALYGORSKITE SYSTEM

Nathália D. Bernardino*, Vera R. L. Constantino, and Dalva L. A. de Faria

Instituto de Química, Universidade de São Paulo, CP 26077, 05513-970, São Paulo, Brasil
nathaliadelboux@usp.br

Clay nanohybrids are used since ancient times and one of the best examples is the pigment known as maya blue, made of a natural dye (indigo) intercalated into palygorskite [1], a clay that has in its structure nanopores able to accommodate neutral molecules like water. One of the most remarkable characteristics of maya blue is its chemical stability [2] which was recognized since the very first investigations [3]. There are, however, several aspects of such stability that are yet to be clarified; it is now clear that the accommodation of the organic dye in the nanopores is responsible for its extended chemical stability but the mechanisms of interaction are still not well established. Recent studies on a simulant of the maya blue pigment detected the presence of the oxidized forms of indigo, dehydroindigo and isatin, which would be responsible for the pigment greenish-blue color [4, 5].

The preparation of maya blue simulants involves heating, which provides stability to the pigment [1]. The Raman spectra of the indigo and palygorskite (ind+paly) mixture unheated and heated at 130°C, 200°C, 300°C, 330°C and 400°C for 2 hours in air are shown in Figure 1.

![Raman spectra](image)

Figure 1. Raman spectra ($\lambda_0 = 632.8$ nm) of indigo (ind, green), ind+paly unheated mixture (black), ind+paly heated at 130°C (red), 200°C (navy), 300°C (khaki), 330°C (brown) and 400°C (purple).

The Raman spectrum of the ind+paly unheated mixture correspond to the resonance Raman spectrum of indigo but some differences upon heating at 130°C and 200°C are observed, with the most significant changes at 552, 759, 946, 1380, 1493, 1635 and 1680 cm$^{-1}$. Such changes are in agreement with previously reported data for both original and simulants of maya blue [2]. Samples heated at 300°C and above presented a grayish color indicating thermal degradation.
In the simulants here reported, DMF (N,N-dimethylformamide) was used to wash out the indigo in excess after heating the indy+paly mixture at 130°C; the treatment was repeated till the solvent was completely colorless. The dried solid retained a greenish-blue color and its Raman spectrum (not shown) agrees with the maya blue one [6].

Dehydroindigo was synthetized using a modification of the procedure described by Kalb [7], resulting in a dark purple solid, without detectable amounts of indigo. Figure 2 shows the Raman spectra of the so prepared dehydroindigo, isatin, indigo and of the ind+paly composite heated at 130°C for 2 hours.

![Raman spectra](image)

Figure 2. Raman spectra ($\lambda_0 = 632.8$ nm) of indigo (green), dehydroindigo (black), isatin (blue) and ind+paly heated at 130°C by 2 hours (red).

It is clear from the Raman spectra shown in Fig. 2 that neither dehydroindigo nor isatin are responsible for the changes observed in the ind+paly nanohybrid spectrum when compared to pure indigo, indicating that such species are not contributing to the nanohybrid Raman spectrum, thus challenging the studies that describe dehydroindigo as a forgotten colorant in maya blue.

WATER AND ION DIFFUSION IN THE OSMOTIC HYDRATE OF NA-SMECTITE

Ian C. Bourg1*, Ruth Tinnacher1, Michael Holmboe2, Christophe Tournassat3, and Jim Davis1

1Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA: icbourg@lbl.gov;
2Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden;
3French Geological Survey (BRGM), 45060 Orléans Cedex 2, France.

Compacted Na-bentonite (i.e., Na-smectite-rich) clay barriers are widely used in the isolation of landfills and contaminated sites and are considered for use in the geologic storage of high-level radioactive waste. At the conditions that occur in these barriers, a significant fraction of the pore space is located in clay interlayer nanopores with pore widths < 1 nm (the so-called two- and three-layer hydrites). The remainder of the pore space is located in poorly-characterized mesopores. To date, atomistic-level examinations of the pore space of compacted Na-bentonite have focused almost exclusively on the interlayer nanopores despite the potentially strong influence of mesopores on water flow, anion and salt diffusion, aqueous geochemistry, and chemo-mechanical coupling in compacted Na-bentonite. In this talk, we present a new set of experiments and simulations (macroscopic scale diffusion experiments, pore scale model calculations, molecular dynamics simulations) that examine the diffusion of cations, anions, and uncharged species in Na-smectite mesopores. Results obtained at different scales are broadly consistent with each other and provide insight into the aqueous geochemistry and transport properties of Na-bentonite barriers.
MOLECULAR DYNAMICS SIMULATIONS OF CATION ADSORPTION AT MICA-WATER INTERFACES

Ian C. Bourg¹, Christophe Tournassat²

¹Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA: icbourg@lbl.gov;
²French Geological Survey (BRGM), Orléans, France.

Muscovite mica, a 2:1 layered aluminosilicate isotstructural with the clay minerals illite and smectite, is an important reference material in fundamental studies of mineral-water interfaces because it can be cleaved to expose an atomically smooth siloxane surface with macroscopic dimensions. In recent years, X-ray reflectivity (XRR) measurements by scientists at the Advanced Photon Source (APS) has provided an unprecedentedly detailed view of cation adsorption from liquid water onto the basal surface of muscovite mica [Lee et al., *Langmuir* 28:8637 (2012); Lee et al., *Geochim. Cosmochim. Acta* 123:416 (2013)]. Molecular dynamics (MD) simulations are known to be highly synergistic with spectroscopic studies. Here, we present new MD simulation results on the adsorption of cations at mica-water interfaces and we discuss the implications of these results for the interpretation of the XRR data.
ASSESSING AUX VASES AND CYPRESS SANDSTONE HETEROGENEITY IN THE ILLINOIS BASIN FOR POTENTIAL EOR PROJECTS USING CLAY MINERALOGY, POROSITY, AND PERMEABILITY

Shane K. Butler*1, Nathan D. Webb1, Evan J. Gragg2, and Kyle D. Rehak2

1Priairie Research Institute, Illinois State Geological Survey, University of Illinois at Urbana-Champaign, Urbana, IL 61820-6918, USA: sbutler4@illinois.edu
2Department of Geology, University of Illinois at Urbana-Champaign, Urbana, IL 61801-2919, USA.

The Chesterian (Upper Mississippian) Aux Vases and Cypress Sandstones are significant oil reservoirs in the Illinois Basin (ILB), and may be the target of future enhanced oil recovery (EOR) projects. Most oil fields in the ILB were discovered in the early twentieth century; many fields are waterflooded and are nearing the end of their economic production window. However, these fields still contain recoverable mobile oil and are undergoing screening for potential EOR operations. Past studies have detailed the clay mineralogy of individual oil fields, but the spatial distribution of clay mineral heterogeneity within the Aux Vases and Cypress is not entirely understood. The focus on characterizing individual oil fields in the ILB has created mineralogical data gaps across the Aux Vases and Cypress formations. This is because past studies were never integrated into a basin-wide model to understand the mineralogical variation of clay in the oil reservoirs. The compiled previous data was mapped to determine areas in the basin that lacked sufficient coverage. New samples were collected from existing cores to improve clay mineralogy data coverage in the areas that lacked information from the two formations across the ILB. X-ray diffraction (XRD) of powder mounted samples and orientated clay mineral slides were used to identify the clay mineral assemblage of 61 samples from 29 distinct cores taken from the two formations (29 from the Aux Vases, 32 from the Cypress). Qualitative XRD spectra analysis provided data that allowed for determination of semi-quantitative clay content in the sandstones. Measurements of permeability and porosity of core plugs taken at or near the same depths as the clay mineral samples helped determine how the clay mineralogy impacted those parameters. The clay mineralogical data should provide new insights and detailed information for understanding the diagenetic evolution of the Aux Vases and Cypress Sandstones in the ILB. The two formations have distinct differences in their clay mineral assemblages that have bearing on future EOR efforts. The synthesis of the new data with those compiled from previous studies of the Aux Vases and Cypress Sandstones pertaining to clay mineral content, permeability, and porosity is expected to demonstrate spatial variations in the diagenetic alteration of each formation. Recognizing the spatial variations in clay mineralogy of reservoir rock in the Aux Vases and Cypress in the ILB will aid in future discoveries and could improve the overall oil recovery through proper implementation of EOR techniques with implications for similar reservoirs around the world.
LOOKING TO THE FUTURE TO PRESERVE THE PAST: THE CLAY MINERALS SOCIETY AND THE USE OF SOCIAL MEDIA TO INCREASE COMMUNICATION AND VISIBILITY

Shane K. Butler*

Illinois State Geological Survey, Prairie Research Institute, University of Illinois at Urbana-Champaign, Urbana, IL 61820-6918, USA: sbutler4@illinois.edu

The Clay Minerals Society (CMS) is holding its 51st annual meeting in 2014. The meeting itself allows people from different disciplines, including professors, students, and private sector employees to come together and share ideas centering on the field of clay mineralogy. During these 51 years, the community has seen many changes, especially with advancements in technology. These advances have lent themselves to various scientific breakthroughs. They have also lent themselves to breakthroughs in how we, as a community, can communicate with one another. One of the newest developments has been social media. The CMS has been slow in adopting social media. This may be, in part, related to the demographics of the CMS members, as many may not be comfortable with the exact workings of social media and networks. In order to ensure that there is a 101st meeting, the CMS must adopt new forms of communication and mass media presentation. While the general membership may be unfamiliar with things such as Twitter or LinkedIn, younger generations look to these social media outlets for news, information and social interactions. Facebook is already nearly a decade old, yet CMS has no presence there. There is no listing on Wikipedia of what CMS is. These are simple, yet overlooked, mediums on which CMS should have a presence in order to increase visibility to a demographic of young scientists and students that are just starting in the field. Other scientific societies, such as the Geological Society of America (GSA) have adopted the use of these outlets, which allow for more visibility, a more diverse membership and, in turn, sustained membership numbers. We saw at last year’s CMS meeting that the session on the history of the society (run by Dewey Moore) was a huge success. Many reflected on their great mentors and what they learned from their experiences as a student. The session provided a great forum for younger members to learn about important figures in the field. While some may not realize it, it can be intimidating for young scientists or students to reach out or ask about such stories. Inexperienced students may be intimidated to talk to a Dewey Moore face to face at a conference, or just not have the opportunity to introduce themselves. Social media allows for such interactions the same way that email and message boards enabled quick electronic communications at the dawn of the internet age. These same types of memories and teachings can be distributed to younger members and potential members via new methods such as social networks. Students can see what CMS members are currently working on, or look at an abbreviated vita or reference of works. Creating group pages can provide communication outlets, break down barriers, and improve visibility of the CMS and its members. It can also provide more links to the CMS home page. In turn, it could be a great method to promote CMS membership to young scientists.
PHOSPHOROUS-FILLED NANOBRICK WALL MULTILAYER THIN FILM ELIMINATES POLYURETHANE MELT DRIPPING AND REDUCES HEAT RELEASE ASSOCIATED WITH FIRE

Amanda A. Cain*1, Craig R. Nolen1, Yu-Chin Li2, Rick Davis2, and Jaime C. Grunlan1

1Department of Mechanical Engineering, Texas A&M University, 3123 TAMU, College Station, Texas 77843, USA: AmandaACain@gmail.com.edu; 2Flammability Reduction Group (Bldg. 224/Rm. A265), National Institute of Standards & Technology (NIST), 100 Bureau Dr., MS-8665, Gaithersburg, MD 20899, USA.

Newly developed trilayer thin films of sodium montmorillonite (MMT), poly(allylamine hydrochloride) (PAH) and poly(sodium phosphate) (PSP), prepared via layer-by-layer assembly, completely stop melting of open-celled flexible polyurethane foam when exposed to direct flame of a butane torch. QCM and EDX measurements confirm presence of PSP within this novel trilayer nanocoating, transforming traditional nanobrickwall systems into multilayers of exfoliated clay platelets that are intercalated with intumescent polymeric mortar. Cone calorimetry confirmed all coated foam reduces peak heat release rate by at least 50% relative to the uncoated control. SEM images reveal coatings swell around urethane walls to suppress flame spread and reduce heat transfer. Using layer-by-layer assembly, this work combines two common flame-retarding components, MMT clay and phosphorous (PSP), into one system in the presence of a blowing agent (PAH) and provides a foundational platform for new environmentally benign flame-retardant treatments for polyurethane foam.
GEOCHEMICAL CONTROLS FOR THE PRESERVATION OF HUMAN REMAINS AND MUMMIES: SOR JUANA INES DE LA CRUZ, LA REINA ROJA, AND PEPITA.

Javiera Cervini-Silva¹*, Lourdes Muñoz², Arturo Romano-Pacheco³⁴, Elizabeth Mejía-Pérez Campos⁵, Ximena Chávez-Balderas⁶, Eduardo Palacios⁷, Paz del Angel⁷, Ascención Montoya⁷, Eduardo Ramos⁴, and Fanny López⁸

¹Departamento de Procesos y Tecnología, Universidad Autónoma Metropolitana, México, D.F., México: jcervini@correo.cua.uam.mx; ²Departamento de Genética y Biología Molecular, Centro de Investigación y Estudios Avanzados del Instituto Politécnico Nacional, Zacatenco, Estado de México, México; ³Universidad del Claustro de Sor Juana, México, D.F., México; ⁴Instituto Nacional de Antropología e Historia, México, D.F., México; ⁵Instituto Nacional de Antropología e Historia, Querétaro, México; ⁶Instituto Nacional de Antropología e Historia, Templo Mayor, México; ⁷Dirección de Investigación y Posgrado, Instituto Mexicano del Petróleo, México, D.F., México. ⁸Instituto Nacional de Antropología e Historia, Montealban, Oaxaca, México.

The preservation of human remains and mummies in nature is intrinsically associated to protection against the action of biological or physicochemical processes. The preservation of the remains of three Mexican females was studied using high resolution microdiffraction and microscopic analysis. The samples selected varied in temporality, and degree of preservation, and consisted of modern and ancient human remains and mummies. The remains belonged to: (a) Sor Juana Ines de Asbaje y Ramirez de Santillana (Sor Juana Ines de la Cruz; Nepantla, México, 1695-México, D.F., México 1695) was a self-taught scholar and poet of the Baroque school, and Hieronymite nun of New Spain. (b) Pepita is a 2,300 Y.O. naturally-preserved mummy, belonging to a two-year and eight month girl, found inside a cave located in Altamira, Querétaro, México (21°40´-20°01´; 99°03´-100°36´). The cave was found in Sierra Gorda, an orographic region with a relief of sedimentary origin from the Gulf of Mexico, composed by high mountains with altitude values surpassing 3,000m above sea level, with ample and steep canyons, and a prominent role on the exploitation and distribution of cinnabar (HgS). And, (c) La Reina Roja (The Red Queen; 700 A.C. reported vs 3,000 B.C ≤ as determined recently; unpublished data) found at Palenque, Mexico, are examples of cinnabar (HgS) application to royal remains during pre-Hispanic times. La Reina Roja remains are those of a ca. 30-35 yr-old female and present a striking similarity to the remains of another Mayan woman found at Copán, Honduras.

Preservation was explained because the presence of geochemical components. For instance, the skin of Pepita showed the presence of small-size spherules, containing Al (≤ 43%) in the most exposed regions (5-10 μm depth). Thin layers and structural microdomains covered small and large spheres. Structures conformed by stacked, nano-sized particles located far-from-the bunches contained C (<45%), Zn and Si (<10%), and minor amounts of Ca (<2.6%). By contrast, regions between spheres contained high amounts of Ca (<23%) and Al (<15%), but lacked Zn and Si. Carbon spheres showed two distinctive compositions, a signature that their formation might have occurred in a least two different stages via concentric growth mechanisms, with the incorporation of Zn and Al at a later stage.
Besides, *La Reina Roja* remains showed the presence of nanotubular organic minerals comparable in composition and molecular dimensions to collagen fibrils, and in spatial ordering to collagen fiber networks. Fungal structures are rare in the geological record because of poor preservation potential. Micrographs revealed the preservation of fungal signatures, with morphology comparable to parasitic fungal-coral matrix associations, consistent with the idea that fungal remains can be preserved in environments which contain high Hg concentrations. The well-preserved signatures of fungus-animal interactions and primary osteogenesis in the Red Queen remains are attributed to the long-term antibacterial activity of HgS and the association of sulfur components with nanotubular structures.


ANTI-INFLAMMATORY AND ANTI-OXIDANT ACTIVITY, AND CYTOXICITY OF HALLOYSITE SURFACES

Javiera Cervini-Silva1,*, Antonio Nieto-Camacho2, Eduardo Palacios3, Ascención Montoya3, Virginia Gómez-Vidales4, and María Teresa Ramírez-Apán2.

1Departamento de Procesos y Tecnología, Universidad Autónoma Metropolitana, México, D.F., México: jcervini@correo.cua.uam.mx
2Laboratorio de Pruebas Biológicas, Instituto de Química, Universidad Nacional Autónoma de México, México, D.F., México.
3 Dirección de Investigación y Posgrado, Instituto Mexicano del Petróleo, México, D.F., México.
4 Laboratorio de Resonancia Paramagnética Electrónica, Instituto de Química, Universidad Nacional Autónoma de México, México, D.F., México.

Halloysite is a naturally-occurring nanomaterial occurring in the thousands of tons and that serves as biomaterial, with applications in the areas of biotechnology, pharmaceutical, and medical research. This study reports on the anti-inflammatory, cytotoxic, and anti-oxidant activity of halloysite Jarrah-dale (collected at ~45 km SE of Perth, Western Australia; JA), Dragon Mine (provided by Natural Nano Inc., Rochester, New York; NA), and Kalgoorie Archean (collected at Siberia, ~85 km NW of Kalgoorlie, West Australia; PA). Prior to biological testing, halloysites were characterized by 27Al and 29Si Nuclear Magnetic Resonance Spectroscopy, the anti-inflammatory activity was determined by (a) the mouse ear edema method, using 12-o-tetradecanoylphorbol-13-acetate (TPA) as anti-inflammatory agent; and (b) the myeloperoxidase enzymatic activity method (MPO). Cell viability was determined using the MTT method. Sample characterization by NMR method showed similar symmetry and atomic environments, with no evidence of distortion(s) due to shiftings in atomic ordering or electron density. The anti-inflammatory activity followed the order: PA > JA > NA, and remained invariant with time. Prolonged anti-inflammatory activity related inversely to surface area and lumen space. The low extent of infiltration at shorter reaction times confirmed a limiting number of active surface sites. EPR intensity signals followed the order: JA > NA > PA. The poor stabilization of RO• species in PA suspensions was explained by tube alignment provoking occlusion, thus limiting transfer of H+ or e− from-and-to the surface, and decreases in acidity associated to Al\textsuperscript{III}. Cell viability (%) varied from one surface to the other, PA (92.3 ± 6.0), JA (84.9 ± 7.8), and NA (78.0 ± 5.6), but related directly to S\textsubscript{BET} values.

AFLATOXIN B1 REMOVAL ON BENTONITE INTERCALATED BY SURFACTANTS

Ya T. Chan*, Yu-Min Tzou

Department of Soil and Environmental Sciences, National Chung Hsing University, 250 Kuo Kuang Road, Taichung 40227, Taiwan: ytchan@drogan.nchu.edu.tw

Aflatoxins B1 (AfB1) is one of mycotoxins, which may lead to a potential impact to the agricultural products due to its toxicity and its occurrence as a natural contaminant of feed stuffs. The applications of pristine clay or organo-clay composites to scavenge the organic pollutants, including AfB1, have received considerable attentions during the last two decades. However, the influences of the organic components in clays on the removal efficiencies of organic pollutants remain unclear. This study evaluated the effectiveness of AfB1 removal on bentonite intercalated with different species and ratios of non-ionic surfactants. The preliminary results demonstrated that the intercalated surfactants could improve the removal ability of AfB1; nonetheless, AfB1 removal decreased with an increase in the concentrations of surfactants intercalated in the bentonite interlayers. The results indicated that the conversions of the surface properties of clays from hydrophilic to hydrophobic would enhance AfB1 sorption, but bentonite with excess surfactants was unfavorable for AfB1 removal. Further studies are required to clarify how the structural arrangements of surfactants as a function of concentrations in the interlayers of bentonite affect AfB1 interactions.
ADSORPTION AND INTERACTION OF CIPROFLOXACIN AND PROBE COMPOUNDS WITH PALYGORSKITE

Po-Hsiang Chang*1, Wei-Teh Jiang1, Zhaohui Li1,3, Qing-feng Wu2, Jiin-Shuh Jean1, Guo-Cheng Lv4, and Chung-Yih Kuo5

1 Department of Earth Sciences, National Cheng Kung University, 1 University Road, Tainan 70101, Taiwan: tectonicion@yahoo.com.tw
2 College of Physics and Technology, Yangtze University, Jingzhou, Hubei, 434023, China.
3 Department of Geosciences, University of Wisconsin-Parkside, 900 Wood Road, Kenosha, WI 53144, USA.
4 School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China.
5 Department of Public Health, College of Health Care and Management, Chung Shan Medical University, No. 110, Sec. 1, Chien-kuo N Road, Taichung 40242, Taiwan.

Interactions between soil or sediment components and antibiotics are subtle and can be complicated by the presence of different functional groups. In this study, interactions between a highly sorptive, fibrous 2:1 layer silicate, palygorskite (PFl-1) and ciprofloxacin (CIP), a second generation of quinolone antibiotic and stereochemically-related probe compounds, phenylpiperazine (PP) (–NH2+) and fluorochloroquinolone carboxylic acid (FCQCA) (–COOH) in aqueous solution were investigated to deduce the interaction mechanisms of ciprofloxacin with PFl-1 under different pH conditions.

The CIP, PP and FCQCA adsorption on PFl-1 obeyed the Langmuir isotherm at pH 2, 7, and 11 except the FCQCA adsorption at pH 2. The capacity for CIP and PP adsorption onto PFl-1 was 119, 160, and 98 mmol/kg, and 154, 135, and 99 mmol/kg at pH 2, 7, and 11, respectively. In neutral solution, the total amount of desorbed exchangeable cations was well correlated with the adsorbed quantities of CIP and PP with a positive slope of 0.96 and 0.87, respectively, indicating that cation exchange was the dominant mechanism for CIP and PP adsorption onto PFl-1. As for FCQCA, the adsorbed amount was 27, 57 and 46 mmol/kg at pH 2, 7, and 11, respectively, and the amount of desorbed exchangeable cations was small and had a slight decrease with increasing amount of adsorbed FCQCA in neutral solution, implying that surface complexation or cation bridging was dominant in the adsorption. All of the adsorption was mainly on the external surface of PFl-1 as no lattice-size changes were detected from the $d_{110}$ spacing at 10.5 Å by X-ray diffraction before and after the CIP, PP, and FCQCA adsorption. Subtle differences in the amount of adsorption with different initial pH at low initial concentrations suggested that CIP in cationic and zwitterionic forms (pH < pKa2), PP in cationic form (pH < pKa), and FCQCA in anionic form (pH > pKa) have a much higher affinity for PFl-1 surfaces and are less likely affected by the initial H+ concentration. At high initial adsorbent concentrations, the fact that the capacity for CIP adsorption on PFL-1 in acidic solution was lower than those in neutral solution could be due to a decrease of the cation exchange capacity of PFl-1 in acidic solution, and a lower fraction of cationic form in PP could have caused the lower adsorption of PP on PFl-1 in neutral solution. On the other hand, the silanol groups at external surfaces of PFl-1 can be deprotonated and cause a slight decrease of the amount of FCQCA adsorption on PFL-1 in high pH solution.
The FTIR spectra of PP and FCQCA absorbed on PFl-1 in neutral solution showed evident band shifting that included the ring-stretch vibration modes for PP and the stretching modes of the keto carbonyl group for FCQCA, indicating strong interactions with PFl-1. Although no significant signals could be obtained from FTIR analysis for CIP adsorbed on PFl-1, the results obtained from the probe compounds collectively imply that in the interaction of CIP with PFl-1, the piperazine amine group could play an important role in cation exchange interaction in acidic to neutral solution, while the deprotonated keto carbonyl group could actively partake in hydrogen bonding with the silanol groups or water molecules or surface complexation with metal cations adsorbed on the surfaces of PFl-1 when the CIP was mainly in anionic form in alkaline solution.
THE EFFECT OF HYDRATED LIME ON THE LINEAR AND NON-LINEAR VISCOELASTIC PROPERTIES OF KAOLINITE SLURRIES

Yadeta C. Chemeda¹²*, Dimitri Deneele¹², and Guy Ouvrard¹

¹Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France: Yadeta.Chemeda@cnrs-imn.fr
²Institute Français des Sciences et des Technologies des Transports, de l'Aménagement et des Réseaux (IFSTTAR), BP 4129, route de Bouaye, 44332 Bouguenais, France

Using local soft geo-materials that usually encounter in construction sites after stabilisation is an alternative in minimizing environmental impact of construction works. Consequently, the stabilisation of clayey soil by lime addition finds broad application in various construction activities and it has been widely researched. However, still the physico-chemical mechanisms, which are considered as key parameters in soil stabilization, are yet not well understood. For instance, the role of Ca-ion in improving the mechanical property (UCS and shear strength) of clayey soil, particularly kaolinite, in the early stage of lime-clay interaction (i.e. prior to the precipitation of secondary phases (CSH and/or CASH)) is not fully appreciated. This has usually been explained by the effect of Ca-ion on the reduction of the thickness of diffused double layer. Indeed, calcium as a surface cation causes an instantaneous agglomeration of clay particles, leading at a macroscopic level to the reduction of the soil plasticity and swelling tendency. However, it has been observed that CaCl₂ solution, having similar concentration of calcium ([Ca²⁺]=22 mmol/l) with that of saturated lime solution, doesn’t exhibit similar effect on the short-term mechanical property of clayey materials [1]. That means, cation exchange reaction and compression of diffused double layer alone could not explain the short-term improvement in mechanical property of lime treated clayey soil. Thus, to understand the causes, microstructural organisation of clay particles in calcium rich alkaline condition should be determined.

The organisation of clay particles and strength of particle-particle interaction, which controls the mechanical property of flocs, can be indirectly assessed by using rheological measurements. Especially, viscoelastic investigation (oscillatory) technique is very sensitive to microstructure and it can provide detail microstructural information [2] at very low deformations. This work, thus, examines the effect of hydrated lime (Ca(OH)₂) on the linear and non-linear viscoelastic property of concentrated kaolinite (20 – 30%) slurry in order to understand the microstructural origin of immediate gain in strength of lime treated clayey soils. The influence of other factors such as volume fraction, type of cation (Ca vs Na), pH (Ca(OH)₂ vs CaCl₂) were also studied. The interfacial chemistry of kaolinite suspensions were analysed with zeta potential measurements. For this purpose, two kaolinites, namely KGa-2 (high defect) and KGa-1b (low defect), have been used.

In the linear viscoelastic regime, where the gel structure is stable, the storage modulus (G’) and cohesive energy density (Ec) provide information on the strength of particle-particle linkages. Two-stage change in G’ and Ec were observed with increasing concentration of Ca(OH)₂ (i.e. first decreases at lower concentration (≤ 5.5 mmol/l) and increases at higher concentration), which revealed the combined effect of pH and Ca concentration on aggregation of kaolinite particles. In contrary to Ca(OH)₂, both G’ and Ec decreased monotonously with
increasing the concentration of NaOH, suggesting the effect at higher pH depends on the type (valency) of cation. This is in agreement with kaolinite particle-solution interfacial chemistry (zeta potential). In non-linear viscoelastic regime, attention has been paid to the strain hardening or hump in $G''$ curve. Kaolinite slurries in de-ionized water and saturated lime solution showed different behaviours in terms of width of strain hump, strain max. (strain at $G''_{\text{max}}$) and intensity of strain hardening (Fig 1). These differences are attributed to the difference in interaction and microstructural organisation of clay particles in the two conditions. The slurries in CaCl$_2$ solution showed no strain hardening indicating the simultaneous occurrence of Ca-ion and OH-ion (higher pH) is necessary for densely packed gel structure. The classification of gel in to attractive and repulsive gel is proposed based on the data from linear and non-linear viscoelastic regime (Fig 2). Change in mechanical property of the kaolinite suspension with varying amount of Ca(OH)$_2$ is explained based on the aggregation microstructure of kaolinite particles.

Keywords: Kaolinite, linear and non-linear viscoelastic property, strain hardening

---

Fig 1. Reduced $G''$ vs strain

Fig 2. Variation of strain max. and cohesive energy as a function of Ca(OH)$_2$ concentration.

Reference:
GAS BARRIER PROPERTIES OF NATURAL RUBBER/MECHANOCHEMICAL TREATMENT COAL BEARING STRATA KAOLINITE NANOCOMPOSITES PREPARED BY MELT BLENDING

Hongfei Cheng*, Qinfu Liu

School of Geoscience and Surveying Engineering, China University of Mining & Technology, Beijing, 100083 P.R. China

Nanocomposites materials are two-phase systems that consist of a polymeric matrix and dispersed inorganic particles of nanometer scale (Choudalakis and Gotsis, 2009). The clay is one of the most common inorganic particles as dispersed phase in polymer matrix to fabricate such “hybrid organic-inorganic nanocomposites” (Okada and Usuki, 1995; Xu et al., 2006). The use of organic clays as precursors to nanocomposite formation have been extended into various polymer systems including epoxys, polyurethanes, polyimides, polyesters, polypropylene, polystyrene, polysiloxanes, nitrile rubber, styrene-butadiene rubber, natural rubber, isobutylene–isoprene rubber and ethylene propylene diene monomer (Liu et al., 2008; Takahashi et al., 2006). Kaolinite-rich rocks are very abundant in the Permo-Carboniferous coal-bearing strata of North China and are widely used (Liu et al., 2001). Thereafter, coal bearing strata kaolinite has been applied to incorporate the layered silicates in polymer hosts by in situ polymerization, solution intercalation or simple melt mixing. Recently, much of the work clay application in the rubber has been done to improve the barrier performance of rubbery materials with organic montmorillonite particles (Zulfiqar et al., 2008), and there are relatively few reports on organic kaolinite in this application.

The X-ray diffraction pattern at room temperature indicated that the intercalation of potassium acetate into kaolinite causes an increase of the basal spacing from 0.718 to 1.42 nm, and with the particle size reduction, the surface area increased sharply with the intercalation and exfoliation by ball-milling. Contrary to what is observed in the grinding treatment, ball-milling after intercalation did not result in the amorphization of kaolinite, and the particulates have high aspect ratio according SEM images (Fig.1). It is also shown coal bearing strata kaolinite layers are finely dispersed into the natural rubber matrix and orientationally arranged in parallel. These highly filled natural rubber/mechanochemical coal bearing strata kaolinite (NR/MBK) nanocomposites exhibit outstanding mechanical properties, excellent gas barrier properties and much higher thermal stability compared to the pure natural rubber. The significant improvements in the mechanical properties (Table 1), thermal stability and gas barrier properties (Fig.2) may be attributed to the restriction of the parallel kaolinite platelets to the free movement of rubber molecule chains and the retardation of the impermeable kaolinite layers to the progress of gas molecules through the rubber composites.

Table 1. Mechanical properties of NR composites filled with various MCBK loadings

<table>
<thead>
<tr>
<th>MCBK content (phr)</th>
<th>Hardness (HA)</th>
<th>Stress /MPa</th>
<th>Tensile strength /MPa</th>
<th>Elongation at break /%</th>
<th>Permanent set /%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>300%</td>
<td>500%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>37</td>
<td>1.89</td>
<td>5.49</td>
<td>23.2</td>
<td>745</td>
</tr>
<tr>
<td>70</td>
<td>55</td>
<td>4.35</td>
<td>14.2</td>
<td>25.2</td>
<td>663</td>
</tr>
</tbody>
</table>

63
Acknowledgment

The authors gratefully acknowledge financial support from The Natural Science Foundation of China (51034006).


INTERACTION BETWEEN BENTONITE AND VARIOUS METALS MIMICKING SPENT NUCLEAR WASTE PACKAGES AT ELEVATED TEMPERATURES AND PRESSURES.

Michael C. Cheshire*1, Florie A. Caporuscio1, and Carlos Jove-Colon2

1Los Alamos National Laboratory, Environmental and Earth Sciences, Los Alamos, NM, 87545: Cheshire@lanl.gov
2Sandia National Laboratory, Nuclear Waste Disposal Research and Analysis Department, Albuquerque, NM, 87185.

Bentonite interaction with nuclear waste packages at temperatures greater than 150°C is important to the U.S. repository program, which is investigating solutions for disposal of approximately 140,000 MTU of commercial spent fuel. Clay-based buffer and backfill materials are elements of alternative disposal concepts for clay, shale, or crystalline rock in the U.S., but waste packages could be larger and hotter than those being considered by international disposal programs. The focus of this experimental work is to expand our understanding bentonite’s hydrothermal stability under a range of geochemical, mineralogical, and engineering conditions.

Hydrothermal experiments were performed at 150 – 160 bars and temperatures up to 300°C for five to six weeks. Unprocessed Wyoming bentonite, containing primarily montmorillonite with minor amounts of clinoptilolite, was saturated with a K-Ca-Na-Cl-bearing water (~1,900 mg/L total dissolved solids) at a 9:1 water:rock mass ratio. The bentonite and solution combination contained either steel plates (i.e., 304SS, 316SS, or low-carbon steel) or Cu-foils and were buffered to low Eh using magnetite and metallic iron.

There was strong interaction between bentonite and steel plates in each experiment producing authigenic Fe-smectites with some occurrences of chlorite. Early-stage pentlandite ((Fe,Ni)9S8), millerite (NiS) and/or pyrrhotite (Fe1-xS) formed in association with Fe-phyllosilicates. The Fe-phyllosilicates formed a 10 – 100 μm thick ‘corrosion’ layer with their basal planes near perpendicular to steel substrate (Figure 1A). The Fe-rich smectites have 06ℓ diffraction bands ranging from 1.547 to 1.523 Å (9.264 and 9.216 Å b-parameters), corresponding to trioctahedral smectite (i.e., Fe-saponite) with no evidence of mixed-layering (i.e., corrensite). Preferential leaching of iron from the stainless steel plates was likely the iron source for saponite/chlorite formation, in addition to producing a Cr-enriched passivation layer. However, low-carbon steel does not have Cr or Ni to produce a passivation layer, therefore, experienced extensive pitting corrosion.

The primary corrosion product associated with the ~ 63 μm thick copper foils is chalcocite (Cu2S). Chalcocite formation was most likely in response to pyrite decomposition forming H2S(г,aq). Corrosion seemed to take place with an initial dissolution of the copper developing dissolution features on the surface of the copper (Figure 1B). Chalcocite ranged from discrete hexagonal plates to completely coalesced patches on the copper surface. The chalcocite formed a ~ 13 μm thick layer over a 15 μm corroded/pitted layer. Corrosion depths reached ~ 32 μm corresponding to an average 0.76 μm/day corrosion rate during the isothermal, 300°C experiments. Surfaces within the rolled copper foil were relatively uncorroded.
Figure 1. SEM images (plan view) of A) Fe-saponite and Fe,Ni-sulfides (pentlandite and millerite) using 316SS as a growth substrate from isothermal, 300°C heating profiles and B) copper surface showing corroded copper surfaces and chalcocite (Cu₂S) corrosion products.

Mineral growth on the waste containers was influenced by the container material, buffer, and fluid compositions, in addition to pressure and temperature conditions. However, it is apparent that the various steels have a stronger interaction with bentonite’s silicate fractions, whereas, copper appears to only be reacting with sulfide. Results of this research show that the waste container may act as a substrate for mineral growth in response to corrosion. However, it is presently unknown the roles these corrosion products will have regarding waste canister stability or radionuclide attenuation.

LA-UR-14-21308
DESORPTION OF PHOSPHATE FROM KAOLINITE KGa-1b

Hyen Goo Cho*, Soon-Oh Kim

Department of Earth and Environment Sciences and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, Korea: hgcho@gsnu.ac.kr

The characteristics of phosphate desorption from kaolinite KGa-1b at pH 4, 5, 7, and 9 were studied by batch adsorption–desorption experiments. Sequential extraction was used as the desorption procedure. The phosphate adsorption–desorption reaction seems to be irreversible rather than reversible. Most of phosphate adsorbed on kaolinite tended to be fixed onto the surface. At pH 7 and 9, the Freundlich equation yielded the closest fit in comparison to the Temkin and Langmuir equations. At pH 4 and 5, the closest fit was shown at short reaction times for the Freundlich equation but long reaction times for the Temkin equation. The desorption process seems to be composed of an initial fast reaction, middle medium-rate reaction, and late slow reaction. Percent desorption generally declined with increase in the adsorbed phosphorous concentration. The average percent desorption decreased with increasing pH.
SYNTHESIS AND CHARACTERIZATION OF IRON/MANGANESE OXIDE COMPOSITE AND ITS SORPTION CAPACITY FOR HEAVY METALS AND PHOSPHATE FROM AQUEOUS SOLUTION

Chul-Min Chon¹, Seung-Bum Roh¹,², Soh-joung Yoon*¹, In-Hyun Nam¹, Hocheol Song², and Jae-Gon Kim¹

¹Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon 305-350, South Korea: syoon@kigam.re.kr
²Department of Environment and Energy, Sejong University, Seoul 143-747, South Korea.

A sorbent that can remove a wide range of contaminants simultaneously has a great potential for an extensive use in water remediation, especially for water containing multiple contaminants. In this study, we synthesized iron/manganese oxide composites as sorbents of multiple contaminants and characterized them using X-ray diffraction (XRD), transmission electron microscope (TEM), field emission-scanning electron microscope (FE-SEM), nanoparticle analyzer, and BET surface area analyzer. Then we evaluated sorption capacities of the synthesized composites for removal of heavy metals and anionic nutrients from aqueous solutions. Iron/manganese oxide composites were synthesized by surface precipitation of manganese ions on iron oxides formed via precipitation of ferrous ions in an alkaline condition, followed by addition of hydrogen peroxide (H₂O₂) into the suspensions. Batch sorption experiments were performed at pH 5-5.5 in 0.5 g·L⁻¹ Fe/Mn oxide composite suspensions using Pb, Cu, Zn, and Cd as metal sorbates and phosphate as an anionic sorbate (20~200 mg·L⁻¹). The synthesized composites consisted of magnetic iron(II,III) oxide (i.e. magnetite) and manganese(IV) oxide (i.e. birnessite), and showed surface areas of 20-100 m²/g and particle sizes of 200-400 nm. The composites synthesized at high Fe to Mn ratio could remove phosphate ions efficiently, while those at low Fe to Mn ratio showed great capacity for removing heavy metal ions. The sorption capacities of Fe/Mn oxide composites for heavy metals and phosphate increased with increasing initial concentrations of both ions, and the sorption isotherms were well fitted by the Langmuir isotherm model. Fe/Mn oxide composite can be an attractive sorbent removing heavy metals and phosphate simultaneously from aqueous solutions to provide time- and cost-efficient treatment of water with multiple contaminants.
ANIONIC CLAY-BIOMOLECULAR INTERACTION SELF-ASSEMBLIES: MULTIFUNCTIONAL NANO-BIO HYBRID MATERIALS FOR GENE AND DRUG DELIVERY

Jin-Ho Choy*

Center for Intelligent Nano-Bio Materials (CINBM), Department of Chemistry and Nano Science (BK21 PLUS Program) and Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Republic of Korea: jhchoy@ewha.ac.kr

Most of researches on drug delivery carriers have been restrictively focused on biomolecules and biodegradable polymers such as plasmid, polyethylene glycol and etc. However there are still many problems unsolved, for example, low delivery efficacy, low expression rate, formation of toxic degradation products, and etc. In the present study, a novel concept of nanohybrid vectors with imaging, targeting and drug delivery functions will be proposed to get breakthroughs in gene and drug delivery system.

In order to examine 2d-structured inorganic nano-material as nanocarrier for gene and drug delivery, an attempt has been made to prepare host-guest interaction mediated nanohybrid assemblies by intercalating the negatively charged biomolecules (CMP, AMP, GMP, DNA, and antisense, etc.) or anticancer drugs (Methotrexate, 5-Fluoro Uracil) into the anionic clay, positively charged layered double hydroxides (LDHs). And eventually we found that the encapsulated biomolecules or drug molecules in the interlayer space of LDHs retained their chemical and biological integrity, and that the present inorganic-bio hybrids showed imaging, targeting and drug delivery functions.

According to the cell line experiments, the drugs or genes encapsulated in LDHs were effectively transferred into the cell by clathrin-mediated endocytosis. Since the LDH nanoparticles are partially soluble in cytosol, the drug concentration in the cell increases and as a consequence, the drug efficacy is maximized.

It is, therefore, concluded that the present multifunctional drug delivery system could provide a promising integrative therapeutic action in chemo-and gene therapy.

SURFACE FUNCTIONALIZED ZIRCONIUM PHOSPHATES: A UNIQUE CLASS OF FUNCTIONAL MATERIALS

Abraham Clearfield*

Department of Chemistry, Texas A&M University, College Station, TX 77843, USA.
clearfield@chem.tamu.edu

α-Zirconium phosphate (α-ZrP) Zr(O₃POH)₂·H₂O has a clay like structure in that it is layered with the Zr⁴⁺ ion six coordinate and the outer layer phosphate groups are four coordinate. However in α-ZrP the phosphate groups are inverted with three oxygens bonded to Zr⁴⁺ and the POH groups pointing away from the metal ions.

The list of uses and potential uses of α-ZrP is quite extensive, but among the most promising ones are ion-exchange, catalysis, photoinduced charge separation, drug delivery, biosensors, and fuel cells, among many others. In order to improve the applicability of these materials, surface modifications of the nanoplatelets are highly desirable. Each modification can be tailored for a specific application. We will describe the modification of the surface of ZrP with different groups, such as silanes, epoxides and different metals. The resulting materials were characterized by XRPD, FTIR, AFM, TEM, XPS, and SIMS, among other techniques. The synthesized materials were used for different applications, including drug delivery, emulsifiers, nanofillers in polymer based nanocomposites and as compatibilizing agents in non-compatible polymer blends. The complete synthesis, characterization, and applications of these materials will be presented.

We will then show how a study of α-ZrP processes may be translated to behavior of smectite clays.
IMPACT OF NONTRONITE ON THE EVOLUTION OF ORGANIC MOLECULES AT THE SURFACE OF MARS

Patrice Coll*1, Olivier Poch2, Maguy Jaber3, Jean-François Lambert3, Thomas Georgelin3, Cyril Szopa4, and Fabien Stalport1

1LISA, Universities Paris-East Créteil, Paris Diderot & CNRS, Créteil, France. pcoll@lisa.u-pec.fr
2CSH, Universität Bern, Bern, Switzerland.
3LRS, Pierre et Marie Curie University & CNRS, Paris, France.
4LATMOS, Universities Versailles St-Quentin, Pierre et Marie Curie & CNRS, Guyancourt, France.

Several evidences suggest that early Mars offered favorable conditions for long-term sustaining water. As a consequence, we can assume that in those days, endogenous chemical processes, or even primitive life, may have produced organic matter on Mars. Moreover, exogenous delivery from small bodies or dust particles is likely to brought fresh organic molecules to the surface of Mars until now. Organic matter is therefore expected to be present at the surface/subsurface of the planet. The search for these organic relics is one of the main objectives of Mars exploration missions. But current environmental conditions at the surface - UV radiation, oxidants and energetic particles - can generate physico-chemical processes that may affect organic molecules.

Here we present results of laboratory investigations dedicated to monitor qualitative and quantitative evolutions of several organic molecules under simulated Martian surface ultraviolet light, mean temperature and pressure, using the Mars Organic Molecules Irradiation and Evolution setup. For each organic molecule, the nature of the evolution products (solid or gaseous) and the kinetic parameters (extrapolated half-life at Mars, quantum yields) were determined experimentally. The results show that when exposed to UV radiation, specific organic molecules lead to the formation of solid residues, probably of macromolecular nature, which could reach long term stability.

On the other hand, we emphasize the study of the evolution of molecules in presence of nontronite, a clay mineral detected at the surface of Mars, highlights a strong protective effect of the clay reducing dissociation rates for some molecules, whereas a possible catalytic effect is tentatively observed for one studied molecule.

These results are essential to support the analyses performed in situ by the past, current and future exploration missions. Moreover, the experimentally determined kinetic parameters provide new inputs for numerical modeling of Mars' current reservoir of organic molecules.
SULFATE FORMATION FROM ACID-WEATHERED PHYLLOSILICATES: IMPLICATIONS FOR THE AQUEOUS HISTORY OF MARS

Patricia I. Craig*,1, Doug W. Ming1, and Elizabeth B. Rampe1

1NASA Johnson Space Center, 2101 NASA Parkway, Houston TX 77058, USA: patricia.i.craig@nasa.gov

Sulfates and phyllosilicates have been identified on Mars in close spatial proximity to each other [Wang, et al., 2006, JGR; Wray, et al., 2010, Icarus; Milliken, et al., 2010, GRL]. During the planet’s global geologic transition from the Noachian to Hesperian eras, prevailing acidic conditions may have altered Noachian phyllosilicates to sulfates [Altheide, et al., 2010, GCA; Craig, et al., 2014, LPSC]. Acid-weathered phyllosilicates may help explain the observed phyllosilicate/sulfate stratigraphies on Mars. The purpose of this study was to characterize the alteration products of acid-weathered phyllosilicates in laboratory experiments. These experiments will help constrain the formation processes of sulfates observed in close association with phyllosilicates on Mars and provide a better understanding of the aqueous history of such regions. Here we focused on three phyllosilicates more commonly identified on Mars by IR spectrometers onboard orbiters: montmorillonite, nontronite, and kaolinite [Carter, et al., 2013, JGR]. Samples obtained from the CMS Source Clay Repository [montmorillonite (STx-1), nontronite (NAu-2), and kaolinite (KGa-1)] were treated with H2SO4 of varying concentrations (0.01, 0.05, 0.1, 0.2, 0.5, and 1.0 M) at 100°C for 72 hrs. Solid materials were characterized by X-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), and near-infrared (NIR) reflection spectroscopy.

The XRD pattern of montmorillonite treated with 0.01 M H2SO4 indicated the formation of alunogen even at the lowest concentration (Fig. 1A). All montmorillonite peaks disappeared by 0.5 M H2SO4 indicating complete weathering of the sample. All new peaks were identified as alunogen with traces of SiO2, which were confirmed by SEM/EDS. In the XRD pattern of nontronite treated with 0.01 M H2SO4, the decreased intensity of the 001 peak at 2θ=6.96° (14.7 Å) and the appearance of the 2θ=10.54° (9.7 Å) peak indicated a partial collapse, but not destruction, of the nontronite layers (Fig. 1B). New peaks representing bassanite appeared in the sample treated with 0.05 M H2SO4. In the sample treated with 0.1 M H2SO4, the 001 peak disappeared indicating complete collapse of nontronite but the 021 peaks remained. All nontronite peaks disappeared at 0.5 M H2SO4, indicating complete destruction of the sample and all new peaks were identified as rhomboclase; Fe and S detected by SEM/EDS supported an Fe-sulfate. Kaolinite was the most resistant to alteration of the three phyllosilicates (Fig. 1C). The XRD patterns remain unchanged until 0.1 M H2SO4, at which point new peaks representing alunogen appeared. The large signature peaks of kaolinite were still visible after treatment with 1.0 M H2SO4 but have significantly decreased in intensity while the alunogen peaks became more prevalent.

NIR spectra of acid-treated montmorillonite indicated weathering by the decrease in intensity of the signature hydration bands at 1.4 and 1.9 µm and the disappearance of the Al₂-OH band at 2.21 µm (Fig. 2A). The H2O/OH bands in the 1.0 M H2SO4 spectrum are representative of the H₂O in alunogen. Similarly, hydration bands were visible in the NIR spectra of acid-
treated nontronite (Fig. 2B) but are likely representative of H₂O in rhomboclase. The 2.29 µm band representing Fe-OH in the octahedral layers of nontronite disappeared in samples treated with 0.5 and 1.0 M H₂SO₄. Signature NIR doublets of kaolinite at 1.40-1.41 µm (OH) and 2.16-2.21 µm (Al₂-OH) were visible in the sample treated with 1.0 M H₂SO₄ but decreased in intensity (Fig. 2C). The band at 1.9 µm increased in intensity representing H₂O in alunogen.

![Figure 1](image1.png)

**Figure 1:** XRD patterns of untreated and acid-treated (A) montmorillonite, (B) nontronite, and (C) kaolinite. “M” is molarity of H₂SO₄.

![Figure 2](image2.png)

**Figure 2:** Near-infrared spectra of untreated and acid-treated (A) montmorillonite, (B) nontronite, and (C) kaolinite. “M” is molarity of H₂SO₄.

Phyllosilicate stability under acidic conditions is vital to understanding Mars’ global change from the Noachian to the Hesperian eras. We showed that acid-weathered phyllosilicates alter to sulfates: nontronite to rhomboclase, montmorillonite and kaolinite to alunogen. In regions of Mars where phyllosilicates and sulfates are found together, the Fe-sulfate is identified as jarosite and the Al-sulfate is alunite (e.g. Farrand, et al., 2009, *Icarus*; Wray, et al., 2011, *JGR*). Two discrepancies arise: 1) absence of K⁺ in our results, which might be explained by the < 2 wt% K₂O in the original samples, and 2) different hydration states. This may result from the environment in which the samples were analyzed. Analyzing the samples under arid conditions may make a difference. Another reason for the difference in hydration may be due to a relatively high water:rock ratio in the experiments. Reducing this ratio might change the end result.
In recent years, studies on nanomaterials for drug delivery systems have been intensified in the nanotechnology field due to the improvement of solubility, stability against decomposition processes, and sustained release of biological species. Layered Double Hydroxides (LDHs) are well known inorganic carriers which have been explored during the development of new materials for medicinal and pharmacological applications. These inorganic materials are biocompatible and are known to have antacid activity. The solubility and chemical stability of guest species can be increased when intercalated between LDH layers. LDHs can support the release of intercalated bioactive species through ion exchange reactions and/or chemical processes mediated by changes in pH.

In this study, synthetic routes and experimental parameters were determined for the confinement of the anionic form of lipoic acid (abbreviated Lip), a natural substance which displays antioxidant activity, and which can be used for the Alzheimer disease and Parkinson's treatment. The inorganic carriers containing the bioactive species were synthesized by the co-precipitation method, using molar ratios of $\text{M}^{2+}/\text{Al}^{3+} = 2$ and $\text{Lip}/\text{Al}^{3+} = 1$. Samples were labeled as $\text{M}_2\text{AlLip}_y$, where $\text{M}$ can either mean $\text{Mg}^{2+}$ or $\text{Zn}^{2+}$, and $y$ denotes one of the following drying processes: (i) lyophilization (lyo) and (ii) room temperature with reduced pressure in a dessicator (des).

XRD patterns of all isolated LDH-lipoate materials (Figure 1) indicate the intercalation of lipoate anions in the interlayer region (basal spacings equal to 2.26 nm for $\text{Mg}_2\text{AlLip}_{\text{des}}$, 2.19 nm for $\text{Zn}_2\text{AlLip}_{\text{lyo}}$, and 2.24 nm for $\text{Zn}_2\text{AlLip}_{\text{des}}$). Those materials prepared with $\text{Zn}^{2+}$ exhibit a more organized stacking of the layers. Evaluating the XRD data by employing the Debye-Scherrer equation for the peak (003), we find that the mean crystallite size of the materials is 15.1 nm for $\text{Mg}_2\text{AlLip}_{\text{des}}$, 20.9 nm for $\text{Zn}_2\text{AlLip}_{\text{lyo}}$, and 22.2 nm for $\text{Zn}_2\text{AlLip}_{\text{des}}$. From the estimated dimensions of lipoate (0.44 x 1.21 x 0.36 nm) and the XRD data, one can suggest an arrangement of a bilayer of the organic anion in the interlayer region. The hydrodynamic diameters of $\text{Zn}_2\text{AlLip}_{\text{lyo}}$ (413 nm) was slightly smaller than the $\text{Zn}_2\text{AlLip}_{\text{des}}$ (455 nm). Thus, the lyophilization drying process decreased the mean particle size compared to the dessicator one. Unlike the dessicator process, the lyophilization process drastically changed the stability of the suspension in water, i.e. the Zeta potential of $\text{Zn}_2\text{AlLip}_{\text{lyo}}$ was +28.2 mV, while that of $\text{Zn}_2\text{AlLip}_{\text{des}}$ was found -7.49mV. Elemental analysis data of the hybrid materials showed that the different compositions of the layered materials used did not alter the organic content in the materials. The amount of lipoate ions (wt.%) in the isolated materials was roughly 39%. FTIR spectra show the bands of lipoate ion:
CH2 stretching (~2928 cm⁻¹), COO- asymmetric stretching (1545 cm⁻¹), COO- symmetric stretching (1399 cm⁻¹). The thermal decomposition of lipoic acid under air begins at 180 °C, while for the hybrid materials that process starts at approximately 230 °C. Hence, the thermal stability of the immobilized species in the LDHs interlayer region was significantly improved. LDHs are potential carriers for lipoate storage and delivery.

![Figure 1. XRD patterns of powdered Zn2AlLip.Lyo, Zn2AlLip.des, and Mg2AlLip.des (from top to bottom).](image)

DISTINGUISHING BETWEEN PORE-FILLING AND PARTITIONING OF NEUTRAL ORGANICS CONTAMINANT SORPTION ON GEOSORBENTS

Kamol Das1*, Cliff T. Johnston2

Kamol Das, Crop Soil and Environmental Sciences, Purdue University, 915 W. State St, West Lafayette, IN 47906

Cliff T. Johnston, Crop Soil and Environmental Sciences, Purdue University, 915 W. State St, West Lafayette, IN 47906

Sorption of neutral organic contaminants (NOCs) on carbon-containing geosorbents has traditionally been described on the basis of partition theory. In recent years, increased attention has focused on the role of condensed carbonaceous materials; broadly known as black carbon, in the attenuation of NOCs in the environment. Sorption of NOCs on black carbon is generally 2 to 3 orders of magnitude greater than that of ‘amorphous’ soil organic matter. We have investigated the interaction of several NOCs on two contrasting geosorbents. We have synthesized and characterized an organoclay geosorbent consisting of Na-SWy-2 smectite modified with dimethyldioctadecyl ammonium chloride. With a d-spacing of 4.2 nm this clay functions as a ‘partition sorbent’ and typical linear sorption isotherms were observed for naphthalene, dibenzo-p-dioxin, and trichloro-ethylene. In addition, we have investigated NOC sorption on a highly porous granular activated carbon. This material shows anomalously high NOC sorption consistent with a pore filling mechanism. Overall sorption mechanisms and behavior of NOC solutes on these two contrasting geosorbents are presented.
MINERAL DIVERSITY IN SOUTH WESTERN AMAZON SOILS, BRAZIL

Elaine Almeida Delarmelinda*1,3, Valdomiro Severino de Souza Junior1, Paulo Guilherme Salvador Wadt2, and Youjun Deng3

1Department of Agronomy, Federal Rural University of Pernambuco, Recife, PE 52171-900, Brazil: elaineadell@gmail.com;
2Brazilian Business of Agriculture Research – EMBRAPA, Rio Branco, Acre, AC 69900-970, Brazil;
3Department of Soil and Crop Sciences, Texas A&M University, College Station, TX 77843-2474, USA.

Soils in the Brazilian Amazon jungle are far more diverse than the perceived simple Oxisols concept. This is largely due to different parent materials, especially sedimentary deposits in this region. In addition to common mineral such as kaolinite and iron oxides observed in highly weathered soils, smectites, vermiculites and interlayered vermiculite and smectite have been reported in South Western Amazon soils. Due to the high charge density of these minerals, they can function either as a sink or a source of acidity in storing or releasing Al and H to the soils. The extent of occurrence of these 2:1 layer silicate mineral in the Amazon soils is still unknown due to limited accessibility of the lands. The objective of this study was to characterize the mineralogical and chemical variations in soils derived from two typical sedimentary deposits in the Amazonian environment and their variations with landscape and age.

Nine soils in the southwest part of Brazilian Amazon were analyzed. These soils are derived from the Upper and Lower Solimões Formation deposited during the Miocene and Pliocene epochs; and the Madeira River sediments deposited during the Pleistocene and Holocene epochs. The soils are located in Humaitá city (07°30’21.2”S 63°04’55.5”W) in south of Amazonas State, Nova California city of Rondônia state; Sena Madureira city (09°00’11.4”S 68°56’53.4”W) and Tarauacá city (07°54’31”S 71°35’30.6”W) of Acre state. The mean annual rainfall is 2000 mm and the average annual maximum temperature is 25 °C. Soil pH; exchange calcium, magnesium, potassium, sodium, and aluminum; and particle-size (clay, silt and sand) distribution were measured. To study the layer silicate minerals, soils were size fractionated and the iron oxides in the clays were removed. Each fraction was analyzed by X-ray diffraction on a Shimadzu DRX 6000 X-ray diffractometer with a Cu Ka source operated at 40 kV and 30 mA.

The first chronossequence consist of soils derived from Madeira River sediments with ages of 1.8 Ma (soil P2) and 0.01 Ma (soils P1 and P3), respectively. Soil P1 is formed on the slightly older alluvial terrace than soil P3. The dominant pedogenic process is clay accumulation in the B horizons of the soils and an argillic horizon containing 488 g kg⁻¹ caly is developed in the oldest soil P2. The contents of exchange bases in these three soils are similar but the exchange Al increased from 0.77 cmol, kg⁻¹ in the youngest soil P3 to 7.10 cmol, kg⁻¹ in soil P2. The XRD analysis (Figure 1) indicated that vermiculite, mica, kaolinite and quartz occur in the clay fractions of the three soils. The oldest soil P2 is dominated by kaolinite while the youngest soil P3 contains the greatest amount of mica and soil P1 has the greatest amount of vermiculite. The silt fraction of these soils are dominated by quartz. With decreasing abundance, mica, kaolinite,
rutile, and anatase also occur in all soils. The XRD analysis indicated decreasing mica abundance from C to A horizon in all profiles.

Figure 1. Clay XRD patterns of B-horizons of soils developed of sediments in South Western Amazon, Amazonas State. P2 - Içá Formation (1.8Ma); P1 – Deposit of river terraces (0.01Ma); P3 – Alluvial deposits (0.01Ma).

Acre and Rondônia states. Soils P4 and P5 derived from the sediment of the Lower Solimões Formation (20-5 Ma, Miocene) and soil P7 from the upper Solimões Formation (5-1.7 Ma, Pliocene). Soil P4 had the highest degree of weathering and formed an Oxisol that is dominated by kaolinite and iron oxides. This soil had a lower exchangeable aluminum between 0.42-1.86 cmol\(\cdot\)kg\(^{-1}\) than soil P2, presumably due to the absence of 2:1 layer silicates in the Oxisol. Soil P5 is clayey with exchangeable aluminum between 6.4-12.82 cmol\(\cdot\)kg\(^{-1}\) and high values of calcium (11.53-37.66 cmol\(\cdot\)kg\(^{-1}\)). Soil P7 derived from the Upper Solimões Formation is also clayey with high exchangeable aluminum (2.76-13.01 cmol\(\cdot\)kg\(^{-1}\)) but the exchangeable calcium (0.44-1.67 cmol\(\cdot\)kg\(^{-1}\)) is lower than soil P5. Kaolinite is the predominate clay mineral in soil P1, smectites in soil P5, and vermiculite in soil P7.

Figure 2. Clay XRD patterns of B-horizons of soils developed of sediments in South Western Amazon, Rondônia and Acre State. P4 and P5 – Lower Solimões Formation (20-5 Ma) P7 – Upper Solimões Formation (5-1.7 Ma).
SYSTEMATICS OF BENTONITE BY NEAR-INFRARED SPECTROSCOPY

Aglaia Deligianni\textsuperscript{1}, Vassilis Gionis\textsuperscript{2}*, and Georgios D. Chryssikos\textsuperscript{2}

\textsuperscript{1}S&B Industrial Minerals S.A., Kifissia, GR-14564, Greece
\textsuperscript{2}Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, GR-11635, Greece: vgionis@eie.gr

This is a near-infrared (NIR) spectroscopic survey of >950 montmorillonite-rich bentonite samples from different localities (among them: Milos, Greece; Montana, USA; Nador, Morocco; Turkey etc.). These samples are benchmarked against CMS source montmorillonite clays SWy-1, SWy-2, STx-1 and SAz-1. All samples are natural, bulk, ground to <200 μm and equilibrated to ambient temperature and humidity. NIR spectra are collected by an optical fiber bundle probe in a non-invasive manner. The technique is sensitive to the O-H combination and overtone modes of both the structural OH groups and molecular H\textsubscript{2}O. The information content of the spectra is enhanced by 2\textsuperscript{nd} derivative analysis which allows for the accurate determination of the maxima of sharp peaks with little influence from broad features or curved baselines.

The spectra serve as fingerprints of montmorillonite because they reflect its compositional variability, i.e. the extent and type of octahedral and/or tetrahedral substitution, as well as the nature and hydration of the interlayer cations. They are also sensitive to other accessory clays (especially kaolinite) or hydrous non-clay minerals. As such they are suitable for identification and classification purposes, or for the evaluation of drill cores, especially if coupled with chemometric analysis.

![Figure 1. Correlation between the (ν+δ) combination modes of AlAlOH structural hydroxyls and interlayer H\textsubscript{2}O in montmorillonite-rich natural bentonite.](image-url)
Opposite to fingerprinting, a survey of the big picture must rely on ubiquitous spectral features, common to all samples and sufficiently intense to be observed in the presence of common admixtures. Such features are the wavenumbers of the AlAlOH and H2O combination modes active in the NIR spectral region. Within our set of samples, the former takes values between 4517 and 4537 cm\(^{-1}\) and is employed intuitively as a proxy for the layer structure (samples containing kaolinite are excluded due to its strong sharp absorption at 4527 cm\(^{-1}\)). The latter ranges between 5240 and 5260 cm\(^{-1}\) and can be considered as probing the interlayer. Interestingly, and despite uncertainties stemming from the mineralogical and chemical variability of the natural samples, the two quantities appear well correlated (Fig. 1).

Further, a hint about the effect of the interlayer cations on the correlation in Figure 1 is offered by the comparison of a subset of \(\sim\)130 bentonites from Milos, Greece in their natural Ca-form and after laboratory Na-exchange (Fig. 2). The position of the AlAlOH combination mode is little affected by the exchange confirming that this band is a useful probe of layer structure with little dependence on the interlayer at ambient. On the contrary, the wavenumber of the H2O combination mode increases systematically upon Na-exchange and the effect is more pronounced for bentonite samples of low energy AlAlOH position.

![Figure 2. Dependence of the \((\nu+\delta)\) AlAlOH (left) and H2O (right) modes on the Na-exchange of natural Ca-bentonite from Milos, Greece](image)

A detailed rationalization of the above trends in terms of layer charge, charge localization and nature of interlayer ions is in progress on the basis of well characterized clay-fractions.

Acknowledgements: Funding for NHRF was provided mostly by S&B Industrial Minerals S.A. and, recently, by the project POLYANO-KRIPI 447963/GSRT-Greece of TPCI-NHRF. During the course of this study, VG and GDC benefited from challenging discussions with Stefan Kaufhold (BGR) and George Christidis (Techn. Univ. Crete).
Fungi and Their Useful Role in Soils

Joe B. Dixon*,1, Muhammad Wasim2, Ana L. Barrientos Velázquez1, and Youjun Deng1
1Department of Soil and Crop Sciences, Texas A&M University, College Station, TX 77843-2474, USA: mjdjbd@suddenlink.net
2PAKISTAN Agric. Res. Council, Islamabad, PAKISTAN

Previous transmission electron microscopy analysis of a Tirnaul (soil series) surface soil from Pakistan showed the presence of fungal mycelia containing iron oxides as ferrihydrite and lepidocrocite, with phosphorus associated within these structures.

The developments in fungal phases reveal potential for learning and better utilization of organic systems and better environmental utilization for improved segment of natural environment e.g. colder climates of the USA and of Canada where fungi occur in scale. Also, fungal phases from Brazil would be a logical inclusion for this proposed research to include a wider range of climates where P is known to be a concern.

We are now motivated to improve food production by new avenues for more collaboration with colleagues in neighboring countries such as fungal use potential e.g. Canada and other small nations with growing populations. They may be attractive collaboration nations because they have humid areas where fungi grow providing variety for plant growth examples compared to local conditions. New roles of soil research by new solutions of improved by P use efficiency. Improved instruments for use in instruction and land use planning may be appropriate.

More collaboration in Texas and internationally is needed to maintain a selection program by better instruction methods at Texas A&M University for domestic and visiting students and fellow scientists. Improved high resolution electron microscopy methods in current laboratories at TAMU and by replacement of instruments in electron microscopes for graduate teaching and for research is required. Research and exceptional graduate instruction to develop and maintain a leading research and graduate training program of the best quality as an international leading research and graduate instruction program. Such a quality program is needed to attract better graduate participants among local and guest participants to yield exceptional participants and productive graduates as needed by graduate participants and graduates. Fungi of interest are commonly found by chance. Collaborations nationally and internationally are important because P and other important nutrient elements may be more likely to be found via chance if we can expand it geographically where resources can be shared e.g. electron microscopes and x-ray diffraction instruments.
MICROBIAL REDUCTION OF HUMIC ACID

Amber Douglas\textsuperscript{1*}, Dr. Shannon Weigum\textsuperscript{2}, and Gary Beall\textsuperscript{3}

\textsuperscript{1}Materials Science, Engineering, and Commercialization, Texas State University-San Marcos, San Marcos, TX 78666-4684, adl1216@txstate.edu;
\textsuperscript{2}Department of Biology, Materials Science, Engineering, and Commercialization, Texas State University-San Marcos, San Marcos, TX 78666-4684, sw57@txstate.edu;
\textsuperscript{3}Department of Chemistry and Biochemistry, Materials Science, Engineering, and Commercialization, Texas State University-San Marcos, San Marcos, TX 78666-4684, gb11@txstate.edu

Graphene is a two-dimensional sp\textsuperscript{2}-hybridized carbon-based material possessing extraordinary properties including, excellent electrical conductivity, ballistic thermal conductivity, tensile strength exceeding that of steel, high flexural strength, optical transparency, and the ability to adsorb and desorb atoms and molecules.

Because of these characteristics, graphene is a candidate for applications in integrated circuits, electrochromic devices, transparent conducting electrodes, desalination, solar cells, thermal management materials, polymer nanocomposites, and biosensors. Despite the above mentioned properties and possible applications, very few technologies have been commercialized with graphene. This is due to the high cost associated with the raw materials and complicated processes required in graphene’s fabrication.

In an effort to contribute to the commercialization of graphene on a large scale, the current work includes a low-cost synthetic process of graphene from humic acid obtained from an inexpensive carbon source, leonardite coal. It has been suggested that graphene can be derived from functionalized graphene via microbial reduction of graphene oxide. This process utilizes specific bacteria which have the ability to use both organic and inorganic compounds as terminal electron acceptors in their respiratory pathway.

It is hypothesized that these bacteria may also reduce humic acid to graphene using low-cost and non-toxic starting materials and energy efficient processes. The work includes the validation and characterization of the humic acid starting material versus graphene oxide and the study of the reduction potential of the selected microbes.
PyXRD: CAN WE IMPROVE AUTOMATIC PARAMETER REFINEMENT FOR FULL-PROFILE X-RAY DIFFRACTION FITTING OF DISORDERED LAYERED STRUCTURES USING A MULTI-SPECIMEN APPROACH?

M. Dumon¹*, E. Van Ranst¹

¹ Department of Geology and Soil Science (WE13), Ghent University, Krijgslaan 281/S8, B-9000 Ghent, Belgium

It is generally accepted that obtaining quantitative mineralogical data allows to study soil properties and formation in greater detail. However, when quantifying minerals in soil clay fractions, the complex assemblages of partially weathered, partially intact and mixed-layer phyllosilicates prevent the use of simple approaches to obtain an accurate quantification. In these cases dedicated software is needed which can calculate the X-ray diffraction patterns for such (dis)ordered phases, thus removing the need for measured standards. The (dis)order and structure of these phases can be described (and adjusted ad hoc) using a number of parameters which allows to improve the fit between the calculated and observed patterns. Although simpler mineral assemblages (e.g. 2 or three phases) might be automatically refined using computer algorithms, in most non-trivial cases, strong correlation between some of the parameters results in unrealistic solutions. As a result, currently the most reliable way to refine complex samples is using a time-consuming trial-and-error approach.

From a theoretical viewpoint the automatic refinement failure is due to a poorly constrained or over-parametrized model, in which the objective function (the residual error) has several (local) minima. This could be alleviated by reducing the number of model parameters compared to the number of observations. This can be achieved by using a multi-specimen approach, combining X-ray diffraction patterns from several treatments (e.g. an air-dry, glycolated and heated to 350°C) for the same sample in a single model. This way, the unaffected parameters can be shared among the different treatments.

PyXRD is a new open-source program able to calculate X-ray diffraction patterns for oriented, disordered layered structures. The mathematical model behind PyXRD is similar to other computer programs such as Sybilla©, MLM2C and MLM3C. However, PyXRD was created from the start with the multi-specimen approach in mind. PyXRD allows the user to link the phases and their parameters together. This allows to selectively keep some parameters (e.g. coherent scattering domain size, octahedral iron contents, ...) linked and keeping the treatment-dependent parameters (e.g. basal-spacing, interlayer contents, ...) unlinked.

The effectiveness of this linked set up for automatic parameter refinement was compared with the standard unlinked set up. To this end, calculated patterns for fictive mineral assemblages with known parameter values where used as input data for the reverse model after scrambling a selection of parameters. Initial results indicate that the linked multi-specimen set up indeed improves the results, but the improvement is highly dependent on the complexity of the theoretical mineral assemblages used.
ALTERATION OF AMORPHOUS AND CRYSTALLINE PHASES, FORMATION OF CLAY MINERALS IN GEOLOGICAL SUCCESSIONS, A PROJECT PRESENTATION

Henning Dypvik\textsuperscript{1,2*}, Helge Hellevang\textsuperscript{1}, and Stephanie Werner\textsuperscript{2,1}

\textsuperscript{1}Department of Geosciences, University of Oslo, P.O.Box 1047, Blindern, NO-0316 Oslo, Norway, \textsuperscript{2}CEED, University of Oslo, P.O.Box 1048, Blindern, NO -0316 Oslo, Norway: henning.dypvik@geo.uio.no

Alteration of unstable, amorphous and crystalline phases is commonly encountered processes in sediments and sedimentary successions in our planetary system. In this connection the water/porewater - rock interactions are crucial. Such mineralogical alterations create compositional changes and severe problems in e.g. in petroleum and water reservoirs, by reducing the permeabilities and changing the pore geometries. These so-called diagenetic reactions may result in dramatic changes in reservoir characteristics and clay mineral formation in sediments containing volcanic fragments or intrusions, with corresponding changes in porosity and permeability.

Comparable mineral alterations and the formation of clay minerals are/have been key processes active on the surface of the Earth and the planets, highly controlled by water/atmosphere/rock interactions. These alterations are to a large extent responsible for generating soils and regoliths. On the Earth these processes are extremely complex, e.g. due to the influence of both flora and fauna, in addition to different local input caused by human activity. The surface of Mars, however, is less complex in that respect and an interesting site for studying such alterations (Ehlmann et al. 2011, Werner et al. 2011). In this respect it is of particular interest to mention the Near Infrared spectroscopy (NIR) analysis executed on the surface of Mars. The NIR analyses have displayed a common presence of several clay minerals (see review by Ehlmann et al. 2011.) with compositions most likely reflecting the original alteration of impact/volcanic glass or volcanic rocks (Hellevang et al., 2013).

Figure 1. Reaction bomb set up with experimental results to the right; SEM of unaltered glass (A) and altered basaltic glass showing crenulated flaky smectite (Hellevang et al., 2013)
On Mars, the presence of clay minerals is often associated to impact crater interior outcrops, and thus it is debated whether the majority of these minerals is an excavated relic of the ancient possible warmer and wetter past of Mars or could still be formed at present climatic conditions.

This is a newly started project with a scientific aim to better explain and understand the alteration processes of glass/melts and less stable crystalline phases, e.g. volcanic rocks. We will approach these issues by different means, e.g. in describing natural rock samples by standard petrographical techniques, by laboratory experiments (in reaction bombs) and by geochemical simulations. Through these analyses we hope to shed new light on both surface and diagenetic alterations of sedimentary particles along with the related precipitation of clay minerals and other phases as, e.g. zeolites.

![Figure 2](image-url)

Figure 2. To the left bulk XRD run of untreated basaltic glass (lower trace) and the reaction product after experiment in the reaction bomb (upper trace). The right plots show results of geochemical simulation of the experimental set up used (Hellevang et al., 2013).

The new information gained will have great general importance, as here illustrated by two end-members cases; the evaluation of petroleum reservoir quality and our understanding of the composition of surface of Mars. The wide span of these two examples illustrates how such alteration studies represent basic knowledge in the formation of clay minerals and clays.

References
COMPOSITION OF CLAY MINERALS ON MARS FROM ORBITING INFRARED SPECTROSCOPY: KEY MINERALS AND KEY QUESTIONS

Bethany L. Ehlmann1,2*

1Division of Geological Sciences, California Institute of Technology, Pasadena, CA, 91125; ehlmann@caltech.edu;
2Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 91109.

Since 2004, orbiting infrared spectrometers with up to 10-nm spectral resolution and 18m/pixel spatial resolution have identified multiple phyllosilicates on Mars (Table 1). Most common are Fe/Mg phyllosilicates, including smectites (e.g. ferrosaponite) and chlorites (e.g. clinochlore). Phyllosilicates are found in characteristic assemblages with other secondary minerals including iron oxides, sulfates, chlorides, carbonates, and other hydrated silicates (for review, see Ehlmann & Edwards, Ann. Rev. Earth Plan Sci., 2014). Phyllosilicates mappable from orbit are restricted to Mars’ earliest geologic epochs, the Noachian and Hesperian, over 3 billion years ago. Multiple environmental settings are indicated: hydrothermal, metamorphic, diagenetic, and, weathering. Here we review the major geologic settings of clay minerals, spectral characteristics permitting identification, and key outstanding questions relevant to clay mineralogy and the geologic history of Mars.

Table 1. Phyllosilicates identified or proposed from orbital IR spectroscopy, grouped by Dana classification. Judgments of certainty are based on the degree to which the ID is spectrally unique and/or has been made by more than one independent group. Even though phases are structurally distinct, they are included together where they cannot be spectrally distinguished with available Mars datasets.

<table>
<thead>
<tr>
<th>Group</th>
<th>Specific phases consistent with spectra</th>
<th>Commonality of occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Phyllosilicate Sheets of Six-Membered Rings with 1:1 layers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolin group</td>
<td>kaolinite, halloysite</td>
<td>minor</td>
</tr>
<tr>
<td>Serpentine groups</td>
<td>lizardite, antigorite, chrysotile</td>
<td>rare</td>
</tr>
<tr>
<td>Allophane group</td>
<td>allophane, hisingerite</td>
<td>(possible)</td>
</tr>
<tr>
<td><strong>Phyllosilicate Sheets of Six-Membered Rings with 2:1 layers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrophyllite-talc group</td>
<td>Talc</td>
<td>(possible)</td>
</tr>
<tr>
<td>Mica group</td>
<td>muscovite, illite, margarite, vermiculite</td>
<td>rare, (possible)</td>
</tr>
<tr>
<td><strong>Phyllosilicate Sheets of Six-Membered Rings with 2:1 clays</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dioctahedral smectites</td>
<td>beidellite, montmorillonite, nontronite</td>
<td>rare, rare, common/minor</td>
</tr>
<tr>
<td>Trioctahedral smectites</td>
<td>(ferro)saponite</td>
<td>common</td>
</tr>
<tr>
<td><strong>Phyllosilicate Sheets of Six-Membered Rings interlayered 1:1, 2:1, and octahedral</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorites</td>
<td>Clinochlore</td>
<td>common</td>
</tr>
<tr>
<td>Interstratified chlorite-smectite</td>
<td>Corrensite</td>
<td>common?</td>
</tr>
<tr>
<td><strong>Phyllosilicate Two-Dimensional Infinite Sheets with Other Than Six-Membered Rings with 4-membered rings</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Prehnite</td>
<td>minor</td>
</tr>
<tr>
<td><strong>Phyllosilicate Modulated Layers with joined strips</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palygorskite</td>
<td>(possible)</td>
<td></td>
</tr>
<tr>
<td>Sepiolite</td>
<td>(possible)</td>
<td></td>
</tr>
</tbody>
</table>
CLAY MINERALOGY OF AN ALLUVIAL AQUIFER, RIFLE, COLORADO

W. Crawford Elliott*1, David Lim1,2, Rebecca Pickering1, Laura K. Zaunbrecher1, Kenneth H. Williams3, and Philip E. Long3

1Department of Geosciences, Georgia State University, Atlanta, GA 30302-4105 USA: wcelliott@gsu.edu
2Department of Geology and Geophysics, University of Wisconsin-Madison, Madison, WI, 53706 USA;
3Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720 USA.

Alluvial aquifers along the Colorado River corridor in central to western Colorado can be important hosts for legacy contamination including U, V, As and Se. These alluvial aquifers are thought to provide important “hot spots” and “hot moments” for microbiological activity controlling organic carbon processing and fluxes in the subsurface. Relatively little is known about the clay mineralogy of these aquifers in spite of the fact that they include lenses of silt-clay materials. These lenses are commonly more reduced than coarser grained materials. The clay mineralogy of an alluvial aquifer located in Rifle, CO (USA) is composed of chlorite, hydroxy-interstratified vermiculite (HIV)-smectite intergrade, smectite, illite, kaolinite and quartz. The clay assemblage reflects the mineralogically immature character of the sediments. This assemblage is consistent with soils that formed in a moderately low rainfall climate and suggestive of minimal transport of the alluvial sediments from their source areas. Chlorite and smectite-HIV are the likely phases involved in the sorption of organic carbon and related microbial redox transformations of metals in these sediments. Chlorite, smectite-HIV and smectite therefore exert a primary control on the fixation of contaminants and are important determinants of biogeofacies in these alluvial sediments.
SPATIAL VERSUS SPECTRAL RESOLUTION: MAPPING HOT SPRING CLAYS USING METER SCALE SATELLITE DATA AND GROUND TRUTH MINERALOGY

Laura E. Fackrell*1, Paul A. Schroeder1

1Department of Geology, University of Georgia Athens, GA 30602-2501, USA lauraelf@uga.edu

Easy collection of high spatially resolved (~1 m²) four-band spectral reflectance data from remote volcanic areas subject to rapid change is now an economically feasible reality. One such area of the world is the active Uzon Caldera, located in Kamchatka, far-eastern Russia. We test the hypothesis that statistically significant relationships exist between the four-band spectral data and ground truth mineralogy. Mineralogical data includes X-ray powder diffraction (XRD), short wave infrared reflectance (SWIR) spectroscopy, and color as collected by digital camera. Ground samples used were collected from the Orange Thermal Field (OTF) and White-Orange-Red (WOR) slope; OTF and WOR areas display gradients in in extent of hydrothermal acid and redox alteration.

Data input into statistical models included 1) quantitative XRD phase analysis using an internal standard and Rietveld refinement method, 2) raw SWIR spectra collected in the field from dry powdered samples, 3) RGB color values from ~ 1mb of pixels averaged from a photo covering 1 m² taken ~ 1 m above the sampling site, and 4) Quickbird® four-band spectral reflectance data. Statistical modeling was performed using R-code to perform non-metric multidimensional scaling (MDS) on both SWIR and XRD data and correlated to collected color and satellite spectral data using Spearman correlation. A facies model was constructed using discriminant function analysis to distinguish among dominant mineral species found along hydrothermal acid and redox alteration gradients.

Results show that with proper ground truth constraint, mineral facies surrounding Uzon hot springs are grouped as 1) iron oxide-, 2) sulfate-, 3) high-T siliceous-, 4) volcanic-, 5) sulfur-, 6) low-T siliceous-, 7) sulfide-, and 8) chloride-dominated. As noted in a previous study (Schroeder et al., 2011), phases like goethite, hematite, alunite, gypsum, cristobalite, andesine, glass, opal-A, pyrite, halite, kaolinite, and smectite may be found within any one facies, but the dominance of one or more mineral influences the classification of facies types. High spatial resolution satellite data lack spectral detail (i.e., only four values) but their collective response to the complex mixture of mineral and biological components does provide meaningful insight. This facies concept is useful in conveying the dominance of particular phases and environmental factors that influence thermophilic microorganisms and the redox, temperature, and hydrologic conditions in which they thrive. Biogeographic mapping of such assemblages can benefit from additional mineralogical and remote sensing efforts. Contrasting satellite images acquired at times apart also allows for the assessment of temporal facies changes in remote terrestrial hot spring systems.
EGYPTIAN “BENTONITIC CLAYS”: MINERALOGY, CEC, AND ORIGIN

Ray Ferrell¹*, Mohamed Agha², and George Hart¹

¹Department of Geology and Geophysics, Louisiana State University, Baton Rouge, LA, 70803, USA. rayferrell@cox.net
²Department of Geology, Fayoum University, Fayoum, Egypt

Tertiary “bentonitic” clays from 12 locations in northern Western Desert of Egypt were characterized by QXRD, AgTU CEC (Ag thiourea), SEM, and DFA (discriminant function analysis). The clays are used in a variety of industrial applications. Most are typically smectite-rich but may have diverse, non-volcanic origins indicating that they are not bentonites in the strict sense. The most abundant minerals are Fe-rich smectite, S-poor I/S, coarsely crystalline kaolinite, and finely crystalline kaolinite. DFA revealed mineral differences that vary with province, age and quarry, related to their genesis. Changes in the kaolinite/smectite ratio are linked to two wet-dry climatic cycles. For the CEC determinations, the use of 2 sample weights, 0.15 and 0.3 g, assessed the influence of soluble minerals. Lower sample weight values in meq/100 g are higher when calcite is present. Cation exchange properties influenced by soluble calcite and halite vary with location. The effective CEC often exceeded the AgTU CEC.

Analytical results and sedimentary features indicate deposition in fluvial and near-shore environments. In a few instances, there are altered spherical microspheres that may have been of volcanic origin.
MINERALOGICAL ANALYSIS OF MUDSTONE AND CLAYSTONE SAMPLES BY MINERAL MAPPING: HOW ACCURATE CAN THAT BE?

Claire I. Fialips*1, Jean-Paul Laurent1, Bernard Labeyrie1, Benoit Lasserre1, François Umbhauer1, and David Haberlah2

1Mineral Geochemistry Team, Total, Technical Center CSTJF, avenue Larribau, 64018 Pau, FRANCE: Claire.Fialips@total.com
2Center of Excellence for Natural Resources, FEI, Brisbane, QLD, Australia.

The interpretation and calibration of wireline logs of gas/oil shale formations and clay-rich caprocks require accurate mineralogical analyses of statistically representative sets of core/cutting samples. It is particularly important to accurately assess the total clay minerals, total carbonates and pyrite contents of the studied core or cutting samples. Bulk quantitative mineralogical analyses relying exclusively on the analysis of powder X-Ray Diffraction (XRD) patterns often encompass significant uncertainty, with errors on total clay minerals content often greater than 15 mass%.

Our in-house approach to quantitative mineralogy, called QM, has been developed over the last decade to optimize accuracy and robustness, especially for clay-bearing samples. This method fully integrates standard XRD analyses of bulk powders and extracted fine fractions with a large suite of additional chemical and physical measurements performed on the exact same samples. Recent developments also include the use of μ-X-Ray Fluorescence (XRF) analyses of individual mineral grains and matrix materials in thin-sections of rocks on a Scanning Electron Microscope (SEM) to better identify individual clay minerals. Although our integrated QM method provides great added value in quantitative mineralogy investigations in that it provides key elements to check internal consistency, hence reliability, it remains a time-consuming labor-intensive method.

Mineralogical mapping of rock samples by automated Energy-Dispersive X-ray Spectroscopy (EDS) in (SEM) has been widely employed over the last decades. EDS-based approaches to mineralogical identification and quantification in unconventional reservoir rocks were however limited because the fine-grain size and mineralogical heterogeneity of shale rocks commonly results in mixed X-ray spectra within the electron-beam interaction volumes. Recent developments of a new Spectral Analysis Engines (SAE) now allow the automatic identification and 2D-quantification of mineral grains and organic components within each electron-beam interaction volume.

In the present study, the quantitative evaluation of minerals in a series of core samples from a shale formation was assessed by SEM mineralogical mapping of thin sections using the new SAE. Results were compared with quantitative data obtained on crushed plugs using the QM method. Although the studied surfaces may not be perfectly representative of the crushed plugs due to small-scale heterogeneity, a close match (to +/- 5 mass%) was obtained for more than 60% of the samples for both the total clay minerals and total carbonates contents. The main discrepancies occur when the clay minerals content is higher than 25 mass%. The observed overestimation of clay minerals content by mineralogical mapping may be related to the presence
of non-quantified porosity within the clayey materials (porosity below the resolution of the method). It may be possible to address this systematic overestimation by high-resolution SEM imaging and quantification of nano-/micro-porosity within the clayey materials.

Further tests are ongoing to evaluate the reliability of a portable well-site mineralogical mapping equipment using the same approach and SAE. If found reliable, the sub-continuous analysis of freshly recovered cuttings and/or cores using this well-site technology may allow the interpretation and calibration of wireline logs in a much more timely manner than ever before.
IMPACT-INDUCED STRUCTURAL CHANGES DIFFER BETWEEN TWO SMECTITE SPECIES, NONTRONITE (NAU-1) AND SAPONITE (SAPCA-2): POSSIBLE IMPLICATIONS FOR THE REMOTE SENSING OF THE MARTIAN SURFACE

Lonia R. Friedlander*1, Timothy D. Glotch1, David L. Bish2, Thomas G. Sharp3, M. Darby Dyar4, and Joseph R. Michalski5

1Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100, USA: lonia.friedlander@stonybrook.edu
2Department of Geological Sciences, Indiana University, Bloomington, IN 47405-1405, USA; 3School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-1404, USA; 4Department of Astronomy, Mount Holyoke College, South Hadley, MA 01075, USA; 5Planetary Science Institute, London, W2 5PJ, United Kingdom.

Introduction: Clay minerals have been identified in several locations on Mars by visible-near infrared reflectance (VNIR) spectroscopy1–7 and by Curiosity in Gale Crater8,9. Many of these identifications are in old, heavily bombarded terrains10–15, suggesting that phyllosilicate minerals on Mars may have experienced shock metamorphism, which alters mineral spectra16–20. In addition, recent work has identified shock-metamorphosed nontronite at Mawrth Vallis21, and thermally altered nontronite has been identified at Nili Fossae22. Thus, impact processes are important for the remote sensing of clay minerals on the martian surface.

In previous work, this group and others have shown that the characteristic mid-IR (MIR) spectral features of phyllosilicates are more sensitive to impact-induced structural change than VNIR features23–25. This result partially explains the apparent disconnect between thermal-infrared and VNIR spectral results from the remote sensing of Mars6,23,25. However, up to now, this has been demonstrated only for nontronite25, and comparisons among different clay mineral species shocked over similar pressure ranges have not yet been made. In addition, variable responses by different minerals to shock pressure might significantly alter their combined spectral signal. Thus, it is important to characterize the effects of shock metamorphism on many mineral species. Because smectites have previously been identified as common phyllosilicates on the martian surface4,13,26–28, we compare the effects of shock on two smectite group clay minerals, saponite (Mg-rich) and nontronite (Fe-rich).

Methods: We conducted our experiments on the Clay Minerals Society Source Clays saponite (SapCa-2) and nontronite (NAu-1). Chemical compositions for both materials have been previously reported in29. The clays were ground, sieved, and separated by centrifugation to remove contaminants commonly found in the >2 μm size fraction29–31. The samples were then washed in acetic acid to remove carbonate contaminants. The clean, < 2 μm size samples were sent to the Flate Plate Accelerator at NASA’s Johnson Space Center where six shock-reverberation experiments were performed on each sample, producing impacts at approximately 10, 20, 25, 30, 35 and 40 GPa pressure. A suite of spectral and structural analyses was then performed on the shocked samples: VNIR reflectance, MIR attenuated total reflectance, MIR emissivity, Mössbauer and Raman spectroscopy, in addition to X-ray diffractometry (XRD), and transmission electron microscopy.
Results and Discussion: Unlike nontronite, saponite retains its layer structure even after impacts up to ~40 GPa (Figure 1). It is possible that the preservation of saponite emissivity spectra after laboratory impacts, relative to nontronite (Figure 2) may result from the resistance of the saponite structure to impact effects and/or to differences in thermal stability between the two minerals. Our samples were also unvented, which has been shown to affect clay mineral devolatilization. Nonetheless, the spectral differences between the two samples have important implications for the use of remote sensing data in detailed mineral identifications.

Figure 4. XRD patterns for the 02l (A) and 001 (B) regions of saponite, compared with the 001 region of nontronite (C). The saponite 02l band was retained up to 39.8 GPa, indicating that saponite’s layer structure is preserved after impacts up to ~40 GPa (A). The 001 peak was also retained (pre-impact has been rescaled for clarity, higher intensity is due to a greater amount of sample), and observed changes are most likely related to differences in relative humidity during measurement (B). These results contrast with those for nontronite’s 001 peak (C), which shifted slightly to higher 20 and was nearly undetectable after impacts of 25 GPa and higher. The nontronite results indicate progressive amorphization and increasing structural disorder with higher-pressure impacts.

Figure 2. MIR emission spectra before and after laboratory impacts at ~40 GPa for nontronite (A) and saponite (B). The nontronite sample lost nearly all characteristic features after impacts at ~40 GPa, except a weaker, broader Si-O fundamental stretch (~1000 cm⁻¹). Nontronite’s characteristic Fe-O-Si deformation (~500 cm⁻¹) and Si-O bending (~420 cm⁻¹) features were completely eliminated. In contrast, saponite retained its characteristic emissivity features, even after impacts up to ~40 GPa.

A PHOSPHATE ADSORBENT FROM HETEROCOAGULATION OF MONTMORILLONITE AND LAYERED DOUBLE HYDROXIDE

Fangqun Gan¹,², Xiaoshuai Hang³, Hongting Zhao⁴, Jianmin Zhou⁵, and Yijie Ma⁵

¹Department of City Science, The City Vocational College of Jiangsu (Jiangsu Open University), Nanjing 210017, China; gfqjy@sina.com.
²Department of Soil and Crop Sciences (Texas AgriLife), Texas A&M University, College Station, TX 77843-2474, USA;
³Nanjing Institute of Environmental Science, MEP of China, Nanjing 210042, China;
⁴College of Materials & Environmental Engineering (Institute of Environmental Materials & Applications), Hangzhou Dianzi University, Hangzhou 310018, China;
⁵State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China.

Excess phosphorus (P) discharged from waste water or agriculture applications to lakes, lagoons, rivers, and seas result in eutrophication of the water bodies. Removing phosphate from waste water by adsorption has emerged as one of the most promising methods in preventing eutrophication. Researchers have focused on development of advanced adsorbents, which are often too expensive to be used in practice. The broad availability, great specific surface area, and charged layer structures of natural clay minerals, such as smectites, have enabled their many adsorption applications. The common clay minerals, however, are negatively charged and, as have been demonstrated in many research work and practical uses, are effective in cation removal. They do not have high adsorption capacity for phosphate anions. Synthetic layer double hydroxides (LDHs) are positively charged and can be used to adsorb anionic species. Due to their small particle size and swelling colloidal properties, it is difficult to apply LDHs as flow-through filtration media. It is desirable to enhance the stability of LDHs in water treatment without losing their adsorption capacity for phosphate. The objective of this study was to seek a low-cost and practical solution in using LDHs for phosphate remediation. Heterocoagulation of montmorillonite and LDHs was used to form composites capable of adsorbing both cations and anions. The potential use of resulting composites in removing P was assessed.

The Mg/Al layered double hydroxide (LDH) solid was prepared according to the method of Gan et al (2011). The montmorilloinute (Mt) clay mined from the Tuokexun County (China) and < 2 μm fraction of Mt was separated from the clay. Ten grams of extracted montmorillonite were dispersed in 500 mL water first. Different amounts of LDH were added to the dispersions to obtain LDH-montmorillonite (LDH-Mt) composites. The mineralogy and surface properties of composites were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDS). Phosphate (P) removal from aqueous solution was evaluated by using batch adsorption method. Phosphate adsorption kinetics and the effect of pH on the adsorption were investigated.

The XRD analysis (Fig. 1) suggested that the stability and abundance of LDH in the composites were consistent with what have been expected. The phosphate adsorption isotherms (Fig. 2) could be fitted with Freundlich and Langmuir equations. The maximum adsorption capacity of LDH-Mt for P increased with LDH loadings, and the removal was favorable in acidic
media. Kinetic data revealed that 90% of adsorption onto LDH-Mt was completed within 1 h and the adsorption process was explained with pseudo-second-order model.

The results demonstrated that heterocoagulation of montmorillonite and layered double hydroxide could preserve the adsorption capacity of LDH for phosphate and enhance the stability of both clay minerals. High cation removal capability from the composites could be expected due to the presence of negatively charged montmorillonite, which will be verified in future work.

Fig. 1. XRD patterns of LDH, natural montmorillonite (Mt) and LDH heterocoagulated montmorillonites (LDH-Mt1, LDH-Mt2, LDH-Mt3).

Fig. 2. Adsorption isotherms of LDH, natural montmorillonite and LDH heterocoagulated montmorillonites plotted as equilibrium adsorbed amount ($q$) vs. equilibrium aqueous phase concentration ($C_e$) at 25 °C.

ASSESSING AND MODIFYING CHINA BENTONITES FOR AFLATOXIN DETOXIFICATION

Fangqun Gan*1,2, Yijie Ma3, Qiaoyun Huang4, and Youjun Deng1

1Department of Soil and Crop Sciences, Texas A&M University, College Station, TX 77843, USA; gfqy@sina.com.
2Department of City Science, The City Vocational College of Jiangsu (Jiangsu Open University), Nanjing 210017, China;
3Institute of Soil Science, Chinese Science of Academy, Nanjing, Jiangsu Province, 210008 China;
4Faculty of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China.

Using bentonites to bind aflatoxins, a group of carcinogenic mycotoxins produced by fungi Aspergillus flavus and A. parasiticus, is a promising practical solution in dealing with the mycotoxins worldwide. Numerous animal feed and human diet trials in the last three decades have illustrated that natural clays, particularly smectite-rich bentonites, can reduce the toxicity of the mycotoxins. Aflatoxicosis in animals and human is a severe problem in China due to frequent occurrence of the mycotoxins caused by high humidity, high temperature, and insect stress on crops. China is also one of the largest bentonite producers with an annual production of more than two million tonnes. The general goal of our study is to assess and to improve the effectiveness of Chinese bentonites in aflatoxin detoxification. Due to the large variations in genesis, parent rock types, sedimentation and diagenetic environments, it is unlikely that all of the natural Chinese bentonites can be used as aflatoxin binders. Recent spectroscopic studies and molecular dynamic calculation indicated that only certain smectites could irreversibly adsorb the mycotoxins into the interlayer space of the minerals. The selectivity and affinity of the smectites for aflatoxins are affected by the layer charge density and type of exchange cations. These factors determined the size and polarity of the adsorbing domains and therefore the fitness and affinity of aflatoxins on the surfaces. The specific objectives of this study were to 1) correlate aflatoxin adsorption capacities of natural Chinese bentonites with their mineralogy properties, 2) to modify low-aflatoxin-affinity bentonites to improve their binding efficiency; and 3) to determine the thermodynamic constants in the aflatoxin-smectite interactions before and after the modifications.

Thirteen bentonites from eight provinces or autonomous region (Henan, Jiangsu, Jilin, Liaoning, Shanxi, Tianjin, Xinjiang, and Zhejiang) in China were collected. They represent the major types of bentonites on the market in China. Preliminary mineral characterization indicated that montmorillonite was the dominant mineral in all of the 13 bentonites. Accessory minerals, namely opal-cristobalite, clinoptilolite, gypsum, feldspars, calcite, dolomite, and quartz, were found in different abundances.

Single point aflatoxin B1 adsorption test showed a 6-fold difference among the 13 natural bentonites. The adsorption appeared to be not only affected by smectite content, but also by exchange cations. The Na-bentonite from Xinjiang had the lowest adsorption of 0.05 mol kg⁻¹, and the Na-bentonite from Jilin had the highest adsorption of 0.294 mol kg⁻¹. The Ca-bentonites
had adsorption varied from 0.07 mol kg\(^{-1}\) to 0.18 mol kg\(^{-1}\). These values are lower than the maximum adsorption capacity of 0.7 mol kg\(^{-1}\) reported for a pure Ba-smectite. The test did not show a higher aflatoxin adsorption by the Ca-bentonites than by Na-bentonites as expected based on previous study. These discrepancies are likely caused by the layer charge density of smectites and the accessory minerals in the bentonites, which will be verified in the ongoing and future experiments. Smectites will be concentrated from these bentonites by fractionation and be modified with divalent cations to maximize their adsorption capacity. Heat generated during aflatoxin adsorption on the clays will be measured and used to calculate the enthalpy, an indicator of bonding strength, of the aflatoxin-smectite interactions. It is expected stronger bonding between aflatoxin and the smectite when the clay mineral is saturated with divalent cations than those saturated with monovalent cations. The preliminary results suggested that certain bentonites in China can be used as aflatoxin binders.
NEAREST NEIGHBOR DISTRIBUTIONS IN SMECTITES

Will P. Gates¹,²*, John D. Cashion³

¹ Senior Research Fellow, Department of Civil Engineering, Monash University, Clayton, Vic 3800 Australia will.gates@monash.edu
² SmecTech Research Consulting, 24 Chapel Road, Moorabbin, Vic 3189, gateswp@smectech.com.au
³ Adjunct Associate Professor, School of Physics, Monash University, Clayton Vic 3800 Australia

Mössbauer spectroscopy has had variable success as a method to determine the site occupancies of the octahedral sheet of smectites. While the Mössbauer effect ‘sees’ the influence of the surrounding chemical environment of 57Fe, satisfactory analysis of the signal has proven difficult. Analysis of Mössbauer spectra of clay minerals is complicated by overlapping lines from different components and also by the fact that a particular configuration, e.g. octahedral Fe(III), can have more than one set of quadrupole splitting parameters due to different nearest neighbour arrangements in the octahedral sheet. In the case of cis-vacant ferruginous smectites, the doublet with the largest splitting has been shown recently to be due to a cis-Fe(III) ion with at least one Mg ion as an octahedral neighbour. For trans-vacant nontronites, however, substitutions of Mg in the octahedral sheet are negligible and another explanation for the occurrence of two doublets in nontronites is needed. Within the dioctahedral sheet of a smectite structure each octahedral Fe atom has three nearest octahedral cation neighbours (generally a mixture of Fe, Al or Mg) and also eight nearest tetrahedral cation neighbours (mainly Si, but with small amounts of Al or Fe as well). Recent results using multinomial distribution calculations indicate that substitutions of Al and Fe in tetrahedral sites contribute non-randomly to both the inner and outer doublets in nontronites.
TREADING THE APPLIED–BASIC RESEARCH ROAD: TWO ROUTES TO ENHANCED HYDRAULIC BARRIER PERFORMANCE OF BENTONITES

Will P. Gates¹²*

¹SmecTech Research Consulting, Moorabbin Victoria, Australia, gateswp@smectech.com.au;
²Department of Civil Engineering & Centre for Green Chemistry, Monash University, Clayton, Victoria Australia.

Australian energy exploration industries produced in excess of 15,000 ML of coal seam gas (CSG) waters during exploration in 2013, largely in Queensland. Due to the often high saline/saline-sodic chemistries of CSG waters, above ground temporary containment poses threats to ground and surface waters. Regulatory authorities increasingly require impoundments to be lined with composite liner systems comprised of a geomembrane primary barrier and one or more low-permeability mineral layers to minimise migration of brines into surrounding surface and ground waters. The mineral liners are expected to maintain a saturated hydraulic conductivity, k, lower than the design value (typically k of 1x10⁻¹⁰ m/s) for the projected lifespan of the containment facility. Note that a k value of 1x10⁻¹⁰ m/s is equivalent to advective transport of ~3 mm per year. Liner lifetime expectancies are unknown in these environments and estimates are usually unsubstantiated by rigorous investigation, thus most containment designs should incorporate leachate collection. An increased use of geosynthetic clay liners (GCLs) for containment of CSG process waters throughout CSG localities in Australia is due to their ready availability, technical equivalence to traditional compacted clayey liners and ease of deployment. GCLs are manufactured in ~8x30 m rolls comprised of ~5-10 mm of sodium bentonite contained between two synthetic geotextiles (usually one woven and one non-woven) held together by needle-punching or stitch bonding. Bentonite is processed (e.g., sodium beneficiated) to impart favorable sealing characteristics: during hydration the geotextiles provide internal confinement for the bentonite to swell against, thereby closing the active advective pore space. However, the general salinity of CSG waters and specific requirements for GCLs used in CSG applications (low confining stress, high hydraulic head) necessitate GCLs functioning under geochemical conditions that are generally adverse to containment. Interaction of GCLs with CSG waters having elevated salinity (generally I>0.3 M) has potential for hydraulic incompatibility resulting in increased hydraulic conductivity of the liner (to k>1x10⁻¹⁰ m/s) and therefore loss of barrier integrity.

Two different approaches to develop modified bentonite able to withstand high saline or saline-sodic conditions typical of CSG applications will be discussed. The first approach was publically funded and used ‘green chemistry’ principals to synthesize modifying agents to impart a saline-stable sodium smectite. Glycerol carbonate (GC), synthesized from glycerol and urea, was found to provide significant protection of sodium smectite from chemical desiccation induced by up to 2 M CaCl₂. Further work showed that derivatives of GC could be similarly synthesized to serve as monomer building blocks of in situ polymerization within smectite interlayer space. The chemical durability of these nanocomposites are promising and further funding for scale-up tests with sodium bentonite are being sought. The second approach to produce a saline-stable bentonite product for use in a variety of civil engineering applications was solely industry funded. In this context, a research, to development, to market scheme of
three years was accomplished. The product has outstanding hydraulic barrier performance to saline waters, ranging from seawater (~0.7 M) to 20% (I≈2.7 M) sodic brines. Saturated hydraulic conductivity of the product in mock GCLs when exposed to 20% sodic brines were \( k < 1 \times 10^{-11} \) m/s whether pre-hydrated with water or not and were well below comparable values for traditional GCLs (\( k > 1 \times 10^{-10} \) m/s). The product is currently undergoing rigorous testing by industry partners prior to full release into the Australian market.

The author thanks Arumpo Bentonite, Pty. Ltd., for funding of the “applied” portion of this research through ongoing consultancy contracts and the Australian Commonwealth for funding the “basic” portion through the Australian Research Council’s Discovery Projects Scheme (DP1095129). The author is also indebted to many colleagues from both academia and industry that have provided wisdom, support and advice during the course of these two projects.
A NOVEL 2-D MATERIAL FOR HIGH EFFICIENCY, REDUCED FOULING, REVERSE OSMOSIS DESALINATION COMPOSITE MEMBRANES

Marcus Goss*1, Gary W. Beall1,2

1 Department of Chemistry and Biochemistry, Texas State University- San Marcos, 601 University Dr., San Marcos, TX 78666, USA: mg75@txstate.edu
2 Physics Department, Faculty of Science, King Abdulaziz University, Jeddah, 21589, Saudi Arabia

The availability of freshwater in many areas of the world is insufficient to sustain human populations. The technology of converting seawater or other saline water supplies to freshwater is desalination. Methods for the production of desalinated water are often prohibitively expensive. Improvements in membrane science have resulted in a shift from expensive thermal processes to more economical solutions such as reverse osmosis (RO). Composite polymeric membrane technology is a mature science and recent work on other materials show promise. Current, commercial, RO membranes composed of thick layers of polymeric materials are less efficient than thin engineered materials like porous graphene or ceramic membranes. Even so, fabrication limitations and high processing costs make these new materials less attractive. A novel 2-dimensional crystalline material composed of cyanide-bridged metal nanosheets with a square planar framework has been developed. The advantage with this material is its ease of synthesis and absence of atomic scale manipulation owing to a low cost fabrication. Thin crystal growth followed by an effective exfoliation process into atomistically thin, 2-D sheets allows for the formation of a large area, pristine matrix lining onto a robust substructure capable of ion selectivity and efficient desalination while also being resistant to fouling by scale or biofilms.

Presented here is a series of dynamic molecular simulations that provide an understanding of the purification mechanism and performance estimates of the efficacy of this novel material for use as a desalination RO membrane. These computer models were constructed using typical force field models and dynamic iterative processes to assess the system parameters and physical limitations. Energy profiles for the passage of water and ionic species through the porous areas of these nanosheets has been formed and reported.

The membrane is constructed of crystalline sheets of di-aquairon(II)tetracyanonickelate hexahydrate or other combinations of transition metals with transition metal salts. Characteristics of the square planar sheets are tailored by choice of these metals. The hydrophilicity of the sheet and the size of the pore areas are affected as well as the affinity of substances to the identity of the metal. Other physical characteristics of the membrane including the adherence to the polymeric substrate can be controlled by the composition of the sheet. Scanning electron microscopy and x-ray diffraction were utilized to evaluate the crystal formation and characterize structure and verification of the formation of square planar sheets. Crystal growth of the material unto a substrate polymer able to add structural strength is studied as well as discussion of limitations and techniques to yield continuous crystalline sheets in two dimensions capable of practical application.
THE DEVELOPMENT OF NOVEL ANTIBACTERIAL POLYMER-CLAY COMPOSITE SYSTEMS

Ashley R Hamilton*, Matthew Roberts, Gillian A Hutcheon, and Elsie E Gaskell

School of Pharmacy and Biomolecular Sciences, Liverpool John Moores University, Liverpool, L3 3AF, UK. a.r.hamilton@2011.ljmu.ac.uk

Much research activity has focused on investigating the interaction between organic molecules and clay mineral surfaces. A number of research teams have reported the adsorption of antimicrobial agents such as clindamycin, tetracyclines, and quinolones (Hamilton et al., 2014) amongst others. In the UK a new antimicrobial stewardship programme has called for a new approach to the management of infection, including the development of novel drugs and technologies (Davies, 2011). This call to action presents a unique and topical opportunity to develop new antimicrobial agents utilising clay minerals as key materials.

In this work the antibacterial molecules ciprofloxacin (CIP), tetracycline (TC), and doxycycline (DC) were adsorbed onto a wide range of clays; kaolin (KN), refined montmorillonite (rMMT), an acid activated montmorillonite (MMTK10), Laponite® RD (LRD), and Laponite® XL21 (LXL21). The adsorption kinetics and isotherms were determined, the mechanism of adsorption was confirmed with XRD and FTIR, and the antibacterial properties were demonstrated with zone of inhibition testing against Propionibacterium acnes, Staphylococcus epidermidis, and Pseudomonas aeruginosa.

KN was shown to be the poorest adsorber of drug molecules due to its minimal surface area and cation exchange capacity (CEC), whereas rMMT, LRD and LXL21 adsorbed large amounts of drug onto their surfaces. A dispersion pH of 7.4 for CIP, 5.0 for TC, and 5.5 for DC was shown to enhance drug molecule adsorption onto the clay mineral surface compared to other pH values tested. At these pH values the drugs are predominantly in their zwitterionic state, which possibly allows for optimal orientation at the clay mineral surface. Adsorption isotherms fitted the Langmuir model well and the kinetics of adsorption followed the pseudo second order. The effect of the clay-drug composites on bacterial growth positively correlated with drug-load and drug-type, with CIP-containing composites performing much better against P. aeruginosa.

Once the optimal conditions had been determined formulation of drug-containing polymer-clay composites was achieved using sodium alginate. By using oven-drying and freeze-drying methods it was possible to obtain films and wafers, respectively (figure 1). These composites were analysed for structural and visual properties and the nature of the composite was determined through XRD, FTIR and scanning electron microscopy.

The ratio of phyllosilicate to polymer appeared to dictate the physical properties of the composites, in terms of thickness and flexibility. Composites that contained low amounts of alginate did not form intact films. The individual components of composites containing the non-swelling clays KN and MMTK10 appeared to separate from the alginate when cast. The films had two distinctly different surfaces and clay minerals clearly separated from the alginate in the wafers, indicating poor interaction between these clay minerals and the alginate. The same effect
was not seen for composites made with swelling clays (rMMT, LRD and LXL21), meaning their colloidal properties were more favourable to composite formation with alginate.

![Image](a) ![Image](b)

**Fig 1.** rMMT-Alginate composites containing 37.5 mg/g CIP formed through (a) oven-drying and (b) freeze-drying.

CIP was successfully incorporated into the composites at various concentrations. However, it was not possible to obtain structurally sound wafers and films from composites containing high concentrations of CIP (≥100 mg/g). High drug loading onto swelling clay minerals can result in their flocculation, which may explain why it was not possible to obtain usable materials after drying. Regardless, this work proves that a composite system containing clay minerals and alginate, alongside an antibacterial drug molecule, can be obtained.

The creation of both films and wafers means it could be possible for these materials to be used to treat infected wounds. The possible behaviour of these composites in a wound environment was determined on weak gels formed from gelatine held in horizontal and vertical orientations. The behaviour of the composites on these gelatine surfaces could be related to their components and how they interacted.

This work shows promise of developing candidate dressings for the treatment of infected wounds, which are often treated with systemic antibacterial agents. Such therapies can cause adverse effects for the patient and can contribute to the development of drug resistant bacteria. Being able to deliver antibacterial molecules directly to the site of infection, whilst also supporting the wound-healing process, is very attractive not just for patients but also for the management of antibacterial resistance (Hamilton et al., 2014).

**References**


TEACHING CLAY MINERALOGY IN AN UNDERGRADUATE GEOCHEMISTRY CLASS

Pat Harris*

Department of Geography and Geology, Sam Houston State University, Huntsville, TX 77341-2148, USA: pat-harris@shsu.edu

Students in upper-level geology courses at Sam Houston State University have difficulty retaining knowledge of key concepts from one exam to the next. I introduced a project-based learning approach to an undergraduate geochemistry class to see if students developed a deeper understanding/better retention of the material. Students were organized into groups of four and each group was given a unique mixture of two clay mineral standards to identify. Each group prepared two oriented samples for X-ray diffraction: one sample was saturated with potassium and placed on a vycor slide for heat treatment; the other sample was saturated with magnesium. Each group wrote a report describing the methods and steps taken to identify the unknown clay standard mixtures. The students were given X-ray diffraction patterns of clay samples taken from various geologic environments to interpret as part of the final exam. Every student in the class was able to correctly identify the peaks from at least one of the clay minerals for each X-ray pattern. The answers given on the final exam to other questions related to clay mineralogy suggests that the students have a deeper understanding of clay mineralogy as a result of the project-based learning approach.
CHALLENGES FOR FORCE FIELDS OF CLAY MINERALS AND NEW KAOLINITE PARAMETERS

Hendrik Heinz1*, Valentina Erastova2, and H. Christopher Greenwell2

1 Department of Polymer Engineering, University of Akron, Akron, Ohio 44325, US *
hendrik.heinz@uakron.edu
2 Department of Earth Sciences and Department of Chemistry, Durham University, Durham, DH1 3LE, UK

The complexity of molecular recognition and assembly of biotic and abiotic clay interfaces on a scale of 1 to 1000 nm can be understood more effectively using simulation tools along with laboratory instrumentation. Current capabilities and limitations of atomistic force fields will be discussed and a strategy explained to obtain dependable parameters for inorganic compounds, including clay minerals, that has been developed and tested over the past decade. Parameters have been developed for layered silicates as well as other silicates, aluminates, oxides, sulfates, and apatites, summarized in what we call the INTERFACE force field. The INTERFACE force field operates as an extension of common harmonic force fields (PCFF, COMPASS, CHARMM, AMBER, GROMACS, and OPLS-AA) by employing the same functional form and combination rules to enable simulations of inorganic−organic and inorganic−biomolecular interfaces. The parameterization builds on an in-depth understanding of physical−chemical properties on the atomic scale to assign each parameter, especially atomic charges and van der Waals constants, as well as on the validation of macroscale physical−chemical properties for each compound in comparison to measurements. The approach eliminates large discrepancies between computed and measured bulk and surface properties of up to two orders of magnitude using other parameterization protocols and increases the transferability of the parameters. As a result, a wide range of properties can be computed in quantitative agreement with experiment, including densities, surface energies, solid−water interface tensions, anisotropies of interfacial energies of different crystal facets, adsorption energies of biomolecules, thermal and mechanical properties. In particular, new parameters for kaolinite and their validation will be introduced, extending the series of mica, montmorillonite, and pyrophyllite in the INTERFACE force field.

Specific challenges for clay minerals will also be addressed. (1) A key property of all force fields are atomic charges that represent quantitatively the balance between ionic and covalent bonding, and relate to chemical reactivity. Accurate atomic charges of clay minerals have been described previously and included in the INTERFACE force field (+1.1±0.1e on tetrahedral Si, +1.45±0.1e on octahedral Al). However, the widely used CLAYFF employs significantly overestimated charges (+2.1e for tetrahedral Si) and, as a consequence, computed surface tensions of clay minerals and adsorption energies of organic molecules are up to 100% higher than measured in experiment. (2) The accuracy of water models has major impact on simulations of clay-water interfaces. Several water models (SPC, TIP3P, TIP4P) underestimate the dipole moment of liquid water by circa 30%, while TIP5P water reproduces the dipole moment exactly and is most suited for calculations. The use of SPC, TIP3P, or TIP4P water models therefore underestimates water-clay dipole-dipole attractions and and leads to higher computed contact angles on clay surfaces compared to experiment. Both INTERFACE or CLAYFF exhibit this trend, whereby CLAYFF performs better due to overestimated atomic charges for the clay. Best results are
possible using INTERFACE-CHARMM or INTERFACE-PCFF with TIP5P water, and any organic molecules, biopolymers, or ions. A “patch”-like fix to reproduce computed contact angles with SPC water using INTERFACE is possible by adjustment of Lennard-Jones parameters of the clay surface atoms (Si and O) towards higher attraction. However, improvements to the standard water models and associated organic parameters in the long term will be chemically more realistic than aiming at a cancellation of errors, i.e., “falsify” perfectly suitable clay parameters to complement “deficient” water parameters for the best reproduction of water interfaces, and accept overestimates in adsorption of everything else including the cohesive energy of the clay itself. (3) Another challenge in force field development is the act of balancing covalent and ionic contributions to bonding across a smoothly variable scale in clay minerals and LDHs. Current force fields rely on two options: (a) include only nonbonded interactions (CLAYFF and INTERFACE) or (b) include both nonbonded and bonded terms (INTERFACE). The decision in INTERFACE is made on the basis of atomic charges and pairwise atomic distances from X-ray data. (a) If the contribution by covalent bonding is 50% or more, bonded terms are added (harmonic bond stretching and angle bending) and, by convention, added exclusions of nonbond interactions between 1,2; 1,3; 1,4 bonded atoms tremendously change the interpretation of Lennard-Jones parameters. Moreover, the addition of bonded terms in full strength is not realistic so that elastic moduli can be overestimated (INTERFACE). (b) Without bonded terms, covalent contributions to cohesion are fully dismissed and cohesion is typically too weak to generate a structurally stable model. Therefore, the strength of atomic charges and of LJ interactions is often artificially increased and results in unrealistic interfacial and reactive properties (CLAYFF).

To overcome such remaining limitations, we envision a new generation of models that allow partial covalent bonding and abandon the limits imposed by exclusion conventions of nonbond interactions between neighboring bonded atoms. Opportunities and plans will be presented.
CHARACTERIZATION OF HUMIC ACID DERIVED FUNCTIONALIZED GRAPHENE AND MECHANICAL EVALUATION OF ITS POLYURETHANE BASED COMPOSITES

Brandon G. Henderson¹*, Gary W. Beall¹

¹Materials Science, Engineering, and Commercialization Program, College of Science and Engineering, Texas State University, San Marcos, TX 78666-4684, USA: bh1352@txstate.edu

Leonardite is a humic substance composed of three fractions: fulvic acid, humic acid, and humin. The humic acid fraction is characterized by its solubility in basic aqueous solutions and of intermediate molecular weight between that of fulvic acid (low MW fraction) and humin (high MW fraction). This combination of solubility and intermediate particle size led to studies evaluating the properties of humic acid and its derivatives, specifically, those of reduced humic acid. Therefore, humic acid has been isolated from leonardite and chemically reduced. The resulting product has recently become commercially available under the trade name Graphenol®. The proposed structure of Graphenol® is that of functionalized graphene sheets with hydroxyl groups located at the edges. Initial characterization of Graphenol® has been performed, including atomic force and scanning electron microscopy. An investigation of Graphenol® as mechanically reinforcing nanofiller has been performed in a water soluble polyurethane matrix. Mechanical properties of the resulting composite were evaluated utilizing dynamic mechanical analysis. The results of these investigations will be outlined and discussed.
Uranium series methods are very important for dating the geological events of the last 0.5 million years. The basic assumption of the $^{230}\text{Th}/^{234}\text{U}$ dating method is that the material being dated was free of Th and contained only U at the time of its deposition. This is possible because uranium is co-precipitated with CaCO$_3$ from waters essentially free of Th. Thus, the activity ratio at the time of deposition for the carbonates should be equal to zero. Subsequently, $^{230}\text{Th}$ is produced from the decay of uranium and its amount should grow with time. Therefore, the amount of $^{230}\text{Th}$ can be used as a direct measure of the age of the carbonate. This approach is only valid for clean carbonates. Unfortunately, clean carbonates are rather rare in Quaternary deposits.

Uranium and Thorium isotopes are commonly incorporated by adsorption in many materials like clay minerals, ferro-hydroxides, etc. Such materials are likely to be incorporated in Quaternary carbonates. Those carbonates are called dirty carbonates. The major problem related to dirty carbonates dating is that contaminants like clays contribute $^{234}\text{U}$, $^{238}\text{U}$, $^{230}\text{Th}$, $^{232}\text{Th}$ isotopes to the leachate during the acid treatment. Therefore, measured $^{234}\text{U}$, $^{238}\text{U}$, $^{230}\text{Th}$, activities are the sum of activities from calcite and from contaminants source. Then some correction methods are introduced to subtract from the total measured activities of $^{230}\text{Th}$, $^{234}\text{U}$ and $^{238}\text{U}$, those portions, which have originated in detritus. Isotope $^{232}\text{Th}$ is not a member of $^{238}\text{U}$ decay series, and it could be used as a marker of non-radiogenic (for a given system) source of Thorium and Uranium. The first U-series dating correction method B0 developed (Kaufman and Broecker, 1965) used $^{232}\text{Th}$ isotope as a proxy estimator for the amount of non-radiogenic (detrital) $^{230}\text{Th}$. The B0 method has two weaknesses: it only corrects for the $^{230}\text{Th}$ contamination, and it is necessary to know the $^{230}\text{Th}/^{232}\text{Th}$ ratio in the detritus. Since it is usually impossible to know precisely the $^{230}\text{Th}/^{232}\text{Th}$ ratio for the carbonate contaminants, the application of the B0 method is always based on a certain assumption. An alternative to the B0 approach is based on using isochrones with the assumption that sediments consist of two components: (1) chemically precipitated calcite free of Th at the time of deposition; and (2) detritus, which are not inert during acid treatment, releasing some non-radiogenic U and Th into the leachate. The classical method of isochrones is based on the analyses of several coeval samples. Those samples should be of the same age and should contain different amounts of contaminant.

Therefore classical isochrones model can’t be used for homogeneous sediments. It is possible to obtain a few samples from a homogeneous layer with different proportions of uranium and thorium from calcite and from contaminant by the method of full leaching of calcite. In this case, several samples are dissolved using different acids. Experimental results
show that it is possible to estimate isochrones for the samples analyzed by the full leaching method. But the estimated isochrone ages are still incorrect despite well-defined isochrones. This means that the assumptions of the method are not fully satisfied. In these experiments, we do know that the assumption of a close system is satisfied and that the samples are coeval. Hence, the assumption that the activity ratios leached from the detritus are unvarying in each sub-sample must be wrong. As a result of this experiment a new tri-component model was proposed. In this model 3 fractions are considered: U and Th from calcite; easily leachable U and Th from clays; and poorly soluble U and Th from clays. During full leaching process all U and Th from calcite and easily leached detritus can be leached to the solution, only the amount of last fraction depends on the concentration of acid used to dissolve the sample (stronger acid dissolves more of the detritus). This model explains why age estimates by the isochrone method are not correct. It is not the calcite age but the “mixed-age” of the calcite and the easily leached detritus fraction containing non radiogenic for the given system thorium and uranium. The tri-component model explains also why the classical isochrones method does work correctly for non-homogeneous samples. In that case, uranium and thorium content from the easily leached fraction is also different so the isochrones age is estimated only for calcite fraction.

In order to better understand the observed physico-chemical behavior of U and Th in clay contaminants we used molecular dynamics (MD) computer simulations. As the first step, MD simulation is applied to study the mechanism of U and Th absorption on a clay surface. Kaolinite was selected as a model surface because it is a 1:1 clay which have two different surfaces: siloxane silicon tetrahedral and gibbsite type aluminum octahedral. In addition, kaolinite is the simplest clay without any isomorphic substitutions in both layers. A model of kaolinite simulation cell was based on the structure determined by Bish (1993). The 4×4×2 crystallographic was put in contact with aqueous solution containing 1800 H2O molecules, 8 UO2^{2+} and 16 Cl− ions. The gibbsite surface of kaolinite has been kept fully protonated to simulate strong acidic conditions. All interatomic interactions in the model were calculated using the CLAYFF force field (Cygan et al., 2004). After an initial equilibration of the system at constant NPT conditions (T = 300 K, P = 0.1 MPa), the equilibrium MD simulation run was performed for 500 picoseconds in the NVT statistical ensemble. The structural and dynamics results show that under ambient conditions there is no UO2^{2+} absorption on the protonated gibbsite surface, but significant inner-sphere and outer-sphere adsorption of uranyl is observed on the siloxane surface of kaolinite. This initial result supports the hypothesis that the easily soluble component of the contaminant is absorbed on the gibbsite surface.
SIZE AND SURFACE CHARGE DEPENDENT BLUE GREEN ALGAE FLOCCULATION OF ANIONIC CLAYS

In-Taek Hong*1, Tae-Hyun Kim1, and Jae-Min Oh1

1Department of Chemistry and Medical Chemistry, College of Science and Technology, Yonsei University, Wonju, Gangwondo, 220-710, Korea :it_hong@yonsei.ac.kr

Sudden bloom of blue green algae, also known as harmful algal blooms (HABs) in water, has seriously affected water quality, local economies, environment and human health. It is known that *Microcystis aeruginosa* (*M. aeruginosa*) is one of the major biological species responsible for HABs. We investigated *M. aeruginosa* flocculation by size and surface charge controlled anionic clay. We prepared anionic clays, having chemical formula of Mg1-xAlx(OH)6(CO3)x·mH2O, with controlled size and surface charge. The particle diameter was controlled to have average size of 100, 300, 1800, 2600 nm. In order to control surface charge, the Mg/Al ratio was systematically manipulated and we obtained anionic clays having zeta potential 32.87, 28.83, 19.01 mV at pH 7.5. Algal suspension containing cultured *M. aeruginosa* (~5 x 10⁶ cells/mL) was treated with anionic clay/water suspension with algae/clay ratio of 1.39 x 10⁷ (cells/g·ml). We found that the algae flocculating activity increased with increasing particle size showing maximum flocculating activity ~ 100% with 2600 nm sized anionic clay. Surface charge dependent assay exhibited higher algae flocculation with more less positively charged anionic clays.
SMECTITE CRYSTAL STRUCTURAL AND SURFACE FACTORS IN DETERMINING THE BINDING EFFICACY FOR ZEARALENONE

Chun-Chun Hsu*, Youjun Deng

Department of Soil & Crop Sciences, Texas A&M University, College Station, Texas, USA: *chunchunhsu@tamu.edu

Zearalenone is an anabolic estrogen produced mainly by *Fusarium graminearum*, and *F. culmorum*. It frequently contaminates corn, wheat, barley, oat, sorghum, hay, and other crops. Minimizing the health risks and economic losses from zearalenone contamination are crucial issues. Inspired by reported high adsorption capacity of many smectites for aflatoxins, and the similarity in molecular weight, functional groups, and polarity between zearalenone and aflatoxins, we are taking efforts to seek clay minerals to detoxify/decontaminate zearalenone by adsorption. The objective of this study was to 1) study the adsorption capacity of natural and modified smectites for zearalenone and the effect of pH on the adsorption, 2) compare the adsorption efficiency of smectites for zearalenone to other mycotoxins, ochratoxin A and deoxynivalenol, and 3) investigate the bonding between zearalenone and smectite before and after the clay was modified by surfactants.

For zearalenone adsorption under different pH, the 4 ppm solution was adjusted to desired pH with HCl and NaOH. The adsorption efficiencies of six different smectites were performed with zearalenone, ochratoxin A, and deoxynivalenol. Experimental results indicated in the pH range from 3 to 12, the highest zearalenone adsorption was at pH 5 with 0.16 mol/kg adsorption capacity. At high pH, it was likely that the mycotoxin hydrolyzed and became negative charged and therefore, could not be adsorbed by smectite. The best adsorption efficiency of smectites for zearalenone, ochratoxin A, and deoxynivalenol were 0.028, 0.043, and 0.030 mol/kg with smectites 7AZ, 37GR, and 8TX, respectively. Fourier transform infrared analysis indicated that the zearalenone did remain on smectite both before and after the surfactant modification. Furthermore, infrared bands of zearalenone shifted after surfactant modification, which suggested the change of bonding type after the modification.

Overall, the preliminary results indicated that the pH of highest adsorption capacity was near their original pH. Although the three mycotoxins can be adsorbed by smectites, the adsorption capacities were still low compared to their adsorption capacity for aflatoxins. The highest adsorption capacities of these three mycotoxins varied with different smectites may implied the adsorption was affected by the charge density. The optimal mineralogy properties for zearalenone adsorption are under further verification and will be reported.
STRUCTURE CHANGES OF FERRIHYDRITE AS AFFECTED BY COPRECIPITATION WITH NATURAL ORGANIC MATTER

Liang-Ching Hsu*1, Jui-Che Sung2, Yu-Min Tzou1, Chiung-Fen Chang2, and Yu-Ting Liu2

1Department of Soil and Environmental Sciences, National Chung Hsing, Taichung 402, Taiwan.
lгла1982@gmail.com
2Department of Environmental Science and Engineering, Tunghai University, Taichung 407, Taiwan.

Ferrihydrite is a poorly crystalline Fe hydroxide that distributes ubiquitously in soils, sediments, and other aqueous environments. Due to the large specific surface area and reactive functional groups at the surface, ferrihydrite serves as an efficient sorbent for nutrients, metals, and organic matter (OM). In soil and waterways, poorly ordered Fe hydroxides are likely associated into complex assemblages with Al hydroxides and organic matter in terms of substitution or coprecipitation. Interactions between dissimilar solid phases could particularly alter the pathway of biogeochemical Fe cycling and subsequently the sorption behavior of ferrihydrite. Whereas the physicochemical properties of Fe hydroxides depends on structural changes caused by coprecipitation with abundant Al or OM, knowledge about molecular-scale transformations in Fe octahedral linkages is limited. In this study, we aimed to determine the mechanistic mechanism at a molecular scale for the formation of Fe(III) hydroxides with coprecipitated humic acid in order to improve our understanding in the bioavailability and reactivity of Fe hydroxides.

Coprecipitates of Fe hydroxide (FH) and humic acid (HA) were synthesized by hydrolyzing Fe(NO3)3·9H2O using 1 M KOH to pH 7.5 in the presence of various soil HA with the C/Fe molar ratio from 0 to 0.5. Three types of HA were tested in this study: yangming mountain HA (YHA), changhua HA (CHA), and aldrich HA (AHA). The YHA and CHA was collected from Yangming mountain and Changhua county, respectively, wherein YAH is enriched with Fe content and CHA contains relatively less Fe. The sample of AHA is a commercial product. The application of purification process before its usage resulted in the lowest metal concentration in AHA. The local structure environments of FH-HA coprecipitates were characterized using Fe K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy. Spectra for EXAFS were collected at Beamline BL17C1 at the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan.

The Fe K-edge EXAFS spectra for samples with HA coprecipitates are similar to that of pure Fe hydroxide. However, irregular changes in shoulder intensity for the high-shell backscattering in the Fourier Transformed (FT) spectra were found with presence of HA. Such changes in the shoulder intensity suggested the variance in the coordination number (CN) for Fe octahedral linkages. A change in octahedral linkages could be further translated as the alteration in number of linked FeO6 polyhedra, i.e., domain size. With increasing HA coprecipitation, a decrease in higher-shell Fe coordination can be interpreted as an increase in the proportion of terminal octahedra. The EXAFS data suggested that coprecipitation of HA affected the development of edge-shared Fe octahedral linkages in Fe domains. Of all the tested HA, YHA changed the structure of FH most intensely. The most possible explanation is that YHA contains
more metal impurities that disrupted the structure development of Fe hydroxide. This study indicates that coprecipitated HA likely plays a critical role in structural transformation and stability for poorly crystalline Fe hydroxides.
K-BENTONITES IN THE UPPER ORDOVICIAN OF THE SIBERIAN PLATFORM

W.D. Huff*1, A.V. Dronov2

1Department of Geology, University of Cincinnati, OH 45221, USA; warren.huff@uc.edu
2Geological Institute, Russian Academy of Sciences, Pyzhevsky per.7, 119017, Moscow, Russia.

Eight K-bentonite beds have been discovered in the Upper Ordovician of the Siberian Platform. This discovery is significant not only for their value in local and regional chronostratigraphic correlation but also for global geochronology, paleogeography, paleotectonic and paleoclimatic reconstructions. Individual K-bentonite beds have been identified in the Baksian, Dolborian and Burian regional stages, which correspond roughly to the Upper Sandbian – Katian Global Stages. All K-bentonite beds have been found within the Upper Ordovician cool-water carbonate succession. The four lowermost K-bentonite beds, which were sampled, are located within the Mangazea and Dolbor Formations (Baksian and Dolborian regional stages, respectively). Modeling of the powder X-ray diffraction tracings using NEWMOD showed the samples consist of R3 ordered illite-smectite with 80% illite and 20% smectite plus a small amount of corrensite. The K-bentonites provide evidence of intensive explosive volcanism on or near the western (in present day orientation) margin of the Siberian craton in Late Ordovician time. The timing of volcanism in the Ordovician of Siberia is surprisingly close to the period of volcanic activity of the Taconic arc near the eastern margin of Laurentia. Thus, it appears that both arcs were activated by the same plate tectonic reorganization.
TEACHING CLAY SCIENCE IN A PROJECT-ORIENTED FORMAT

Warren D. Huff*

Department of Geology, University of Cincinnati, Cincinnati, OH 45221 warren.huff@uc.edu

The study of clay science is offered in two formats in the Department of Geology: a traditional lecture-based, lab-based format in the fall semester and a project-based format in the spring. The spring course requires students to have completed the fall class in order to have some basic understanding of clay mineral concepts and analytical methods. At the beginning of the spring term the class meets as a group to discuss possible projects, including several that are offered by the instructor. Topics will vary depending upon the background of the students, which can include civil engineering, archaeology, anthropology and physical geography. Once agreement is reached then sample collection and analytical methods are discussed. The group meets formally once a week, but during the rest of the time the group may travel together or as individuals to collect appropriate samples for the project. Often, this may mean simply mining departmental storage facilities. We attempt to employ as wide a variety of analytical methods as possible in order to give everyone the experience of using techniques such as FTIR, XRF, SEM and Raman spectroscopy that were not discussed in the fall term. As the project draws to a close the class is asked to select one of its members who will serve as the first author on an abstract that will be submitted to the Annual Meeting of the GSA. That individual prepares a draft that is then discussed and, if necessary, modified by the rest of the class. That individual also receives an expenses-paid trip to the Annual Meeting to present either an oral or a poster report on the project. Examples of past projects will be presented.
STRUCTURES OF SERPENTINE-CHLORITE MIXED-LAYER MINERALS FROM HYDROTHERMAL SYSTEMS

Sayako Inoué *1, Toshihiro Kogure 1

1 Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan: sinoue@eps.s.u-tokyo.ac.jp

Mixed-layer structures are one of the distinct features of clay minerals. Serpentine-chlorite (S-C) mixed-layer is among them but compared to the others (e.g., illite-smectite) its occurrence and stability have not been well understood. This may be due to the fact that S-C interstratification does not influence conventional XRD patterns apparently because the basal spacing of serpentine is always almost a half of that of chlorite. Instead, high-resolution transmission electron microscopy (HRTEM) is effective to characterize the interstratified structure of S-C, because S and C layers can be distinguished by their distinct contrasts (Ahn and Peacor, 1985).

In this study, Fe-rich chlorites and/or S-C mixed-layer minerals from five hydrothermal ore deposits in Japan (Toyoha, Osarizawa, Yatani, Arakawa and Ashio) were investigated by HRTEM to find aspects for the occurrence and stability of S-C mixed-layer minerals. Ashio mine is classified into a mesothermal(300-200ºC) ore deposit and the others into epithermal (100-200ºC) ore deposits. The chlorites from these deposits show a wide range of Fe content (Fig. 1).

Regardless of the formation temperatures (epithermal or mesothermal), chlorites with high a Fe/(Mg+Fe) ratio (Toyoha, Yatani, Ashio) always contain S-C interstratification. On the other hand, no interstratification was observed in chlorite with Fe/(Mg+Fe) ratios around 0.5 (Osarizawa; Arakawa). Two-dimensional HRTEM imaging of randomly interstratified S-C indicates a mixture of different polytypic sequences in chlorite and serpentine (Fig. 2).

Several previous works suggested that regularly or randomly interstratified S-C are transformed from serpentine or chlorite by subsequent metamorphism (Slack et al., 1992; Banfield and Bailey, 1996; Xu and Veblen, 1996). The results of hydrothermal synthesis suggested that 7Å phase (serpentine) is formed first at a low temperature then it converts to chlorite via S-C mixed-layer phase (e.g. Cho and Fawcett, 1986). Hence S-C interstratification is considered as a low temperature metastable phase of chlorite. In our case, randomly interstratified S-C didn’t suffer subsequent metamorphism. And the occurrence of S-C interstratification seems not to be related to the formation temperature because the sample formed under a higher temperature condition (Ashio) also contains the interstratification. Fe content is probably critical for the occurrence and stability S-C mixed-layer minerals.
Figure 1. Al content in (Si, Al)$_4$ vs. Fe/(Fe+Mg) in the octahedral sheets for the “chlorites” from various hydrothermal ore deposits in Japan.

Figure 2. HRTEM image (processed for noise reduction) of randomly-interstratified S-C from Ashio mine. The arrowheads indicate serpentine layers. The horizontal lines connect the equivalent sites in the adjacent layers. Symbols (0, +, −) indicate the stagger directions from the underlayers.
INTERCALATION OF MACROSCOPIC VERMICULITE PARTICLES INTO NANOPARTICLES WITH ANIONIC SURFACTANTS

Sevim İşçi*, Yavuz İşçi,

İstanbul Technical University, Department of Physics, Maslak 34469, İstanbul, Türkiye.
iscisev@itu.edu.tr

Layered structure clay minerals have been extensively used as naturally nano-sized particles, low-cost filler to enhance the mechanical and physical properties of polymer composites. Montmorillonite is mostly used as layered clay in many articles, and also in industrial uses. However, compared with montmorillonite, the clay layers in vermiculite have a higher charge density, a key parameter facilitating the incorporation of organic modifiers to generate larger interlayer spacing. Vermiculite forms macroscopic crystals, that are potentially suitable for producing high aspect ratio nanofillers, and its natural abundance makes it economically attractive for industrial applications. Vermiculite was modified with surfactants in order to enable intercalation of vermiculite layers. Since vermiculite has negative charges on its surfaces, it was expected that cationic surfactant would expand the clay layers more than an anionic surfactant. Nevertheless, OH- ions of the vermiculite surfaces were exchanged with negative parts of the anionic surfactant so unexpectedly the expansion of the layer was determined to be fully expanded structure of vermiculite. Colloidal and structural properties of vermiculite dispersions were examined in presence of anionic and cationic surfactants. The results showed that cationic surfactant covered the surface of the vermiculite with a second layer but the expansion of the clay layer was limited compared to the anionic surfactant. The anionic surfactant produced ion exchange with OH- ions of vermiculite and fully expanded the layer structure of the vermiculite.

**Keywords:** Nanoclays, surfactants, colloidal properties, structural properties.
EFFECT OF THE CLAY TYPE ON THE PROPERTIES OF REINFORCED-PVA NANOCOMPOSITES

Yavuz İşçi *, Sevim İşçi

İ.T.Ü., Faculty of Science and Letters, Dept. of Physics, Maslak 34469, Istanbul, Turkey. isciyavuz@itu.edu.tr

Clay/polymer nanocomposites have aroused intense research interest due to their many attractive properties. Different clay minerals were used to prepare to the nanocomposites. Every mineral has different properties according to their crystal structure. In this study, PVA nanocomposites were synthesized with montmorillonite (Mt), sepiolite (Sp) and vermiculite (Vk) by intercalation of polymer from solution method. The structural and morphological characterizations of these nanocomposites were examined by using XRD, TEM and FTIR techniques and the thermal and mechanical properties were determined by DMA and DSC methods. Structural analyses revealed that both Mt and Vk synthesized nanocomposites could be described as exfoliated type and Sp persisted itself in PVA. Besides, FTIR results showed that there are some H-bonding between the clays and PVA. As a result of the preparing nanocomposites with these clays, the mechanical and the thermal properties were improved especially mechanical properties with Vk addition and thermal properties with Mt addition. The delamination of clay layers made difference on the properties of PVA comparing to the undelaminated Sp.

Keywords:
Nanoclays; Clay-Polymer nanocomposites.
MICROBIAL CYCLING OF PHOSPHATE AT THE MINERAL-WATER INTERFACE

Deb P Jaisi1*

1Department of Plant and Soil Sciences, University of Delaware, Newark, DE 19716, USA
*jaisi@udel.edu

Phosphate is present in the natural environment predominantly as a tightly bound form to mineral surfaces. Micro-organisms access phosphate bound to mineral surfaces by a verity of mechanisms including artificially changing chemical equilibria, redox condition, and pH to favor the release of mineral bound phosphate. But the question whether a particular reaction is biological, biologically mediated, or abiotic has remained largely elusive in many cases. Stable isotopes have been increasingly popular methods for understanding interface reactions. In this study, the dynamic interaction of phosphate at the mineral-water interface in the presence of microorganisms and macromolecules was analyzed using phosphate oxygen isotope ratios as a reaction tracer. This tracer was able to identify the role of phosphate and organic macromolecules inhibiting iron oxide mineral dissolution and controlling the pathway of mineral transformation. Similarly, it was able to distinguish and quantify the biotic and abiotic pathways of phosphate cycling at the mineral-water interface. These findings support burgeoning applications of phosphate oxygen isotopes as a tracer of interface reactions as well as an indicator of reaction pathways in different environments.
INCREASED AFLATOXIN AND FUMONISIN ADSORPTION TO FEED ADDITIVES BY REDUCING THE ADSORPTION OF SOLUBLE FEED COMPOUNDS

William Jaynes1, Richard Zartman1

1Department of Plant and Soil Science, Texas Tech University, Lubbock, Texas 79409 USA. william.jaynes@ttu.edu.

Mycotoxins are toxic compounds produced by fungi (e.g. Aspergillus sp., Fusarium sp.) that infest food crops, such as corn, wheat, rye, peanuts, tree nuts, and other seeds. Contamination can occur before harvest and during crop storage. Mycotoxins are acutely toxic at high concentrations, but chronic ingestion at lower concentrations can result in cancers and other medical problems. In the 1960s, the first and most toxic mycotoxins, the aflatoxins, were identified in highly-contaminated peanut meal used as turkey feed. More than 100 mycotoxins have now been identified, but only about 5 are a major problem. The fumonisins are less toxic mycotoxins identified in the late 1980s. Bentonites added to animal feed to absorb moisture and improve the physical properties were also found to bind aflatoxins in feed and reduce the toxicity. Many animal feeding studies have since shown that bentonites and other clay minerals can effectively bind aflatoxins in feed and prevent toxicity. Feed additives have subsequently been examined as a possible remedy for mycotoxin-contaminated food/feed. However, there is a wide range in the chemical and physical properties of mycotoxins and bentonites only effectively adsorb some mycotoxins. The much different properties of aflatoxins and fumonisins can be used to illustrate the different approaches needed to limit mycotoxin toxicity in food/feed. How can effective feed additives to bind mycotoxins in food/feed be identified?

Feed additives that effectively adsorb mycotoxins in water might not effectively adsorb mycotoxins in ingested food and prevent toxicity. Soluble compounds in food, such as proteins, might compete with mycotoxins for adsorption sites on feed additives. Mycotoxin adsorption from food, simulated gastrointestinal digestion, and animal feeding studies might be needed to verify that feed additives can bind mycotoxins in contaminated food and prevent toxicity. To optimize mycotoxin adsorption and toxicity reduction, the negative effects of soluble food compounds must be minimized. Aflatoxins are neutral compounds that are nearly insoluble in water, but soluble in methanol and other organic solvents. Fumonisins are very water-soluble, amphoteric compounds with 4 carboxyl groups and one amine group.

The objective of this research was to show how aflatoxin and fumonisin toxicity in feed can be reduced by minimizing the deleterious effects of soluble food compounds on aflatoxin and fumonisin adsorption to feed additives. Aflatoxin B1 (AfB1) adsorption from water yielded Langmuir-type isotherms consistent with adsorption to a surface at loadings up to 200 g/kg or
more. In contrast, ~100 times less aflatoxin was adsorbed (~2 g/kg) from aqueous corn meal. Activated carbon was about as effective as the clays from water (~180 g/kg), but much less effective from aqueous corn meal (~0.2 g/kg). Sepiolite (SepSp-1) adsorbed less AfB1 from water (~90 g/kg) than Novasil montmorillonite (~250 g/kg) or activated carbon, but relatively more AfB1 from aqueous corn meal (~1.2 g/kg). Soluble compounds in aqueous corn meal must block AfB1 adsorption sites. Much greater AfB1 adsorption by low-charge SWy-2 montmorillonite relative to high-charge SAz-1 montmorillonite indicates that layer charge inversely affects AfB1 adsorption. AfB1 adsorption followed the order hectorite (SHCa-1) > low-charge montmorillonite (SWy-2) > high-charge montmorillonite (SAz-1) > vermiculite (VSC). Proteins are soluble compounds in food that can adsorb to clays and block AfB1 adsorption. Blocking cation exchange sites on clays with small organic cations, such as choline and carnitine, might prevent protein adsorption and permit greater AfB1 adsorption. The much greater surface area of the choline-SWy organoclay (140 m² N₂/g) relative to SWy (29 m²/g) indicates nitrogen-accessible interlayer sites. The choline-SWy organoclay adsorbed AfB1 from aqueous corn meal ~15 times as effectively as SWy and ~47 times as effectively as SAz. Organoclays prepared from low-charge smectites by cation exchange with small non-toxic organic cations might be one of the most effective feed additives to bind aflatoxins in feed.

A different approach and different feed additives are needed to bind fumonisins in feed. An animal feeding/adsorption study has shown that the anion exchange resin and cholesterol-lowering pharmaceutical, cholestyramine, effectively adsorbs fumonisins from water and aqueous corn meal and reduces the toxicity to animals. Unlike aflatoxins, fumonisin adsorption to feed additives is pH-dependent. Fumonisins adsorb to feed additives by ion exchange rather than by adsorption to non-polar surfaces. Montmorillonites effectively adsorb fumonisin B₁ (FuB1) at pH 4, but not at pH 7. Cholestyramine more effectively adsorbs FuB1 at pH 7 than at pH 4. What pH should be used for adsorption isotherms to identify effective fumonisin feed additives? Five times as much FuB1 adsorbed to cholestyramine from water than from aqueous corn meal. Soluble compounds in corn must block FuB1 adsorption to cholestyramine. Phytic acid and phytates are soluble multivalent anionic compounds in corn meal (2%) and other grains that might compete with FuB1 for adsorption sites on cholestyramine. The addition of FeCl₃ to precipitate phytates or phytase enzyme to decompose phytates can reduce phytate interference and enhance FuB1 adsorption to feed additives. Similarly, feed additives in low-phytate corn should more effectively bind fumonisins. Simulated gastrointestinal digestions of FuB1-contaminated corn meal suggest that simple adsorption isotherms from water or corn meal are not sufficient to identify feed additives that can effectively bind fumonisins in feed. Simulated gastrointestinal digestions (pH 1.5 to pH 7) might integrate the many effects of soluble feed compounds, different pHs, and digestion on fumonisin adsorption to feed additives.


AEOLIAN AND AUTHIGENIC CLAY MINERALS IN THE BROWN PEDOSEDIMENTARY SEQUENCE OF PALEOLITHIC SITE, KOREA

Gi Young Jeong*

Department of Earth and Environmental Sciences, Andong National University, Andong, 760-749, Republic of Korea: jearth@anu.ac.kr

Brown clay-silt pedosedimentary sequence occurs on river terrace in Jeongok Paleolithic site, Korea. The origin of the sequence is important for reconstructing the paleoenvironment of the Paleolithic artifact-bearing stratigraphic unit. The lower stratigraphic unit of the sequence is a fluvial silt-sand deposit strongly influenced by local lithology dominated by Jurassic granitoids, whereas the upper units are characterized by brown clay-silt units. X-ray powder diffraction of the oriented clay fractions show that clay minerals from the section are dominated by illitic (illite and illite-smectite mixed layers) and kaolin clays (halloysite and kaolinite). However, the types of clay minerals vary throughout the section. In the lower fluvial units, the dominant kaolin mineral is halloysite with minor gibbsite, while the upper brown clay-silt units are dominated by illitic clay minerals, vermiculite, and chlorite. In the fluvial sandy unit, sand particles are dispersed in the silt-clay matrix. Plagioclase was weathered to halloysite leaving the skeletal grains of plagioclase. Biotite flake had also been subjected to weathering, showing fanning-out textures due to kaolinitization. K-feldspars had been weakly dissolved along the cleavages. In the lower reddish brown clay-silt unit, silt particles are mostly composed of quartz and muscovite with minor K-feldspar and biotite. K-feldspar particles are intensely weathered, leaving skeletal grains. EDS and microscopic analysis revealed that the weathering product of K-feldspar is kaolin, probably halloysite. Plagioclase was completely weathered. The degree of mineral weathering was lowest in the uppermost brown clay-silt unit as shown in the no signature of K-feldspar dissolution and partial dissolution of plagioclase. Chlorite is common and second to muscovite in abundance. The mineralogy of the BCSs indicates a widespread deposition of Asian dust and subsequent weathering in the late Quaternary, forming brown clay-silt pedosedimentary sequences on fluvial sandy deposits. The brown clay-silt pedosedimentary sequences are considered to be the additionally weathered equivalents of the CLP loess–paleosol sequences, having been exposed to the high annual precipitation of the Korean Peninsula. The lower brown clay-silt pedosedimentary units were severely weathered during the warm interglacial period, while the upper units were less weathered during the cold glacial period.
CLAY MINERALS IN ASIAN AIR

Gi Young Jeong*

Department of Earth and Environmental Sciences, Andong National University, Andong, 760-749, Republic of Korea: jearth@anu.ac.kr

Mineral dust interacts with atmospheric incoming/outgoing electromagnetic radiation, changing Earth’s radiative balance, and supplies micronutrient metals, particularly iron, to marine ecosystem. Global climatic changes were recorded in aeolian deposits on land, sea, and ice. Clay minerals are the key constituents of the dust particles. Their mineralogy in the dust should be clarified to understand their contribution to global climatic changes. The small quantity of Asian dust samples collected on air filter was analyzed using scanning electron microscopy and transmission electron microscopy to explore their clay mineralogy. Illite-smectite series clay minerals were the major mineral group followed by quartz, plagioclase, K-feldspar, and calcite. Total phyllosilicates was ~52%. The mineral composition of dust particles varied little throughout the fine (<5 μm), coarse (5–10 μm), giant-S (10–20 μm), and giant-L (>20 μm) size bins, indicating the agglomeration of clay mineral grains to form large particles. The interiors of Asian dust particles were observed for cross-sectional thin slices prepared using focused ion beam. Individual dust particles consist of numerous mineral grains, which were organized into several types of internal structure: single and polycrystalline cores of quartz, feldspars, calcite, and amphibole often with oriented clay coatings; individual clay agglomerates of nano-thin clay platelets showing preferred to random orientations commonly with coarser mineral inclusions; and platy coarse phyllosilicates (muscovite, biotite, and chlorite). Micron to submicron pores were scattered throughout the interior of particles. Clays in the coatings and agglomerates were dominated by nano-thin platelets of the clay minerals of illite-smectite series possibly including illite, smectite, and their mixed layers with subordinate kaolinite and clay-size chlorite. Chemical compositions of the clay minerals were determined by energy dispersive X-ray spectrometry. Average iron content of the nano-thin clusters of illite-smectite series clay minerals was around 6.2 Fe wt% in average assuming 14% H2O. Submicron iron oxide grains, dominantly goethite, were distributed throughout the clay agglomerates and coatings. Accounting for this structural, mineralogical, and chemical makeup may improve the remote sensing retrieval of dust, the evaluation of radiation effects, and modeling the iron supply to remote ocean.
IDENTIFICATION AND QUANTIFICATION OF HEMATITE AND GOETHITE IN SEDIMENTS AND PALEOCLIMATE IMPLICATION

Junfeng Ji*

Key Laboratory of Surficial Geochemistry, the Ministry of Education; School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, China. jijunfeng@nju.edu.cn

Hematite (Hm) and Goethite (Gt) are common in marine, lacustrine and eolian sediments, soils, and a wide variety of rocks. They develop in climatically specific environments suggesting that these two iron minerals are environmentally significant. Moist conditions favor the presence of Gt over Hm, their ratio may provide a record of precipitation changes. Although Hm and Gt are common and important iron minerals, their low concentrations in many geological materials have impeded thorough implementation of their potential uses. Conventional measurements cannot effectively identify it at the low concentrations typical of sediments and soils. In this study we use diffuse reflectance spectroscopy (DRS) to identify and quantify Hm and Gt in sediments, and display its application to marine sediments for paleoclimate reconstruction.

First, we demonstrate that the DRS analysis in combination with thermal treatment provides a technique for definitively identifying Gt in soil when Hm is present. DRS patterns of Gt show a shift of the FDV peak toward longer wavelengths after it is heated to 300 °C. Changes associated with thermal treatment, especially the disappearance of the shoulder on the 565–575 nm peak, can be used to conclusively identify Gt.

Second, DRS is capable of quantifying Fe oxides in sediments with concentration as low as 0.01 % by removing the matrix effect. The target sediments are deferrated to serve as calibration samples for a transfer function for determining the concentration of hematite and goethite.

Third, we apply the method to sediments from the Ocean Drilling Program (ODP) site 1143, southern South China Sea. Using the Hm/Gt we produce a continuous record of monsoonal rainfall variations and reveal low-latitude climate dynamics for the last five million years. This record enabled us to explore its possible interplay with the NHG initiation.

References

ALUMINATE SPECIATION IN ALKALINE ELECTROLYTE SOLUTIONS
SIMULATING HIGH-LEVEL NUCLEAR WASTE

Cliff T. Johnston1*, Jacob G. Reynolds2, and Stephen F. Agnew3

1Crop, Soil and Environmental Sciences, Purdue University, West Lafayette, IN 47907 USA
2Washington River Protection Solutions, LLC, Richland, WA, 99352 USA
3Columbia Energy and Environmental Services, Inc., Richland, WA, 99354 USA

The total amount of aluminum observed in a large number of alkaline high level nuclear waste (HLW) liquors is often significantly greater than what is predicted on the basis of thermodynamic equilibria in the ‘simple’ Al-NaOH-H2O system. Broadly speaking, there are three possibilities that would account for the higher-than-expected dissolved aluminum concentrations in HLW. The first possibility is that some other solid phase other than gibbsite which is considered to be the controlling solid phase, may be present. Second, the precipitation kinetics of gibbsite and bayerite can be relatively slow and these data may indicate that thermodynamic equilibrium has not been achieved. The third possibility is that some ‘other’ constituent present in Hanford waste may contribute to aluminate stability in these solutions. Although the chemical composition of HLW is complex, the specific objective of this project was to examine the role of the aluminate dimer and its impact on aluminum precipitation and stability. Relatively little is known about this solution species and we report on the spectroscopic and thermodynamic properties of the aluminate dimer. We employed Raman and FTIR spectroscopy to study these solutions as a function of time (0 to 127 days) and temperature (25 and 45 °C). Raman spectroscopy is the only unambiguous way to observe the aluminate dimer and was used in this study. In addition to the spectroscopic measurements, macroscopic properties (elemental composition, solution density and water activities) of these solutions were also determined. We developed an improved expression to describe the apparent formation constant of aluminate dimer that corrected for the difference in Raman cross-section between the aluminate monomer and the dimer, and water activity.
HOW DOES METHYLENE BLUE INTERACT WITH THE SURFACE OF KAOLINITE?

Cliff T. Johnston1*, Robert A. Schoonheydt2

1Crop, Soil and Environmental Sciences, Purdue University, 915 W State St., West Lafayette, IN 47907 (USA)
2Center for Surface Chemistry and Catalysis, KU Leuven, Kasteelpark Arenberg 23, 3000 Leuven (Belgium).
cliffjohnston@purdue.edu and Robert.Schoonheydt@biw.kuleuven.be

Cationic dyes are a group of ‘classic’ molecular probe that have been used extensively in the mineral processing industry for the past 65 years. Of these cationic dyes, methylene blue (MB) has been used the most extensively in both applied mining and laboratory research. The interaction of methylene blue, a cationic organic dye, with clay minerals has been studied for many years using a wide range of spectroscopic, sorption and theoretical methods. For clay minerals, much of this work has focused on the interaction of methylene blue with expandable 2:1 clay minerals where sorption, orientation and optical properties of sorbed methylene blue have been clearly related to structure, charge density and charge location. As a simple indicator test method, the partitioning of MB between clay particle and the aqueous phase is used to determine the CEC of the clay using ASTM Method C837-09 and this method has been widely used in diverse clay industries, including the kaolin industry. In oil sands mining, the methylene blue index is one of the most reliable and simple assays to identify ores that have a high clay content (the overall mineralogy of the clay fraction of the Athabasca oil sands ores is dominated kaolinite). Despite it wide-scale adoption and utility in kaolin-related fields, surprisingly little is known about the mechanisms of interaction between methylene blue and kaolinite. The interaction of methylene blue with a suite of kaolins of varying size, aspect ratio, and structural disorder is examined in the present study using sorption and spectroscopic methods. The spectral signature of methylene blue sorbed to kaolinite reveals some interesting spectral features that resemble methylene blue sorbed to a high charge density smectite.
EUROPIUM(III)-PHENANTHROLINE INTERCALATED HECTORITE/ POLYPROPYLENE NANOCOMPOSITE FILM WITH BIFUNCTIONAL PHOTOLUMINESCENT AND SUPERHYDROPHOBIC PROPERTIES

Hyun Jung*, Aran Kim

Advanced Functional Nanohybrid Material Laboratory, Department of Chemistry, Dongguk University Seoul-campus, 30 Pildong-ro 1-gil, Jung-gu, Seoul 100-715, Republic of Korea: chemphile@dongguk.edu

The bifunctional nanocomposite film with photoluminescent and superhydrophobic properties was successfully fabricated through the solution blending method from europium(III)-complex ([Eu(Phen)2]3+) intercalated hectorite and isotactic polypropylene. The obtained film shows the characteristic strong red emission and superhydrophobicity with a water contact angle of 151°. This film also exhibits excellent long term stability of fluorescence against constant humidity (84%) for one month.

Figure 1. Photographs (taken under 254 nm UV lamp) of a water droplet on the bifunctional nanocomposite film.
ONE-POT SYNTHESIS OF HETERO-ION DOPED GRAPHENE BY USING ELECTRON-BEAM IRRADIATION

Myunggoo Kang*1, Dong Heon Lee1, Jeong Hoon Yang2, Mi Ru Jo2, Yong-Mook Kang2, and Hyun Jung1

1Advanced Functional Nanohybrid Material Laboratory, Department of Chemistry, 2Department of Energy and Materials Engineering, Dongguk University-Seoul Campus, 30 Pildong-ro 1-gil, Jung-gu, Seoul 100-715, Republic of Korea: kkang09@dongguk.edu

Hetero-ion (Nitrogen, Boron, Sulfur, etc) doped graphene are successfully obtained by electron-beam irradiation from exfoliated graphite oxide (GO) aqueous solution in the presence of hetero-ion source. The electron-beam irradiation simultaneously allows rapid reduction and hetero-ion doping of GO at room temperature under the ambient. The physicochemical characterizations on the obtained hetero-ion doped graphene have been carried out as a function of irradiation dose, along with the test of their electrochemical property as a supercapacitor.

Scheme 1. Fabrication of hetero-ion doped graphene from graphite oxide by electron-beam irradiation.
RECOGNITION OF SODIUM CARBONATE ACTIVATED BENTONITES

S. Kaufhold\textsuperscript{1}, K. Emmerich\textsuperscript{2,3}, R. Dohrmann\textsuperscript{1,4}, A. Steudel\textsuperscript{3}, and K. Ufer\textsuperscript{1}

\textsuperscript{1}BGR, Bundesanstalt für Geowissenschaften und Rohstoffe, Stilleweg 2, D-30655 Hannover, Germany;
\textsuperscript{2}CMM, Competence Center for Material Moisture, Karlsruhe Institute of Technology, H.-v.-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany; katja.emmerich@kit.edu;
\textsuperscript{3}IFG, Institute for Functional Interfaces, Karlsruhe Institute of Technology, H.-v.-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany;
\textsuperscript{4}LBEG, Landesamt für Bergbau, Energie und Geologie, Stilleweg 2, D-30655 Hannover, Germany.

A large amount of bentonites is used because of its rheological properties such as thixotropy. Examples are drilling mud and paint additive. The rheological properties strongly depend on the type of interlayer cation balancing the permanent charge of the smectites. While few bentonites (smectites) are dominated by exchangeable Na\textsuperscript{+} the rheological properties of Ca/Mg-rich bentonites are improved by adding sodium carbonates for the exchange of natural interlayer cations by Na\textsuperscript{+}. The optimum amount of sodium carbonate to be added to a Ca/Mg-rich bentonite is commonly determined empirically by investigation of the rheology of a set of different bentonites with different ratios of sodium carbonate. Thereby adding slightly more sodium carbonate than the CEC often yields best results.

Technically activated bentonites are produced at production lines all over the world, packed, and shipped to their destination. For customs declaration commonly technically produced and natural materials have to be distinguished. So far suitable methods that can unambiguously distinguish natural Na-bentonites from alkaline activated materials were missing. Steudel et al. (2013) proposed thermal analysis for the detection of technically activated Na-rich bentonite. In order to assess the proposed method different sodium carbonate samples and a set of well characterized bentonites were used.

The most important conclusion of the present study (Kaufhold et al. 2013) is that the presence of any peak or intensity around 200 °C in the MS–CO\textsubscript{2} curve indicates technical activation of bentonite with sodium carbonate. Findings were supported by CEC and FTIR measurements.

ANIONIC CLAYS AS POTENTIAL NANOCARRIERS FOR COMBINATION CHEMOTHERAPY

Tae-il Kim¹, Gyeong Jin Lee¹, Tae-Hyun Kim², and Jae-Min Oh²*

¹Department of Biosystems and Biomaterials Science and Engineering, College of Agriculture and Life Sciences, Seoul National University, Seoul 151-921, Republic of Korea: seal1004@snu.ac.kr
²Department of Chemistry and Medical Chemistry, College of Science and Technology, Yonsei University, Wonju, Gangwondo, 220-710, Korea

We evaluated the anticancer drug delivery efficiency of anionic clays for potential application of combination chemotherapy. Two kinds of anticancer drugs, methotrexate (MTX) and 5-fluorouracil (5-FU), were incorporated into anionic clays through successive dehydration-rehydration reaction, which is also known as reconstruction reaction in anionic clays. Three different kinds of drug-clay hybrids were thus prepared to contain drug only or the mixture. Physico-chemical characterization such as X-ray diffractometer, scanning electron microscopy, infrared spectroscopy, thermal analysis, high performance liquid chromatography, elemental analysis, zeta-potential measurement and dynamic light scattering confirmed that the drug molecules were well introduced into the interlayer space of anionic clays. In order to confirm the enhanced therapeutic efficiency of drug-clay hybrid as combination therapy, we treated those hybrids to the human cervical adenocarcinoma, HeLa cells in concentrations dependent manner, comparing with drug itself. All the hybrids were proven to have higher cancer suppressing effect compared with drug only. It was notable that the hybrid containing both drug together showed the highest anticancer efficacy suggesting that multidrug-incorporated clay hybrid could be potential carriers for combination chemotherapy.
ANALYSIS OF SECONDARY MINERALS FROM BASALT-SEDIMENTS INTERFACE, SOUTH PACIFIC GYRE: IODP EXPEDITION 329

Jinwook Kim1*, Kiho Yang1, Kogure Toshihiro2, Hionsuck Baik3, and IODP Expedition 329 shipboard scientists4,

1Department of Earth System Sciences, Yonsei University, Seoul, Korea; 2Department of Earth and Planetary Sciences, University of Tokyo, Japan; 3 Korea Basic Science Institute (KBSI), Seoul, Korea; 4IODP Expedition 329 shipboard scientists

*jinwook@yonsei.ac.kr

The core samples of basalt-sediments interface at a depth of 74.79 mbsf were collected from the IODP expedition 329 (2010.10.10-2010.12.13) in the South Pacific Gyre (SPG). This is the first time to collect the basalt and sediment samples in the SPG since HMS Challenger expedition (1872). Two distinct regions of yellow and red colored sediments were observed in the basalt.

In the yellow part, K-nontronite, and feroxyhyte (δ'-Fe3+O(OH)) were the dominant mineral phases compared with the magnesium rich smectite (saponite), chlorite, hematite and goethite in reddish sediment. In the more oxic condition, hematite and goethite could be formed from the oxidation of feroxyhyte.

Mineralogy, elemental composition, Fe-oxidation state, and structure of minerals were analyzed by transmission electron microscope (TEM) with the selected area electron diffraction (SAED) pattern, electron dispersive spectrometer (EDS), and electron energy loss spectroscopy (EELS), scanning electron microscopy (SEM), and the micro x-ray fluorescence (μ-XRF) in order to understand the formation of K-nontronite, and Fe-oxides from the basalt alteration.

The existence of K-nontronite and feroxyhyte mineral assemblages at altered part may indicate that there was oxidative basalt alteration between basement aquifer and basaltic crust concerned to the secondary minerals formation. The results of EELS may suggest the oxidation state of Fe and its relations to the K-fixation of smectite resulting in the K-nontronite during basalt alteration.
NONTRONITE AND SI-SUBSTITUTED IRON OXIDE FORMATION IN AN EEMIAN INTERGLACIAL LAKE IN DENMARK

Christian Bender Koch*1, Takeshi Kasama2

1Department of Soil Chemistry, University of Copenhagen, DK-2400 Copenhagen Ø, Denmark: cbk@chem.ku.dk
2Center of Nanoscopy, Technical University of Denmark, DK-4200 Kgs. Lyngby, Denmark.

The Eemian interglacial in Scandinavia represent an approximately 100 kyear period of weathering and biological activity on land and in lake environments. Carbonates and sulphides were leached from the glacial sediments and accumulated in springs and lakes. Within the lakes primary productivity was high and silica accumulated as diatom frustrules. Weischelian glacial activity disturbed most of the lake deposits leaving only one known interglacial lake deposit dominated by calcium carbonate-iron oxide-silica in Denmark. In terms of bulk chemistry the sediment varies between 1 and 53 %wt. CaO, 0 and 60 %wt. Fe2O3, and 0.5 and 45 %wt. SiO2 – Al2O3 is below 1 %wt. throughout the approximately 5 m thick deposit.

The mineralogy was investigated using a combination of XRD, TEM and spectroscopies allowing the identification of a nontronite layer silicate and goethite commonly showing defects correlating with silica in the structure. Taking into consideration the current formation of 1:1 iron silicates recently documented in similar Holocene lake sediments, we suggest that the nontronite does not precipitate directly, but via the 1:1 precursor.
CHARACTERIZATION AND QUANTIFICATION OF WATER IN SMECTITES WITH NUCLEAR MAGNETIC RESONANCE AND SMALL ANGLE X-RAY SCATTERING

Eric Kohler\textsuperscript{1*}, Marc Fleury\textsuperscript{2}, Françoise Norrant\textsuperscript{1}, Serge Gautier\textsuperscript{3}, Jalel M’Hamdi\textsuperscript{1}, and Loic Barré\textsuperscript{1}

\textsuperscript{1}Department of Physics and analyzes, IFP Energies Nouvelles, Rueil-Malmaison, 1-4 Av. de Bois Préau 92500, FRANCE: eric.kohler@ifpen.fr;
\textsuperscript{2}Department of Petrophysic and geochemistry, IFP Energies Nouvelles, Rueil-Malmaison, 1-4 Av. de Bois Préau 92500, FRANCE;
\textsuperscript{3}Department of Experiments and Process, IFP Energies Nouvelles, Rueil-Malmaison, 1-4 Av. de Bois Préau 92500, FRANCE;

A method to estimate the amount of water in smectites has been successfully tested on a homoionic montmorillonite (exchanged with Ca, Na, K, Mg) at controlled humidities. This method can distinguish the interlayer water by removing the contribution of water adsorbed on surfaces and structural hydroxyls. Measurements were performed with Nuclear Magnetic Resonance (NMR) and Small Angle X-ray Scattering (SAXS). The interlayer distance can be connected directly to the amount of water which varies with cations and humidity. The clay used for these experiments is a montmorillonite from Libya. It was saturated with the cations Na, Ca, Mg and K with a conventional method. The smectites were then characterized with X-ray diffraction and scanning electron microscopy to check the crystalline and chemical properties. Each smectite is then equilibrated for several months in humidity controlled media (11 to 97 %RH) to obtain smectites with distinct moistures.

The NMR measurements performed at a magnetic field of 0.5 T were to deduce a distribution of transverse relaxation times T2, the 2D T1−T2 sequence to analyze the mobility of protons, and a free induction decay (FID) sequence to detect very short relaxation time and evaluate the total amount of protons present in the system, including structural hydroxyls. We complemented the NMR data with small angle X-ray scattering (SAXS) to obtain the basal spacing d(001) with a 2D proportional detector located at 0.55 m from the sample.

The measurements of hydroxyls were checked on a mica, a kaolinite and the studied smectite by comparing with the calculation from the structural formulas. For a reference smectite (Ca-Swy-1) well described in the literature, the NMR results are in good agreement with the published data that show in some cases a very large scatter. We found a ranking of the water content in agreement with the ion radius. However, whatever the ion, the interlayer water content is linearly related to the basal spacing d001 at relative humidity smaller than 75%.
ROLE OF CLAYS IN BITUMEN EXTRACTION FROM ATHABASCA OIL SANDS: FROM A RHEOLOGICAL PERSPECTIVE

Brad Komishke*1, Louxiang Wang2, and Kenleigh Pasay3

1Energy Business Unit, Teck Resources Limited, Calgary, AB, T2G 0R3, Canada: Bradley.Komishke@teck.com
2Applied Research & Technology, Teck Metals Ltd. Trail, BC, V1R 4S4, Canada;
3Energy Business Unit, Teck Resources Limited, Calgary, AB, T2G 0R3, Canada.

Similar to mineral processing, clay plays an important role in bitumen extraction from Athabasca Oil Sands using aqueous extraction processing which currently constitutes about 51% of total crude bitumen production and accounts for 29% of the total Canadian oil production. In this process, the oil sands ores are firstly mixed with hot water and chemicals to prepare slurry. This slurry is then pumped to a primary separation cell (PSC) through a 3-5 km transport pipeline where the bitumen liberates from the sand grain under extensive hydrodynamic shear. The liberated bitumen attaches to air bubbles and rises in the PSC to form the bitumen froth at the top of the PSC, while the coarse solids settle rapidly to the bottom of the cell to form the tailing. The middling stream, a mixture of sands, clay, fines, and residual bitumen, is sent to secondary flotation to maximize the recovery. The presence of clay together with fines in this process greatly increases the slurry viscosity, makes the bitumen liberation from sand grain more difficult and hinders the bitumen flotation to the top of the cell, rendering a poor bitumen recovery and even potential no recovery should strong gel form in the PSC.

The role of clay in oil sands processing was investigated in this study by measuring the viscosity/yield stress of oil sands slurry and middling to understand the effect of clay on bitumen liberation in the hydrotransport line and bitumen flotation in the PSC. The focus of this study is to illustrate the effect of clay on slurry and middling rheology and thus the extraction performance. Six different oil sands ores and three chemical aids were used. The results show that the yield stress increased sharply with the increase of fine/clay content in the middling, and a dramatic drop of bitumen recovery was observed with an increased middling yield stress. An elevated slurry viscosity can also be found when high fine/clay content ores were used, and the slurry viscosity dropped dramatically with the addition of the chemical aids by either altering the surface properties of clay and/or mitigating the multivalent cationic interactions with clay/fine. To better understand the effect of rheology on oil sands process, an industry standard batch scale extractor was used. The extraction results indicate the addition of the chemicals improved bitumen extraction recovery and froth quality when the slurry/middling viscosity was reduced.
PRELIMINARY RESULTS OF THE MICROBE-MINERAL INTERACTION IN ACIDO-HYPERTHERMAL ENVIRONMENTS, YELLOWSTONE NATIONAL PARK

Tae-hee Koo1*, Gill Geesey2, and Jin-wook Kim1

1Department of Earth System Sciences, Yonsei University, Seoul, Korea; 2Department of Microbiology, Montana State University, Bozeman, Montana, USA; *ktehee@yonsei.ac.kr; §correspondence: jinwook@yonsei.ac.kr

The biotic/abiotic process in mineralization is a common phenomenon in geothermal habitats. However, there is limited knowledge for the mechanism of the biotic/abiotic mineralization process in extreme environments, for example Yellowstone National Park, USA. The objective of the present study is to understand the microbe-mineral interaction particularly microbial metal-respiration in the acido-hyperthermal region.

The experiments were designed in two sets in order to distinguish the biotic and abiotic process. The first set is the mimic of the natural environment which contains only clay slurry and the hot-spring water (natural sample). The other set contains carbon source, yeast extract, and other ingredients to enhance the microbial activity (enrichment sample). The consequences of changes in mineralogy and chemistry were compared with the control. The pH of the growth medium was adjusted to pH=3.5, similar to the acidity in the field by adding sulfuric acid. The control was prepared in the same condition except adding the glutaraldehyde to eliminate the bacterial activity. Then whole samples were prepared in the serum bottle and N2 gas purged to maintain the anaerobic condition. The sealed serum bottle was incubated at 78 °C (water temperature of the sampling site) for each time point (0 – 12 months).

The x-ray diffraction (XRD) and scanning electron microscope with energy dispersive x-ray spectroscopy (SEM-EDS) were applied in the present study for mineral identification. The XRD data displayed the initial mineral assemblages of kaolinite, alunite, cristobalite, tridymite, and quartz. The changes in water chemistry of experiments for 0, 6, 12 months were measured by ICP-OES with filtrated supernatant. XRD verified the formation of new mineral phase only in the enrichment for the long-term incubation (6-12 months) suggesting that the microbial metal-respiration may be the important mechanism in the formation of new mineral phase. The possible biotic/abiotic mechanism in mineral alteration and formation as a by-product of microbe-mineral interaction in extreme environment will be discussed.
EFFICIENCY AND MECHANISM OF HEAVY METALS SORPTION ON GRAFTED KAOLINITES OF DIFFERENT STRUCTURAL ORDER

Anna Koteja*, Jakub Matusik

*Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Krakow, Poland: *jakub_matusik@wp.pl

Among other clay minerals kaolinite exhibits relatively low sorption capacity. This is mainly because the sorption takes place exclusively on the particle surface while the interlayer space of the mineral is not accessible for ions. Studies on organo-kaolinite derivatives gave the possibility of obtaining new nanomaterials which may be used in industry and environmental protection. The modification routes usually involve intercalation processes and grafting reactions. In particular, the exposed inner surface hydroxyls of the 1:1 layered minerals show reactivity in reactions with selected organic molecules. As a result materials with desired functionalities may be synthesized. Heavy metals are introduced into the environment both in natural processes and as a result of human activity. They are known to have a harmful effect on the living organisms. Therefore, the remediation of aqueous solutions contaminated with toxic metals is of environmental importance. The objective of the research was to test the sorption properties of kaolinite-based materials towards heavy metals. The cation sorption properties of kaolinites of different structural order were improved through interlayer grafting of selected aminoalcohols.

Two types of Polish kaolinites were selected for the experiment: well ordered from Maria III deposit (M) and poorly ordered from Jaroszów deposit (J). The modification involved a preparation of kaolinite-dimethyl sulfoxide pre-intercalates (MDMSO and JDMSO) and their further grafting with diethanolamine (DEA) or triethanolamine (TEA). The obtained MDEA, MTEA, JDEA, and JTEA materials were examined using XRD, IR and CHNS methods. The sorption equilibrium experiments of Cd(II), Pb(II), Cu(II) and Zn(II) were carried out in the 0.005-10.0 mmol/L concentration range at room temperature and initial pH 5. The kinetic experiments were performed in a system containing all four metals in equal 1 mmol/L concentration. The suspension samples were collected after 0.5, 1.0, 1.5, 2, 3, 4, 5, 6, 8, 10, 15 and 20 minutes from the beginning of the reaction. The heavy metals concentration was determined using AAS method.

The XRD patterns of grafted materials confirmed the presence of aminoalcohols in the interlayer space. The d001 values for MDEA, MTEA, JDEA and JTEA increased from 7.2 Å (pure kaolinite) to 10.2 Å, 10.8 Å, 10.1 Å and 11.0 Å, respectively. The formation of kaolinite-aminoalcohol derivatives resulted in an appearance of bands in the C-H stretching region (2800-3000 cm⁻¹) in the IR spectra. Moreover, significant changes of bands in the O-H stretching region (3600-3700 cm⁻¹) were also noticed. It was assumed that sorption improvement will be due to attraction of cations by the nitrogen lone electron pair of the grafted molecules. Therefore, the theoretical sorption capacity of the materials associated with nitrogen, calculated on the basis of CHNS analysis was equal to 184 mmol/kg (MDEA), 223 mmol/kg (MTEA), 122 mmol/kg (JDEA) and 323 mmol/kg (JTEA). It is worth to mention that the cation exchange capacity (CEC) of M and J sample was only equal to 19 mmol/kg and 47 mmol/kg, respectively.
The sorption capacity of modified materials showed increase as compared to the raw kaolinites and the sorption isotherms in most cases followed the Langmuir model. The most significant improvement was observed for the Cu(II) ions where the sorption increased from 65 mmol/kg (J) to 88 mmol/kg (JDEA) and 119 mmol/kg (JTEA). The high sorption capacity values were also noticed for MDEA: 73 mmol Cu(II)/kg and JTEA: 77 mmol Pb(II)/kg. The materials based on the J sample showed 2 or 3 times higher capacity as compared to the materials based on the M sample. Moreover, minerals modified with DEA in most cases showed better improvement of sorption capacity, than those modified with TEA, which arises from the fact that the steric hindrance effect is greater in the case of TEA molecules. The sorption improvement for the modified minerals was due to migration of cations into the interlayer space and their further attraction by the nitrogens lone electron pair. This was in particular efficient for Cu(II) ions which readily form Cu-aminoalcohol complexes in aqueous solutions. Such mechanism resulted in an increase of pH attributed to competitive protons sorption. The kinetic experiments indicated that the sorption equilibrium was achieved already in the first minute of the reaction, with exception of the JTEA sample where it was achieved after about 5 minutes. The experiment in the multi-element system showed that Cu(II) is more likely to bind with nitrogen than other tested metals. In all cases the reactions followed the pseudo-second order model.

This project was supported by the Polish National Science Centre under research project awarded by decision No. DEC-2011/01/D/ST10/06814.
ALTERATION OF CLAY MINERALS DUE TO INFLUENCE OF ACID AND ALKALINE SOLUTIONS ACCOMPANY RADIOACTIVE WASTE IN THE DEEP GEOLOGICAL LAYERS

Victoria V. Krupskaya*1,2, Sergey V. Zakusin2, Anatoliy P. Zhukhlistov1, Andrey A. Zubkov3
1Institute of Ore Geology, Mineralogy, Petrography and Geochemistry, Russian Academy of Sciences (IGEM RAS), Moscow, Russia; krupskaya@ruclay.com
2The Lomonosov Moscow State University, Moscow, Russia;
3JSC "Siberian Chemical Combine"

Radioactive wastes disposal is a quite difficult and demanding technological process. The most hazardous types of solid and liquid radioactive wastes are primarily exposed to solidification and then to underground disposal. However, this approach to big volumes of the low- and mid-level radioactive wastes is not reasonable in most cases. When this occurs subsurface waste injection seems to be the most rationale way of disposal. For this purpose liquid wastes are injected in deep layers that lie much deeper than horizons of water-supply and far from tectonic faults. Such reservoir beds are isolated by thick clay layers with a non-significant permeability and high adsorption capacity in order to prevent pollutants from vertical migration. Horizontal migration is limited by permeability of reservoir rocks.

Liquid radioactive wastes are basically complicated solutions of different pH with a significant amount of unstable isotopes. Obviously they can make a significant influence on a geological environment. Clay minerals are the most chemically reactive component of a geological environment; therefore they become affected by the influence of active solutions. The analysis of the possible transformations and synthesis of the new mineral phases makes it possible to predict migration process of the hazardous substances.

The present research is based on the investigation of clay minerals, extracted from sandy reservoir beds for low-level radioactive wastes. Samples for the study were collected at a safe distance from the radioactivity affected area. The research object is the influence of different level acidity and alkalinity solutions on the geological environment. One of the most important instances is the evaluation of possible transformations due to the interactions between rock and solutions and distinction of them from naturally occurring geological processes.

A suit of methods was used for investigation of the active solutions influence on the reservoir bed rocks. This suit included lithological description, XRF, XRD, IR, SEM, TEM, DTG – analyses, grain-size distribution analysis.

As a result of the work following changes of reservoir rock were revealed. First of all it concerns occurred in abundance process of leaching and synthesis of swelling (smectitic) clay minerals. Also it was found that well-sorted sands provide enabling environment for smectite synthesis. This observation can be explained by better permeability of such sands which leads to more efficient supply of material for reaction. Clay fraction detailed study gave us the information to distinguish neocrystallization due to catagenesis which were taking place in reservoir and buffer horizons. However on the background of naturally occurring processes some technologically induced alterations were found. It concerns neocrystallized smectite (fig. 1), for
which morphological features, crystal-structure particularities and stages of growth were described.

The obtained results allow us to suggest that isolation property of geological environment in the waste site remains sustainable. Feldspar and dark-colored minerals' leaching may cause increase permeability, however new formations of smectite aggregates in big pores most probably will neutralize this effect.

Figure 1. Micromorphological features of authigenic smectite aggregates: a, b – "technogenic smectite", formed under the influence of highly reactive waste solutions; c, d - "natural smectite" formed as the result of catagenetic processes.
A FORGOTTEN BAND–INFRARED SIGNATURE OF THE INTERLAYER WATER IN SMECTITES

Artur Kuligiewicz1*, Marek Szczérerba1, Arkadiusz Derkowski1, Vassilis Gionis2, and Georgios D. Chryssikos2

1 Institute of Geological Sciences, Polish Academy of Sciences, 31-002 Krakow, Poland: ndkuligi@cyf-kr.edu.pl
2 Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens 11635, Greece.

Fourier transform infrared spectroscopy (FTIR) is one of the most commonly used techniques for studying clay minerals and becomes widely used in fields like remote sensing and planetary research. Yet, the unambiguous distinction between the O-H stretching modes of structural hydroxyls (OHs) and interlayer H2O (OHw) in clay minerals, especially dioctahedral smectites, is still a subject of debate. At ambient hydration conditions, these modes overlap and impede both the correlation of the OHs spectra with the octahedral composition and the independent study of H2O confined in the interlayer.

Deuteriation may be an effective tool in avoiding the overlap problem, as it shifts the interlayer H2O bands by a factor of ~1.35 towards lower wavenumbers. Thus, if mild deuteration conditions are employed to prevent the formation of ODs, only OHs bands should be visible in the 3700-3000 cm⁻¹ region and the full spectrum of adsorbed D2O would be clearly deployed at lower wavenumbers (2700-2200 cm⁻¹). Deuteration was widely used in the vibrational study of clay minerals during the 70’ and 80’ (e.g. Farmer and Russell, 1971, Transactions of the Faraday Society 67, 2737-2749) but it has since become scarcely applied, perhaps forgotten.

The aim of this research is to re-evaluate deuteration as a tool to avoid the overlapping of OHs and OHw and to study independently both the layer and interlayer structure of clays at ambient hydration conditions. The study is based on attenuated total reflection infrared spectroscopy (ATR-IR) fitted with a custom-made environmental cell that allows for sample drying and hydration (deuteration) in situ, at ambient temperature, and with real-time infrared monitoring. A collection of six dioctahedral (high-charge beidellite HCB, low-charge beidellite LCB, high-charge montmorillonites SCa-3 and SAz-2, low charge montmorillonite SWy-2, low-charge nontronite SWa-1) and one trioctahedral (saponite, SAP) pure smectites in both Na- and Ca- cationic form, was studied to explore variability in terms of octahedral structure, total charge, charge location and interlayer cation. The FTIR results were confronted with molecular dynamics (MD) simulations of model smectite-H2O systems with different amounts of total layer charge and charge localization.

The FTIR data show that under the mild conditions employed, deuteration of OHs is not observed in any of the samples. Therefore, the interlayer ODw signature at 2700-2200 cm⁻¹ is a good proxy for the OHw signature in the 3700-3000 cm⁻¹ region. Further, the ODw spectra involve, besides the expected liquid-like bands of strongly H-bonded D2O in the interlayer, an additional sharp stretching feature at approx. 2680 cm⁻¹. By analogy, the spectrum of OHw in
H$_2$O-smectites should also involve a sharp OH$_w$ analog at approx. 3620 cm$^{-1}$ that belongs to interlayer water but overlaps with typical OH$_s$ bands (e.g. Al$_2$OH). As a result of this overlap, the sharp, 3620 cm$^{-1}$ OH$_w$ band is frequently missed in the recent literature, or attributed to OH$_s$.

The position of the high-wavenumber sharp OD$_w$ band (determined from the minima in the 2$^{nd}$ derivative) is found to depend mostly on total layer charge and not on charge localization (Fig. 1). The effect of interlayer cation is negligible for Na$^+$ and Ca$^{2+}$ smectites.

![Figure 1. Position of the high energy OD$_w$ stretching band in Na- and Ca-smectites as a function of layer charge.](image)

Comparison of the FTIR results with the MD simulations shows that the sharp, high frequency H$_2$O band originates from water molecules located close to the surface of the 2:1 layer and involved in very weak H-bonding. Mapping the distribution of water dipole moments as a function of the distance from the basal oxygen plane indicates that these surface H$_2$O species have one OH$_w$ group directed towards the basal plane (giving rise to the high energy band) while the other OH$_w$ vector points towards the bulk of the interlayer, in qualitative agreement with early reports about the pleochroism of the high frequency OH$_w$ (OD$_w$) band.

Acknowledgments

Financial support from the projects REGPOT/ATLAB and KRHPIS/Polynano (GSRT) are greatly acknowledged.
DRIFT SPECTROSCOPIC ANALYSIS OF <2μM CLAY SIZE FRACTION IN ARGILLACEOUS SOURCE ROCKS

Yingli Li1*, Jingong Cai1

1 State Key Laboratory of Marine Geology, School of Ocean and Earth Science, Tongji University, Shanghai 20092, China: liyingli369@126.com

The combination mechanism between clay minerals and organic matter combine in the argillaceous source rocks is always the focus concerned by researches. Infrared spectroscopy, especially for the Thermo-DRIFT technique, is a useful tool for this study. With this method, researchers can obtain the information of mineral groups and organic functional groups and their variation according to the temperature. Our study selected 17 mudstone samples from 2200 m~3500 m deep Neocene deposition in the Dongying Depression, East China. We extracted the organo-clay complex(<2μm) to study the bonding mechanism between clay minerals and organic matter by using the DRIFT technique, XRD (X-ray diffraction) and pyrolytic analyzing. We try to reveal the correlation relationship and evolution trend between clay minerals and organic matter which have a great influence on organic matter preservation and hydrocarbon generation and expulsion.

Smectite and illite are the major clay minerals in the sample, with an extra 0~23% kaolinite and chlorite. As the depth increases, the proportion of the smectite decreased from 75% to 8%, and that of the illite increases from 14% to 91%, indicating a transformation from smectite to illite. This process accelerates since the depth of 3100m. Pyrolytic analysis shows that the samples are rich in organic matter, with 1.37-6.75% TOC and increases significantly beneath the depth of 3100m. According to the DRIFT spectra, the OH vibrations within the clay structure and the CH vibrations coexisted, indicating that certain amount of organic matter is adsorbed by the clay minerals and combined together closely.

In addition, the CH vibrations (2926 cm⁻¹, 2852 cm⁻¹, 1481 cm⁻¹) as well as the OH stretching (3300 cm⁻¹) and bending (1630 cm⁻¹) vibrations assigned to adsorbed water appeared simultaneously in the infrared spectra. Further thermo-infrared spectroscopy analysis shows that these two kind of vibrations always existed with rarely any variation of the intensity at 250 °C. This result differs from that of the pure clay minerals and organic matter, which desorbed and pyrolyzed before 250 °C. As it is heated up to 550 °C, the intensity of OH and CH vibrations reduced or even disappeared; The synchronous fluctuation of these two vibrations indicates the organic matter combined with clay minerals through the hydrogen bond, namely the water bridge.

Further analysis on the infrared spectra shows that the vibration peak areas of CH (A2926+A2852) increases with depth, and the adsorbance accelerates beneath 3100 m. This means that the organic matter adsorbing capacity of the clay minerals increases consequently. Besides, beneath the 3100 m deep strata, the variation amplitude of OH bending vibrations is 5-11 cm⁻¹. After 3100 m, the OH bending shifts to a low frequency whereas the variation amplitude increases to 15-31 cm⁻¹, accompanied by the intensity degradation. This indicates that the hydration of clay interlayer adsorbed water gets weakened in this interval, giving rise to the
reduction of the interlayered organic matter adsorbance. Therefore, in the interval beneath 3100m, more organic matter was adsorbed to the external surface of the clay by the water bridge mechanism (Madejova 2003, Frost et al. 2008, Lu et al. 2011). Considering the clay mineral composition and evolution rules of TOC, we can finally conclude that the organo-smectite complex combined by the interlayer water is the main part in the argillaceous source rock above 3100m. In the interval beneath 3100 m, there is mainly organo-illite complex combined by the surfactant water. For this reason, the specific bonding mode and adsorption pattern between clay and organic matter change in different depth of the argillaceous source rocks according to the diagenesis.

This work was supported by National Natural Science Foundation of China (Grant No. 41072089, 41372130), National Oil and Gas Special Fund (Grant No.2011ZX05006–001).


YTTRIUM ADSORPTION ON SOLVATED EDGE SURFACES OF KAOLINITE: INSIGHTS FROM FIRST PRINCIPLE MOLECULAR DYNAMICS

Lei Li*1, Xiandong Liu1, Xiancai Lu1, and Rucheng Wang1

1School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, PR China

REE-bearing ionic-adsorption clays in south China have attracted significant attentions over the past decades. To explore the complexation mechanisms of REEs on kaolinite, we take Yttrium as an example and simulate complexation of Y^{3+} on the (010) and (110) edge surfaces of kaolinite by using first principle molecular dynamics technique. By analysing the results, we derive the complexes structures and interfacial hydrogen bonds. This study provides a fundamental basis for investigating REE adsorption onto clays.
ULTRASTRONG EPOXY NANOCOMPOSITES CONTAINING SELF-ASSEMBLED SYNTHETIC CLAY IN SMECTIC ORDER

Peng Li*1, Kevin L. White2, Chienhong Lin2, Anastasia Muliana2, Riichi Nishimura3, and Hung-Jue Sue1,2

1 Texas A&M University, Department of Materials Science and Engineering, College Station, TX 77843, USA: lipeng0503@gmail.com
2 Texas A&M University, Department of Mechanical Engineering, College Station, TX 77843, USA;
3 Corporate R&D Division, Kaneka Corporation, Osaka 530-8288, Japan.

Epoxy films containing self-assembly of 2D colloidal α-zirconium phosphate nanoplatelets (ZrP) in smectic order have been prepared via a simple, energy-efficient film fabrication process favorable to industrial practices. The ZrP nanoplatelets in epoxy form a chiral smectic mesophase with simultaneous lamellar order and helical arrangements. These epoxy nanocomposite films are transparent and flexible, and exhibit exceptionally high tensile moduli and strengths values. Implication of the present finding for a vast variety of engineering applications is discussed.
MECHANICAL AND GAS BARRIER PROPERTIES OF RUBBER/KAOLIN NANO COMPOSITES

Qinfu Liu*, Yinmin Zhang, and Hongfei Cheng

School of Geosciences and Survey Engineering, China University of Mining and Technology, Beijing 100083, China:*lqf@cumtb.edu.cn

Clay minerals, as an important natural phyllosilicate material, have many attractive structural features [1]. Especially the layered structure and high-aspect ratio characteristic can considerably improve the gas barrier property of polymer composites [2]. 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 [3].

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 nanokaolin 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:

\[
R_p = \frac{1 - \phi_f}{1 + \frac{\alpha}{2} \left(1 + \frac{s}{d_p}\right)^3 \phi_f \cos^2 \theta \xi}
\]

In the model, the author considered the main affect factors: volume fraction of filler \(\phi_f\), the aspect ratio \(\alpha\), the split between kaolin platelets \(s\), the diameter of kaolinite platelets \(d_p\), and the orientation angle of kaolin platelet \(\theta\). Meantime, the combination parameter \(\xi\) was introduced to describe the combination between aggregation of clay and polymer chains. 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 of kaolin platelets in the SBR matrix 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 in filled composite ranged between $30^\circ \sim 45^\circ$. Based on the above result, the author defined that the orientation angle of kaolin platelet is $45^\circ$ when the volume fraction at low level (20~40phr), otherwise, it is chosen as $30^\circ$ in the volume fraction at high level (50~70phr). The fitting of prediction value and measured value was shown in the Fig. 1., which shows that the prediction value is lower than the measured value at low volume fraction, but higher than that at high volume fraction.

![Fig. 1 Fitting between the prediction of model and value of experiment.](image)

**Acknowledgment**

The authors gratefully acknowledge financial support from The Natural Science Foundation of China (51034006).

**References:**

FERRIC CHLORIDE TREATMENT ON HALLOYSITE NANOTUBES

Shu-Ting Liu*1, Ao-Bo Zhang1, Xue-Gang Chen1, and Ying Ye1

1Ocean College, Zhejiang University, Hangzhou, 310058, PR China: liushuting@zju.edu.cn

Halloysite is an aluminosilicate clay mineral with natural nanotubular structures. It is a consensus that the properties of nano-materials are depended on their chemical compositions and microstructures. In this study, we systematically investigated the ferric chloride treatment on halloysite and the effects of ferric chloride treatment on the composition, morphology, and porous characteristics of halloysite. A certain amount of halloysite was added into FeCl3 solution. The mixture was placed in water baths at different temperature (25 °C, 60 °C, and 90 °C) for varying times (1 day, 7 days). The products were filtered, washed by distilled water, dried and grounded.

The chemical compositions of all samples are determined by XRF (Fig. 1). SiO2 and Al2O3 are main components of the halloysite samples with minor amount of Fe2O3, MgO, and others. The Fe content increased with the temperature rising due to the enhancement of the reaction proceeds by higher temperature. The Fe content increase from 1.7 % of halloysite to 14.0 % of sample after 7 days at 90 °C treatment, which may attributed to Fe3+ replace Al3+ in octahedral position. As time increased, the Fe content increase at three temperature set, which is ascribed to the degree of reaction is increased with reaction time. The ratio of Si/Al increased slightly over time due to dealumination. The MgO, CaO and Na2O content drastically decreased at day 1 and keep relatively stable over time, which illustrate that these constituents is more reactive than Al2O3 and SiO2. In addition, the K2O, N2O and TiO2 content basically kept constant at different temperature and time, because they have stable chemical properties in the halloysite.

The crystal structures of halloysite samples were investigated by X-ray diffraction. All samples exhibit similar XRD pattern with characteristic peaks of halloysite, which illustrate the bulk structure after the ferric chloride treatment has no significantly variation. The specific surface area and pore size of all samples were measured by a BET apparatus. As the temperature of ferrite treatment increased from 20 °C to 90 °C, surface area increased, and reached to maximum of 108.8 m2 g\(^{-1}\) after treated for 7 days at 90 °C. The surface areas of all samples increase with time due to the dissolution of [AlO6] octahedral layers. Likewise, the total, micro pore and mesopore volumes of halloysite increase with reaction time and temperature rising, respectively. However, the average pore size decline from 29.4 nm to 16.4 nm after treated 7 days at 90 °C, which is contributed to formation of more micropores. Ferric chloride treatment of halloysite is an effective method to increase the activity of halloysite though increasing the Fe content, which may bring the halloysite electromagnetic properties, and also make a new possibility of developing new properties of halloysite application for adsorption and catalysis proposes.
Fig. 1 Chemical compositions for halloysite samples before and after FeCl₃ treatment
UNDERSTANDING SURFACE ACIDITY OF GIBBSITE USING FIRST PRINCIPLE MOLECULAR DYNAMICS

Xiandong Liu¹*, Jun Cheng², Michiel Sprik², Xiancai Lu¹, and Rucheng Wang¹

¹State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, P. R. China: xiandongliu@gmail.com
²Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom

Using FPMD, we computed the acidity constants of the sites on the basal surface (i.e. (001)) and the edge surface (100) of gibbsite. For the basal surface, the results show that the surface hydroxyls almost have no contribution to the acid-base chemistry. Free-energy calculation indicates that ≡Al(OH₂)₂ (i.e. 6-fold Al) is the dominant site of the edge surface. These sites have very similar 1st and 2nd pKas in 9.0~10.0, which agrees with the experimental PZC range.
URANYL ADSORPTION AT MUSCOVITE SURFACE THROUGH MOLECULAR DYNAMICS SIMULATION: INTERFACIAL STRUCTURE AND ADSORPTION FREE ENERGY PROFILES

Narasimhan Loganathan*,1, Andrey G. Kalinichev1

1Laboratoire SUBATECH, Ecole des Mines de Nantes, 4, Rue Alfred Kastler, La Chantrerie, 44307, Nantes Cedex 3, France : *loganath@subatech.in2p3.fr

The structure of water films at charged clay surfaces is an essential factor controlling the physico-chemical properties of the adsorbed species which can provide fundamental insights into many important geochemical and environmental problems, such as the mobility of contaminants in near surface and subsurface environments. These properties, in turn, strongly depend upon the substrate structure and the nature of the charge compensating ions. The retention properties of aqueous ions in their interaction with clay minerals are pivotal in understanding, since clays are considered as natural and engineered barriers for the containment of toxic wastes.

Uranium is one of the most important long-lived radioactive species with high level of toxicity. The uptake of uranium by clay minerals is one of the principal retention mechanisms for their limited mobility from the storage sites. Molecular computer simulations represent an important tool capable of providing invaluable quantitative atomistic information that helps to understand the underlying physico-chemical processes and to interpret available results of surface-specific experimental measurements.

Classical molecular dynamics (MD) computer simulations using the CLAYFF force field were performed to investigate the UO$_2^{2+}$ adsorption at hydrated muscovite surface. New larger scale models of muscovite were constructed in order to more realistically represent the layer charge distributions in its structure by allowing a significant degree of disorder in the positions of isomorphic Al/Si substitutions. This yielded three different energetically favorable adsorption sites at the basal surface of muscovite. The technique of umbrella sampling calculations was employed to perform calculations of the potentials of mean force (PMF) in order to quantify the profiles of the free energy of adsorption and complexation of UO$_2^{2+}$ ions as functions of their distance from the surface at each of the three adsorption sites. Atomic density profiles and the topology of the interfacial hydrogen bonding network were also analyzed in detail.

The adsorption free energy profiles clearly indicate that for the UO$_2^{2+}$ ion there exist two significantly different adsorption sites characterized by significant difference in their equilibrium inner-sphere vs outer-sphere adsorption probabilities that are solely controlled by the nature of the adsorption site. At larger distance from the muscovite surface, irrespective of the adsorption sites, the energy barrier amounts to 14 kcal/mol. The simulation results are in good agreement with available experimental data and other simulations thereby providing a reliable comprehensive molecular view of the structure and energetics of UO$_2^{2+}$ ion at hydrated muscovite surface.
A representative snapshot of the simulated system indicating the outer-sphere adsorption of UO$_2^{2+}$ near the Al/Si substitution on the muscovite surface. Color codes: purple – U, red – O, white – H, yellow – Si, pink – Al.
Adsorption of Monovalent and Divalent Cations at the Clay–Water Interface Investigated by Molecular Computer Simulations

Narasimhan Loganathan*, Brice F. Ngouana Wakou¹, and Andrey G. Kalinichev¹

¹Laboratoire SUBATECH, Ecole des Mines de Nantes, 4, Rue Alfred Kastler, La Chantrerie, 44307, Nantes Cedex 3, France: *loganath@subatech.in2p3.fr

Safe and sustainable management of nuclear energy poses major scientific and engineered challenges, one of which is the necessity to make the environmental impacts of the long-term nuclear waste storage as small as possible. This requires detailed understanding and prediction of the migration and retention properties of radionuclides in deep geological formations of nuclear waste repositories.

The Callovo-Oxfordian rock formation of the French nuclear repository site is mainly composed of clay minerals (illite, smectite and interstratified illite/smectite), quartz, calcite and non-negligible amount of organic matter. The adsorption of water can change the properties of mineral surfaces, including protonation state, surface charge, structure and reactivity. Despite significant recent advances in surface specific experimental techniques, the results of such measurements are often difficult to quantitatively interpret in terms of the underlying physical and chemical processes. Meanwhile, molecular computer simulations have already become an important tool in the study of such interfacial systems and phenomena by providing otherwise unobtainable information on the fundamental molecular scale.

We performed classical molecular dynamics (MD) simulations using the CLAYFF force field for a series of hydrated monovalent (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺) and divalent (Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Ni²⁺, UO₂²⁻) cations at the surfaces of muscovite and montmorillonite to study the effects of the ionic size and charge on their adsorption behavior. In both the cases, the layer charge distributions were represented more realistically than in earlier simulations by developing a series of new clay models with larger surface area and disordered distributions of the Al/Si and Mg/Al isomorphic substitutions in the tetrahedral and octahedral layers of clay. The effects of this structural disorder on the surface adsorption and mobility of the cations have also been quantitatively investigated.

Atomic density profiles, near-surface atomic distributions and the structure and dynamics of the interfacial hydrogen bonding network were analyzed in detail for both substrate surfaces. The local structural disorder of the substrate charge distribution is clearly responsible for the significant redistribution of water molecules at the interfacial region. In addition, local differences in the layer charge play pivotal role in the distribution of hydrated cations at the interfacial region between inner-sphere and outer-sphere surface coordinations. The lateral diffusion of H₂O molecules is 35% reduced at the surface of muscovite in comparison with the bulk liquid state. The surface diffusion rate of aqueous ionic species is found to be not particularly sensitive to the degree of disorder in the substrate structure of montmorillonite. The calculated hydrogen bond lifetimes between H₂O – H₂O pairs are lower than between H₂O and the bridging oxygens of the muscovite surface.
A representative snapshot of illustrating how cation adsorption is controlled by the structural disorder of isomorphic Al/Si substitutions in the basal surface of muscovite mica. Color codes: red – O, pink – Al, yellow – Si, white – H, cyan – metal ions. For the sake of clarity, only one tetrahedral surface is shown.

Identification of different ion binding sites on the montmorillonite surface: “normal” hexagonal site without substitution (H$_n$), hexagonal site adjacent to a tetrahedral substitution (H$_t$), “normal” triangular site without substitution (T$_n$), substituted triangular site (T$_i$), and triangular site adjacent to a tetrahedral substitution (T$_{n'}$).
TRANSMISSION ELECTRON MICROSCOPY IN ANTIBACTERIAL CLAY INVESTIGATIONS

Sandra C. Londono*, Lynda B. Williams

School of Earth and Space Exploration, Arizona State University, AZ 85287, USA: sandralondono@asu.edu

Transmission electron microscopy (TEM) was used to observe physical contact between minerals and bacterial cells, assess particle size, track the changes in bacterial morphology and texture over time and, identify the composition of electron dense particles and abnormal zones inside bacterial cells. An antibacterial clay from the Colombian Amazon (AMZ) was compared to non-antibacterial clay (kaolinite API#5) when reacted with model Gram-negative and Gram-positive bacteria (E.coli ATCC 29927 & B.subtilis ATCC6633) respectively. The aqueous leachates of these clays are acidic (4.0-4.6), thus to observe the low pH damage on cells, E.coli was incubated under acidic conditions. Bacteria were suspended with clay and sampled in time series over 24 hrs. Cell separation from the bulk of the mineral suspension was required in order to observe cell aggregates. Samples were washed and fixed by standard methods using OsO2 and microtomed to 70 and 50nm sections. TEM imaging was performed using a Phillips CM12 TEM equipped with a Gatan model 791 CCD camera, using a primary energy of 80kV to avoid sample damage and obtain data from the surface. In addition, images in dark field, annular bright field, and bright field were acquired in the TEM/STEM ARM 200F JEOL, equipped with aberration correctors; with resolution is at the atom level (0.8Å). This instrument was used to obtain Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive Spectroscopy (EDS) using carbon-coated samples mounted on Au grids.

Results showed that the control acid solution caused severe cytoplasmic condensation on E. coli (Fig 1, B). AMZ clay induced textural/morphological changes in E.coli that did not appear when kaolinite API#5 was used, e.g., presence of dark particles inside cells (Fig 1, C), and membrane anomalies (Fig 1, C & D). EDS allowed recognition of clay nanoparticles (<100 nm) able to interact with cell membranes and exopolysaccharide. High contrast particles were also observed within the periplasmic space, although they were rounded and not plate-like. Si, Al and S were detected intracellularly. EELS spectra showed C and O, but no other elements were detected. The response of B.subtilis differed in that cells did not allow alien particles through their more complex cell envelopes.

Current results suggest that cytotoxicity is related to Si^{4+}, Al^{3+} and/or clay nanoparticles that compromise the membrane functions. The membrane can lose integrity by lipid peroxidation and replacement of structural Ca^{2+} and Mg^{2+} by Al^{3+}. The membrane functions and properties can be impaired by particles that physically limit the bacterial motility, and efflux response.

We gratefully acknowledge the use of facilities within the LeRoy Eyring center for Solid State Science at Arizona State University and the CLAS Bioimaging Facility - Electron Microscopy Division.
Fig. 1. *E. coli* images after treatment with AMZ clay. A. *E. coli* in the absence of clay. B. *E. coli* treated with 2.8 pH solution. Notice the cytoplasm condensation and the leaking of material C. *E. coli* treated with AMZ showing particles within the membrane. D. *E. coli* treated with AMZ with clays attached and dark zone inside the cell.
HALLOYSITE CLAY NANOTUBES USED FOR FABRICATION OF SUPERAMPHIPHOBIC SURFACES

Wei Ma*,1, Atsushi Takahara1,2

1International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan: m-wei@cstf.kyushu-u.ac.jp
2Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.

Due to the plenty of valuable usage, superamphiphobic surfaces have drawn much research attention in recent years. However, the fabrication of superamphiphobic surfaces is still quite challenging, because low surface tension liquids tend to wet and spread on most solid surfaces. Successful attempts to prepare superamphiphobic surfaces include introducing some special microstructures, such as nanofilaments, overhang structures, and re-entrant surface curvatures. But the fabrication of those structures is usually limited to particular substrates and relies on complicated process control, thus offering very little in the way of real utility. A more straightforward strategy to fabricate superamphiphobic surfaces is to prepare hierarchically structured coatings by using fluorinated polymer grafted inorganic nanoparticles. Whereas, the nanoparticles used in this method are mainly synthetic ones. Considering the undesirable energy consumption and harmful environment pollution during the nanoparticle synthesis process, naturally occurring nanomaterials, such as clays, are expected to have great advantages for fabricating superamphiphobic surfaces.

In this research, we report a superamphiphobic surface based on halloysite nanotubes (HNTs), which is an important clay type composed of Al₂Si₂O₅(OH)₄·nH₂O.¹ Owing to the needle like morphology of individual HNT, the agglomerates could form pincushion structure with connected air pockets. Therefore, HNTs can be potentially used for the fabrication of superamphiphobic coatings. To achieve low surface free energy, a copolymer of 2-(perfluorooctyl)ethylacrylate and dopamine acrylate² (Fig. 1d) was synthesized to modify HNTs surface. Upon dropping on a piece of paper, the surface modified HNTs formed a hierarchically structured surface (Fig. 1b and c) with an excellent superamphiphobicity (Fig. 1a).

References:
ADSORPTION OF 2-NAPHTHOL AND COPPER BY CATIONIC AND ZWITTERIONIC SURfactANTS MODIFIED MONTMORILLONITE: A COMPARATIVE STUDY

Lingya Ma*,1,2, Jianxi Zhu1, Hongping He1, Runliang Zhu1, and Qi Tao1

1CAS Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, P.R. China: malingya@gmail.com
2University of Chinese Academy of Sciences, Beijing 100049, P.R. China.

Organic modification is an important process method in using montmorillonite (Mt) for environmental protection. Organo-montmorillonites (OMt) are commonly synthesized by intercalating cationic surfactants into the interlayer space of Mt through cation exchange reaction. After modification, external and interlayer surfaces of montmorillonite change from hydrophilic to hydrophobic, making OMt high adsorption capacity toward organic contaminants. However, the adsorption capacity of OMt toward heavy metals dramatically decreases as compared with raw Mt. Zwitterionic surfactants contain both positively and negatively charged groups, and one may expect that they can be used to synthesize novel OMt, with the capacity of removing both inorganic and organic contaminants. In this work, hexadecyldimethyl (3-sulphonatopropyl) ammonium as one typical zwitterionic surfactant was used to modify calcium Mt (Ca-Mt). And the capacity of the resulting OMt (Z16-Mt) in adsorbing 2-naphthol and Cu were investigated. For comparison, the adsorption capacity of the two contaminants on hexadecyltrimethyl ammonium bromide modified Mt (C16-Mt) was studied as well.

Results of this work showed that both C16-Mt and Z16-Mt had good and similar capacity in adsorbing 2-naphthol and the adsorption isotherms were nearly linear within the studied concentration range, indicating a hydrophobic partition mechanism for uptaking 2-naphthol to both the two OMt. On the other hand, C16-Mt had much weaker capacity in adsorbing Cu as compared with Ca-Mt, e.g., 3.9 mg/g (C16-Mt) against 14.4 mg/g (Ca-Mt) at the same initial Cu concentration. In the case of Z16-Mt, however, the amount of Cu adsorption (12.9 mg/g) was only slightly lower than Ca-Mt. Adsorption of Cu on Z16-Mt was accompanied by evident release of Ca which implied that a certain amount of Ca ions still existed in the interlayer space of Z16-Mt, balancing the negatively charged groups of Z16. The electrostatic attractions between Cu ions and negatively charged groups of Z16 should be responsible for the adsorption of Cu on Z16-Mt. This work shows that the Z16-Mt as a new type of OMt can efficiently remove both heavy metal cations and organic contaminants from water.
INFLUENCE OF RYEGRASS ON PHYSICOCHEMICAL AND MINERALOGICAL PROPERTIES OF A FRAGIPAN SOIL

C. J. Matocha*¹, L. W. Murdock¹, A.D. Karathanasis¹, J.H. Grove¹, and M. V. Vandiviere¹

¹ Department of Plant and Soil Sciences, University of Kentucky, Lexington, KY 40546-0091, USA; cjmato2@uky.edu

Soils containing fragipan horizons occupy roughly 12% of the land area in the USA¹. These naturally occurring, impermeable horizons form as a result of weathering and cementation of silica and aluminum in association with iron². Fragipan horizons can be found at shallow soil depths. This limits row crop production due in large part to inhibited root growth and effects on plant available water³. There is a need to explore management strategies to degrade or remediate fragipan horizons.

Field experiments at the University of Illinois noted that annual ryegrass as a cover crop impacted properties of a fragipan horizon which allowed the subsequent row crops (corn and soybeans) to have a greater rooting depth⁴. While the growth of ryegrass is known to weather pure clay minerals and soil clays⁵,⁶, its effect on fragipan properties is unclear. The objective of this study is to evaluate the potential of ryegrass to degrade fragipan horizons in greenhouse studies using intact soil cores by evaluating changes in chemical, mineralogical, and physical properties.

Six 1 ¾ inch diameter soil cores were removed from a field site in Western Kentucky from a Zanesville silt loam (Typic Fragiudalf) to a depth of 120 cm. Three cores were seeded to annual ryegrass and the remaining three served as controls. All cores were incubated in a greenhouse during ryegrass growth under controlled conditions. The cores were sacrificed and the horizons determined using standard methods. Water-soluble elements (Si, Al, and K) and pH were determined immediately.

Visual inspection of the cores showed that ryegrass roots made it down into the fragipan horizon (Btx1). Soil pH values were 5.2 in the Ap and decreased to 4.4 in the Btx2 of the control columns. The cores planted to ryegrass exhibited pH values of 5.6 in the Ap and slightly decreased to 5.2 in the Btx2. Water-soluble Si values decreased 1.8-fold in the ryegrass treatments at the Ap horizon and these differences disappeared with depth when compared with control cores (Figure 1A). Potassium levels were also lower in ryegrass cores (Figure 1B). In contrast, solution Al was elevated in ryegrass treatments, particularly in the Ap and Btx2 horizons (Figure 1B). These patterns suggest that ryegrass might be altering the mineralogy of this soil and ongoing experiments using XRD and FTIR are evaluating this possibility. In addition, physical properties of the fragipan clods will be evaluated.
Figure 1. Water-soluble Si (A), Al (B), and K (C) from the control and ryegrass soil cores in different soil horizons.

INVESTIGATING THE SORPTION CAPACITY OF CLAY MINERALS FOR APPLICATIONS IN NUCLEAR WASTE REPOSITORY DESIGN

Edward N. Matteo\textsuperscript{1}, Andrew W. Miller\textsuperscript{1,2}, Jessica Kruichak\textsuperscript{1}, Melissa Mills\textsuperscript{1}, and Yifeng Wang\textsuperscript{1}

\textsuperscript{1}Sandia National Laboratories, \emph{Nuclear Waste Disposal Research and Analysis}, P.O. Box 5800, Albuquerque, NM 87185-0779, USA: enmatte@sandia.gov
\textsuperscript{2}Emporia State University, \emph{Dept. of Chemistry}, Emporia, KS 6680, USA

Clay minerals are likely candidates to aid in nuclear waste isolation due to their low permeability, favorable swelling properties, and high cation sorption capacities. A key challenge to the performance assessment (PA) of nuclear waste repository design is the need to model transport in materials over a time frame on the order of $10^6$ years. Over such a time frame, clay sorption capacity of radionuclide species has significant impact on repository design constraints, as well as evaluation of waste isolation performance.

Over the short term of the repository lifetime, establishing the thermal limit for clay minerals in a nuclear waste repository is a potentially important component of repository design, as flexibility of the heat load within the repository can have a major impact on the selection of repository design. For example, the thermal limit plays a critical role in the time that waste packages would need to cool before being transferred to the repository. Understanding the chemical and physical changes that occur in clay minerals at various temperatures above the current thermal limit (of 100 °C) can enable decision-makers with information critical to evaluate the potential trade-offs of increasing the thermal limit within the repository. Most critical is gaining understanding of how varying thermal conditions in the repository will impact radionuclide sorption and transport in clay materials either as engineered barriers or as disposal media.

In the long term of the repository lifetime, transport behavior of key anionic species, like Iodine-129, can have important bearing on repository performance. Since the basal surface of clay minerals has a fixed negative charge, it is generally assumed that anionic radionuclides are repelled by clay surfaces. This has led to treating anions as non-reactive with clay, which, in turn, translates into anions –by virtue of having lowest retention times and thus fastest transport – being calculated as the largest dose contributors at times $>$10,000 years. However, there are reports in the literature showing that many anions are retarded in clays relative to tritiated water. It is assumed that the retardation occurs due to sorption, which is often quantified with a $K_D$ value. These values are small; for example, iodide $K_D$ values have been reported from $\sim0.001-2.9$mL/g. While these values are relatively low, the assumption that the iodide will have low retention can lead to overestimation of iodine dose in a performance assessment.

Current thought assumes that iodide does not interact directly with clay minerals due to electrical repulsion between the iodide and the negatively charged clay layers. However, a growing body of work indicates a weak interaction between iodide and clays may exist under certain conditions. A reasonable explanation for such an interaction is still lacking. Here we report a conceptual model for iodide interaction with clays by considering clay mineral structures and emergent behaviors of chemical species in confined spaces. To approach the problem, a suite
of clay minerals was used with varying degrees of isomorphic substitution, chemical composition, and mineral structure. Iodide uptake experiments were completed with each of these minerals in a range of swamping electrolyte identities (NaCl, NaBr, KCl) and concentrations. Iodide uptake behaviors form distinct trends with cation exchange capacity and mineral structure. These trends change substantially with electrolyte composition and concentration, but do not appear to be affected by solution pH. The experimental results suggest that iodide may directly interact with clays by forming ion-pairs (e.g., NaI(aq)) which may concentrate within the interlayer space as well as the thin areas surrounding the clay particle where water behavior is more structured relative to bulk water. Ion pairing and iodide concentration in these zones is probably driven by the reduced dielectric constant of water in confined space and by the relatively high polarizability of the iodide species. This new conceptual model has far-reaching implications to the capability of clay materials as a geo-membrane for anion exclusion and isolation.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s Nation Nuclear Security Administration under contract DE-AC04-94AL85000. SAND Number: 2014-2051A
ANALYSIS OF $H_2O$ EVOLVED DURING PYROLYSIS OF CLAY-MINERAL BEARING ROCKS ON MARS

Amy C. McAdam$^1$, Paul R. Mahaffy$^1$, Douglas W. Ming$^2$, Anna E. Brunner$^3$, P. Douglas Archer$^4$, Jennifer C. Stern$^1$, Christopher R. Webster$^5$, Heather V. Graham$^1$, Heather B. Franz$^3$, Brad Sutter$^4$, Richard V. Morris$^2$, Jennifer L. Eigenbrode$^1$, David L. Bish$^6$, Sushil K. Atreya$^7$, and Laurie A. Leshin$^8$.

$^1$NASA Goddard Space Flight Center, Greenbelt, MD 20771: Amy.McAdam@nasa.gov;
$^2$NASA Johnson Space Center, Houston, TX, 77058;
$^3$Center for Research and Exploration in Space Science & Technology, NASA Goddard Space Flight Center, Greenbelt, MD 20771;
$^4$Jacobs, NASA Johnson Space Center, Houston, TX 77058;
$^5$Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109;
$^6$Department of Geological Science, Indiana University, Bloomington, IN 47405;
$^7$Dept. of Atmospheric, Oceanic and Space Sciences, Univ. of Michigan, Ann Arbor, MI, 48109;
$^8$Dept. of Earth and Environmental. Sci., Rensselaer Polytechnic Institute, Troy, NY 12180.

Alteration signatures recorded in the secondary mineralogy of martian materials provide an important mechanism to assess martian environmental history and habitability. Secondary phyllosilicates, especially smectite clays, have been a focus because they are expected from alteration of basalts on Mars, they can give insight into alteration conditions, and in terrestrial settings clay mineral-rich deposits often sequester organic compounds. Clay minerals have been observed or inferred in martian materials from a variety of datasets. Recently, the Mars Science Laboratory (MSL) drilled two samples from the Sheepbed mudstone at Yellowknife Bay, at sites termed John Klein (JK) and Cumberland (CB) and delivered portions to the Chemistry and Mineralogy (CheMin) instrument and the Sample Analysis at Mars (SAM) instrument suite. CheMin found the first evidence of smectite clays in situ X-ray diffraction (XRD), in addition to basaltic primary minerals, magnetite, Ca-sulfates, a substantial X-ray amorphous component (~30 wt%), Fe-sulfides and akaganeite [1]. The XRD patterns indicate that these smectites are trioctahedral and comprise ~20 wt% of the mudstone [1]. SAM detected $H_2O$, $CO_2$, $O_2$, $H_2$, $SO_2$, $H_2S$, $HCl$ and other trace gases during pyrolysis. Here we focus on analyses of evolved $H_2O$.

SAM consists of a quadrupole mass spectrometer (QMS), a gas chromatograph (GC), and a tunable laser spectrometer (TLS), connected by a gas processing system. These instruments analyze volatiles evolved on heating samples, or ingested atmospheric gases. QMS analysis of evolved volatiles comprises SAM’s Evolved Gas Analysis (EGA) mode. EGA data are acquired over the entire run, but volatiles from a selected temperature (T) range can also be sent to either the GC or TLS. The TLS can provide the abundances and isotopic compositions of $CO_2$ and $H_2O$. Samples were heated from ~45 to ~870°C at 35°C/min. Evolved gases were carried to the QMS by He flowing at 0.8 sccm. The pressure of He in the oven was ~25 mb. SAM-like EGA lab systems were used to analyze phyllosilicate reference materials under SAM-like conditions.

$H_2O$ was the most abundant volatile released from JK (1.8-2.4 wt%) and CB (1.7-2.5 wt%) [2]. A majority comes off in a wide low-T peak <~450°C (Fig. 1). The low-T $H_2O$ has many potential sources, including adsorbed $H_2O$, smectite interlayer $H_2O$, structural $H_2O/OH$.
from bassanite, akaganeite or oxychlorine phases, and H\textsubscript{2}O/OH from amorphous phases in the sample [2]. The high-T H\textsubscript{2}O peak near 750°C is consistent with H\textsubscript{2}O from the dehydroxylation of the smectite detected by CheMin. Comparison with SAM-like EGA data from a variety of clay mineral reference materials indicates that a trioctahedral smectite, such as Fe-saponite, is consistent with the high-T H\textsubscript{2}O evolution (Fig. 1). The Fe-saponite griffithite has an 02l XRD band position similar to that reported for CheMin analyses of JK and CB samples [1]. The abundances of smectite clays indicated by SAM H\textsubscript{2}O data also agree well with those determined from CheMin XRD patterns. If the abundances of H\textsubscript{2}O released between 450 and 835°C are attributed to smectite dehydroxylation, the wt% of smectites indicated in the samples analyzed by SAM (~16-17 ± 11-12 wt%) [2] is consistent with the ~18-22 ± 9-11 wt% obtained from CheMin data [1,2].

The D/H ratio of the H\textsubscript{2}O evolved from the mudstone samples was also determined by SAM, both using the TLS and, independently, the QMS [3]. H\textsubscript{2}O evolved above ~450°C, likely dominated by smectite dehydroxylation, showed an H\textsubscript{2}O D/H value lower than that of the current martian atmosphere, though still very high compared with the terrestrial value. H\textsubscript{2}O evolved at lower Ts showed a higher D/H, closer to that of the current martian atmosphere [3]. This lower T H\textsubscript{2}O likely had contributions from H\textsubscript{2}O that is more readily exchanged with the atmosphere such as adsorbed H\textsubscript{2}O and smectite interlayer H\textsubscript{2}O. Assuming the high T H\textsubscript{2}O is dominantly from smectite dehydroxylation, this H\textsubscript{2}O is likely to represent the water from which the smectites originally precipitated. Recent K/Ar formation age dating of the Yellowknife Bay rocks indicates an age near 4 Gyr [4], placing an approximate constraint on smectite formation age. If the D/H of the original martian water reservoir was Earth-like, the D/H of the high-T H\textsubscript{2}O implies that a substantial amount of the H fractionation in the current martian atmosphere had happened by the time the clay minerals at Yellowknife Bay formed. Further fractionation was needed to obtain the higher values of the current atmosphere.

The presence of the smectite clays in the Sheepbed mudstone indicates relatively high water activity, with fluids having near neutral pH and a low salinity. The fact that these clays are not chlorites indicates that their formation environment (and post formation environments) did not exceed ~80°C [e.g., 1]. These smectite clays are a key indicator of a past habitable environment at Yellowknife Bay [e.g., 1, 5]. Comparison of the isotopic composition of the H\textsubscript{2}O evolved during thermal dehydroxylation of the smectites with that of the current martian atmosphere and predictions of the original water inventory may also provide insight into atmospheric change on Mars.

SPECTRAL TRENDS IN AQUEOUSLY ALTERED CM/CI METEORITES

M. M. McAdam*, J. M. Sunshine1, K. T. Howard2, and T. M. McCoy3

1Department of Astronomy, University of Maryland, College Park, MD 20742: mmcadam@astro.umd.edu
2Department of Physical Sciences, Kingsborough Community College, Brooklyn, NY
3National Museum of Natural History, Smithsonian Institution, Washington D.C 20560

Certain families of carbonaceous chondrite meteorites are characterized by the abundant presence of phyllosilicates [e.g. 1]. CM ( Mighei type) and CI ( Ivuna type) carbonaceous chondrites groups are two examples. CM/CI meteorites span a range of degrees in aqueous alteration from highly altered meteorites (e.g. CI1 Orgueil and CM1 SCO 06043) to less altered meteorites (e.g. CM2 Murchison and CM2 QUE 97990). The highly altered meteorites consist of ~90 volume percent (vol. %) or greater phyllosilicates while the least altered meteorites have phyllosilicate abundances of ~60 vol. % [2]. Position sensitive X-ray diffraction (PSD-XRD) experiments [2] describe the compositional and structural nature of the phyllosilicate phases within the meteorites and the total degree of alteration. A large suite of well characterized meteorites are here studied in mid-infrared (MIR) reflectance spectroscopy to determine the spectral manifestations of the trends in aqueous alteration described by [2] and recently reviewed by [3].

CM/CI meteorites underwent pervasive [3], low temperature [4, 5] aqueous alteration on their parent body(ies). Alteration occurred on asteroids post accretion due to radiogenic heating allowing co-accreted water to become liquid. Matrices, Fe-rich silicates, altered followed by chondrules (Mg-rich silicates, Fe-Ni metal and glass) [1, 3]. The first stage of alteration produced Fe-rich phyllosilicates with platy crystals. As magnesium from the chondrules was added to the phyllosilicates, a recrystallization occurred forcing the mineral structure to chance from a dioctahedral phyllosilicate (Fe³⁺ in 2/3 of M sites) into a trioctahedral phyllosilicate (Mg²⁺ and Fe²⁺ occupying all three M sites). The Mg-rich trioctahedral clay is very fine grained [1] and poorly crystalline [2]. The degree to which a particular meteorite is altered could depend on factors including the total accreted water in the asteroid [5] or location within the asteroid [5]. Additional mechanisms such as catastrophic break-up could have halted alteration prematurely. Trends in degree of alteration and mineralogy are also seen in the reflectance spectra of CM/CI meteorites.

Previous visible/near-infrared (NIR) studies of CM/CI meteorites yield few connections between the spectra and mineralogy due to the dearth of spectral features [6]. The MIR reflectance spectra of three representative meteorites are presented in Fig. 1. Spectra of meteorite powders (grain size <30 µm) were obtained from the NASA/Keck Reflectance Laboratory (RELAB) FTIR spectrometer with resolution of 4 cm⁻¹. One particular region of interest is the 1150-800 cm⁻¹ (10-13-µm) feature. This feature has been tentatively interpreted as a combination of tetrahedral layer vibrations of phyllosilicates [7] and the ν1 fundamental stretching vibration in olivine [8]. The highly altered meteorites, typically with larger abundances of Mg-rich phyllosilicates are dominated by a peak closer to 875 cm⁻¹ (11-µm) while the least altered meteorites, with more unaltered silicates are dominated olivine and have a characteristically lower wavenumber (longer-wavelength) peak. The peak position of this feature is correlated with degree of alteration (Fig. 2) and can be used to remotely identify alteration on asteroids.
trends in the nature and composition of phyllosilicates appear in other regions in addition to the 10-13-µm region. Between 800-400 cm\(^{-1}\), highly altered meteorites have a ‘W’ shaped feature, which may be due to the OH-bending vibrations in Mg-rich trioctahedral phyllosilicates (16-µm, 625 cm\(^{-1}\))[6] and the SiO\(_4\) bending vibration at 500 cm\(^{-1}\) (20-µm) [6]. A single feature at 525 cm\(^{-1}\) (19-µm) in the least altered meteorites is thought to be produced by the of the dioctahedral phyllosilicates [9].

The most difficult aspect of these studies has been assignment of spectral features, due to a lack of relevant analog material. Terrestrial phyllosilicates are structurally and thus spectrally dissimilar to the poorly crystalline Mg-rich meteoritic phyllosilicates. Furthermore, while meteoritic phyllosilicates are described as Mg- and Fe-rich, they are certainly not endmember compositions. Terrestrial Fe-rich phyllosilicates almost always have Fe abundances above that of the meteorites.

Trends in the mid-infrared spectra of the CM/CI meteorites can be used to interpret the spectra of dark, primitive asteroids. These asteroids are thought to be aqueously altered [e.g. 10] but have characteristically low albedos and few features in the NIR. Using these insights from the meteorite spectra and mineralogy with archived space telescope data in the mid-infrared (e.g. *Spitzer Space Telescope*), it may be possible to constrain the water abundance in primitive asteroids. Additionally, by observing collisional families, it may be possible to constrain aqueous
CLAYS AND CLAY MINERALS ON MARS: INDICATORS FOR AQUEOUS PROCESSES AND HABITABLE ENVIRONMENTS

Douglas W. Ming*

Astromaterials Research and Exploration Science Directorate, Mail Code KA, 2101 NASA Parkway, NASA Johnson Space Center, Houston, TX 77058, USA; douglas.w.ming@nasa.gov

For centuries humans have looked to the skies and have asked the question - are we alone? Does life exist elsewhere in the universe or is it unique here on Earth? Mars has been the focus of efforts to address this question because it is the most Earth-like planetary body that we can explore with our current state of technology. Nearly 40 years ago, NASA sent the twin Viking landers to the surface of Mars to search for the evidence of life. Viking instruments did not detect life, but the data returned by the X-ray Fluorescence Spectrometers (XRFS) provided the first geochemical information on martian surface materials. Viking “soils” had a basaltic composition enriched in S and Cl, suggesting a “salt” component to the martian fines. However, the Viking payload did not have instrumentation to characterize the mineralogy of these fines.

Mars robotic exploration went on a 30 year hiatus until 1997 with the landing of Pathfinder and minirover Sojourner and the arrival of Mars Global Surveyor (MGS) in orbit. A flotilla of spacecraft since 1997 has vastly improved our mineralogical understanding of surface materials. Orbiters equipped with IR spectrometers have provided new insights on the distribution of clay minerals on Mars, indicating that clay mineral formation was widespread during the early history of the planet. Evidence for the importance of clay mineralogy for deciphering formation conditions on Mars has been amassing in the last decade.

I have had the fortune to be a co-investigator on five spacecraft sent to the surface, although one of those was the ill-fated Mars Polar Lander in 1999. The Mars Exploration Rovers Spirit and Opportunity carried Mössbauer and thermal emission spectrometers as the first mineralogical instruments to operate on the surface. Mössbauer discovered several Fe-bearing phases that formed via aqueous processes including jarosite, goethite, hematite, ferric-sulfate, nanophase ferric oxides (npOx), and Mg-Fe carbonate. Spirit and Opportunity discovered that water has played an important role in the evolution of surface materials. Phoenix was the next lander, carrying a payload that would delight a soil chemist, including the Wet Chemistry Lab with a suite of ion selective electrodes. Phoenix surprised scientists with the discovery of alkaline “soils” containing about 3 wt. % calcium carbonate and 1 wt. % perchlorate salts.

The most recent spacecraft to reach the surface is the Mars Science Laboratory rover Curiosity. Curiosity houses a sample analytical laboratory including the CheMin instrument as the first X-ray diffraction unit to operate on another planetary surface. The most important discovery so far is the occurrence of smectite in a mudstone that appears to have formed in an ancient lakebed. The mudstone preserves evidence of an environment that would have been suited to supporting life. Other secondary minerals that may have formed in the presence of water in the mudstone include bassanite, anhydrite, magnetite, hematite, akaganeite, pyrrhotite, and halite. A large amount of amorphous material was also detected by CheMin in the mudstone...
along with primary minerals such as plagioclase, Fe-forsterite, augite, pigeonite and orthopyroxene.

Laboratory analyses of martian meteorites have greatly improved our knowledge of the geochemical, mineralogical, and chronological characteristics of materials from the martian crust. Although these meteorites exhibit primary mineralogies, several contain minerals strongly indicating indigenous aqueous processes on Mars, showing that water did at least have some influence on martian crustal materials. The martian meteorites provide our only “hand samples” of Mars, but they are all igneous and are poorly representative of martian sediments and weathered materials. These surface materials beg for a sample return mission.

The discovery and characterization of clays and clay minerals is critical to our understanding of aqueous processes and habitability on Mars. A spacecraft akin to Curiosity will launch in 2020 to explore an astrobiologically relevant ancient environment and to decipher its geological history and habitability, assess the biosignature preservation potential within the selected geological environment, search for potential biosignatures, and cache samples as the first step in returning samples to Earth. Clay mineralogy has and will continue to play an important role in the exploration of Mars!
IMPROVEMENT OF METHYLENE BLUE ADSORPTION TEST METHODS FOR BENTONITE

Youko Miyoshi*1, Yu Horiuchi1, and Tetsuichi Takagi1

1Mineral Resource Research Group, Institute for Geo-Resources and Environment, National institute of Advanced Industrial Science and Technology (AIST), Central-7, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8567, Japan: youko-miyoshi@aist.go.jp

Bentonite is fine-grained clayey materials composed mainly of montmorillonite. The content of montmorillonite in bentonite has been estimated by the amount of methylene blue adsorption, because the methylene blue molecules replace exchangeable cations present on the basal plane surfaces of montmorillonite platelets. Methylene blue adsorption test method has generally been used for determining either cation exchange capacities (CEC) or surface areas of bentonite (Kahr and Madsen, 1995, Hang and Brindley, 1970). As the practical industrial use, methylene blue adsorption capacity is employed for quality control of mining products (Kaufhold et al., 2002, Kahr and Madsen, 1995). In Japan, a methylene blue adsorption test method of bentonite was established by Japan Bentonite Manufacturers Association Standard (JBAS) in the 1970s, but it is becoming obsolete. Bentonite will be used for a buffer material of radioactive waste repositories in Japan. The methylene blue adsorption test will be one of the important methods to assess the safety performance of the repositories. Our purpose of this study is to renew the methylene blue adsorption test method of JBAS and publish a new method acceptable for JIS (Japanese Industrial Standards).

We have investigated the methylene blue adsorption test method in 13 manufacturers of bentonite in Japan. Among the 13 manufacturers, 10 manufacturers were conducting a methylene blue adsorption test method. Among the 10 manufacturers, 8 manufacturers were conducting their own procedures based on the conventional method established by JBAS. It was recognized that some of the procedures in the method were different from each manufacturer. The different procedures were (1) drying temperature and time of bentonite samples, (2) preparation of methylene blue solution, (3) dispersion, (4) decision of end point.

(1) Drying temperature and time: In the conventional JBAS method, drying temperature was defined as 105 ~ 110 °C and drying time was not defined. In some manufacturers, bentonite samples were dried under 105 °C for 18 ~ 24 hours, while in other manufacturers, under 110 °C and 2 ~ 3 hours. (2) Preparation of methylene blue solution: In the conventional JBAS method, the moisture content of regent methylene blue powder was determined before making of the solution. In some manufacturers, the moisture content was determined before the making, while in other manufacturers, the moisture content was not determined. (3) Dispersion: In the conventional JBAS method, a 2 % solution of anhydrous tetrasodium pyrophosphate (TSPP) was used both for exchange of Ca²⁺ and Mg²⁺ by Na⁺ and for dispersion. In some manufacturers, the solution of TSPP was used, while in other manufacturers, pure water for dispersion. As the dispersion procedure, both ultrasonic treatment and boiling were described in the conventional JBAS method. In some manufacturers, the dispersion was performed by ultrasonic treatment, while in other manufacturers by boiling. (4) Decision of end point: In the conventional JBAS method, an end point was decided by turquoise halo appearing around peripheries of droplets on
a filter paper. In some manufacturers, the end point was decided by weak halo, while in other manufacturers, by large halo. In other manufacturers, the end point was decided by around 15% halo of the diameter of the droplet on the filter paper.

Among the 10 manufacturers which were conducted a methylene blue adsorption test method, 2 manufacturers were conducting a colorimetric method using absorptiometry, which was not defined by the JBAS. In the colorimetric method, excessive amounts of methylene blue solution were added in the primary solution and the amount of methylene blue in supernatant solution was determined by absorptiometry. In the method, the difference between the amount of methylene blue in the primary and supernatant solutions can be regarded as the amount of methylene blue adsorbed in bentonite. The colorimetric method minimizes an ambiguity of the end point decided by turquoise halo appearing around the droplet on the filter paper and errors arising from differences of individual skills. The colorimetric method is expected to be a potential method for JIS.

Reference
MINERALOGICAL TRANSFORMATION AND TRANSPORT INSIDE ACID MINE TAILINGS AND IN NEARBY RIVER SEDIMENTS IN ZIMAPAN, MEXICO

Luke Morgan*1, Youjun Deng1

1Department of Soil and Crop Sciences, Texas A&M University, College Station, TX 77843-2474, USA: icbneumon@tamu.edu

Currently, more than 6 million tons of mine tailings have accumulated in and around surrounding areas of the city Zimapán, Mexico. Thus, exposing large amounts of oxidizing pyritic material containing high levels of heavy metals and metalloids As, Zn, Cu, and Pb, which make the confinement and remediation of the tailings difficult and costly. In addition to dissolved forms in acidic drainage solutions, formation of colloids and nanoparticles significantly affect the transformation and transport of heavy metals through adsorption/desorption and incorporation/dissolution reactions. The mineral transformation can form heterogeneous mixtures of amorphous and crystalline phases. The quantities, chemical species, and mobility of heavy metals in these new phases are generally poorly understood. Colloids and nanoparticles containing heavy metals are susceptible to dynamic environmental changes because of their large surface area, structural defects, and incorporation of several elements into their structure. The objectives of this study were 1) to characterize the newly formed colloids and nanoparticles in the Zimapan mine tailings and nearby river sediments, 2) to identify and quantify heavy metals adsorbed and incorporated by these new phases, and 3) to investigate the transport of the contaminant particles in the river.

Seventeen tailing and river sediment samples were collected at three tailing heaps and at nearby streams. One of the streams, Rio Toliman, is only a few meters from the heaps (Fig. 1, Right). The tailing samples were selected based on their oxidation status, stratification, color, and solubility (Fig. 1, Left). Analysis of collected tailings consisted of fundamental and comprehensive mineral characterization by size fractionation, XRD with and without treatments, SEM, TEM, FT-IR, and XRF.

Samples contain ~20% carbonates, and up to 1.3% arsenic by mass. The oxidized samples exhibited low pH’s near 2, while silicate minerals such as pyroxenes ((Mg,Fe,Ca)Si2O6), amphiboles (i.e. hornblende Ca2(Mg,Fe,Al)3(Al,Si)8O22(OH)2), and clay minerals were dissolved by acidic conditions resulting in low CEC ~25 cmol/kg. According to XRD and SEM/EDS analysis, samples have an abundance of iron oxides, Cu, Pb, As, and Zn. Observed intermediate and stable mineral phases from the oxidation of sulfide and arsenide minerals in the tailings included: melanterite [FeSO4·7H2O], rozenite [FeSO4·4(H2O)], gypsum [CaSO4·2H2O], starkeyite [MgSO4 · 4H2O], kieserite [(MgSO4·H2O)], gunningite [(Zn,Mn)SO4·H2O], copiapite [Fe2+Fe3+4(SO4)6(OH)2·20H2O], jarosite [KFe3(OH)6(SO4)2], scorodite [FeAsO4·2H2O], goethite and hematite. Among the soluble sulfate phases, it appeared that most of them form separated, relatively pure minerals without incorporating other heavy metals, except the isocrystals. Manganese is a common accessory element in the gunningite. Lead was observed as a trace element in the jarosite. Nearby water sediments contained clays such as montmorillonite and vermiculite, but still having traces of jarosite, silica, and galena (PbS). The size of the colloids...
and nanoparticles (Fig. 2) in the river sediments suggested that they might be mobilized under favored conditions, which can be contamination source of the downstream water and sediments.

Figure 1. Mineral transformations created distinct stratifications in mine tailing heaps. A) Middle, yellow strata consisting mostly of jarosite, while the bottom gray strata has high amount of scorodite. B) The Toliman River runs near a large heap of mine tailings.

Figure 2. A) River sample containing particles of pyroxenes with globular silica and other colloids magnified in image B.  C) Jarosite located in the yellow strata seen in figure 1. D) Scorodite located in the gray strata shown in Figure 1. The small size of the particles implied that they might be easily mobilized and transported into downstream water bodies.
THE ANTIBACTERIAL ACTIVITY OF MINERALS PROVIDES NEW INSIGHTS ON METAL TOXICITY

Keith D. Morrison*, Lynda B. Williams¹

¹School of Earth & Space Exploration, Arizona State University, Tempe, AZ 85287-1404: keith.morrison@asu.edu

Recent evidence reveals that certain clay mineral deposits rich sub-micron iron sulfides have the ability to prevent pathogenic bacterial growth. These antibacterial clays have been shown to prevent the growth of a broad spectrum of bacteria, including methicillin-resistant Staphylococcus aureus MRSA and extended-spectrum beta lactamase (ESBL) Escherichia coli (antibiotic resistant strains) when tested in vitro. Our previous results revealed that mM levels of Fe²⁺, Fe³⁺, and Al³⁺ are leaching from the clays at low pH (2.8-3.1) resulting in increased intracellular iron and the precipitation of iron oxides upon cell death. The majority of studies on bacterial metal toxicity are performed at circumneutral pH (6-8) in buffered nutrient broth which greatly effects metal solubility. The generation of reactive oxygen species (ROS), damage to proteins and membrane lipids along with metal MIC (minimum inhibitory concentration) and MBC (minimum bactericidal concentration) levels have yet to be determined at conditions relevant to the clay bactericide. This research tests the hypothesis that mixed-layered clay minerals containing sub-micron iron sulfides release transition metals at low pH, while generating ROS resulting in lipid peroxidation, protein oxidation and intracellular metal precipitation.

E. coli (ATCC 25922) was reacted with clay suspensions and clay leachates (aqueous solutions equilibrated with clays for 24 hrs). Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the soluble transition metals that are leaching from the clays. Bioimaging using scanning transmission electron microscopy-electron energy loss spectroscopy (STEM-EELS) was used to investigate the precipitation of intracellular mineral particles. Reactive oxygen species (ROS) generated by minerals and mineral leachates were measured using a spectrophotometric hydrogen peroxide assay (H₂O₂) assay. Intracellular ROS and lipid peroxidation were measured using the fluorescent probes, CellROX® Deep Red and BODIPY® respectively. Protein oxidation levels were determined by measuring carbonyl groups using 2,4-dinitrophenylhydrazine (DNPH). E. coli metal MIC and MBC concentrations, pH and Eh measurements of mineral leachates, Fe²⁺, Fe³⁺ and Al³⁺ were determined in 10 g/l Luria-Broth.

Antibacterial susceptibility testing and ICP-MS elemental analysis of the leachates reveals that low pH (2.8-3.1) samples containing mM levels of soluble Fe and Al are antibacterial. The acidic pH is not the only factor contributing to the antibacterial effect. The intracellular particles observed upon cell death were determined to be Fe-oxides by STEM-EELS (Fig. 1). The mineral leachates caused protein oxidation and lipid peroxidation over 24 hours. The adsorption of reduced iron to the cell walls of bacteria can result in lipid peroxidation and the concurrent release of toxic aldehydes. The hydrogen peroxide assay of the mineral leachates indicates that H₂O₂ is being generated in the presence of Fe²⁺, ultimately generating hydroxyl radicals which resulted in the generation of intracellular ROS and precipitation of Fe-oxides.
FIG 1 STEM dark field images and electron energy loss (EELS) in eV of *E. coli* reacted with a 100 mg/ml Blue 1 mineral suspension for 24 hours. (a) Mineral particles outside the cell range in size from 20-100nm; (b) intracellular particles are <10nm; (c) EELS spectra of the oxygen K edge (533 eV) and iron L$_{2/3}$ edge (709.5 eV) with 0.5 eV resolution. Both the extracellular and intracellular mineral particles are composed primarily of iron and oxygen. The iron L$_{2/3}$ edge of the intracellular particles (0.3 eV resolution) reveal the presence of Fe$^{3+}$ at 709.5 eV; Fe$^{2+}$ at 707.5 eV, shown in inset (d) was not measurable.
ELECTROSPUN PolyACRYLONITRILE MAT CONTAINING SYNTHETIC NA-MONTMORILLONITE OR ORDERED MESOPOROUS SILICA PARTICLES: PREPARATION AND CHARACTERIZATION

Sliman Al Muhamed¹, Nabyl Khenoussy¹, Magali Bonne², Laurence Schacher¹, Jocelyne Brendlé*², Dominique Adolphe¹, and Bénédicte Lebeau²

¹Laboratoire de Physique et Mécanique Textiles, EA 4365, UHA, ENSISA, 11 rue Alfred Werner F-68093 Mulhouse Cedex, France ;
²Équipe Matériaux à Porosité Contrôlée, Institut de science des Matériaux de Mulhouse, UMR 7361 CNRS/UHA/ENSCMu, 3b rue Alfred Werner - 68093 Mulhouse Cedex – France.
Jocelyne.Brendle@uha.fr

Electrospinning is an effective technology to produce polymer nanofibers. In a typical electrospinning process, a high voltage is applied to create electrically charged jets of polymer solutions. The jets dry and form nanofibers, which are collected on a target as nonwoven mat. In order to enhance the properties of the nanofibers, inorganic fillers can be introduced. Porous fillers such as montmorillonite or ordered mesoporous silica materials are of interest due to their remarkable properties, such as high surface area, controllable surface chemistry and, in the case of SBA-15 a narrow pore size distribution. Electrospun nanofibers with embedded Na-montmorillonite or SBA-15 type ordered mesoporous silica will therefore present a high potential for various applications in specific areas such as catalysis or controlled drug delivery.

The aim of this present work was to prepare polyacrylonitrile (PAN)/SBA-15 and PAN/synthetic Na-montmorillonite composites by electrospinning. The polymer solution and dispersion process have been optimized and the influence of some electrospinning process parameters was investigated. A series of nanowebs PAN fibers charged by 16, 24 and 30 wt. % of SBA-15 ordered mesoporous silica particles or synthetic Na-montmorillonite have been prepared. Morphology of the nanofibers was examined by using scanning electron microscopy (SEM). The composition was characterized using thermogravimetric analysis. The ratio of accessible pores of SBA-15 particles in nanocomposites was estimated from the determination of the specific surface area, the porous volume and the pore size of pristine SBA-15 particles and (PAN)/SBA-15 nanocomposites by N₂ adsorption/desorption measurements. The accessibility of the interlayer space of montmorillonite embedded in PAN was evaluated by performing an ion exchange between the sodium interlayer cations and hexadecyltrimethylammonium cations. X-Ray diffraction was used to check the increase of the basal spacing.

The addition of SBA-15 has an influence on the diameter and the textural properties of the submicron fibers produced. Thermogravimetric measurements showed that regarding the initial loading percent of SBA-15 particles, 100% of these particles are embedded in the electrospun webs. Collected data from N₂ sorption isotherms reveal that there is a significant percentage (> 50%) of accessible pores of SBA-15 particles in the composite structure.

It was found that Na-montmorillonite aggregates are apparent along the nanofibers axis. Furthermore, incorporating Na-montmorillonite particles into PAN matrix has led to an increasing of the roughness and to a decrease in nanofibers diameter with respect to their pristine
counterparts. It is worthy to note that an ion exchange is still possible once Na-montmorillonite is embedded in PAN. This opens the way to applications in the field of pollutant remediation.
CYANIDE-BRIDGED TRANSITION METAL NANOSHEETS AS PRECURSORS FOR PLATINUM-NICKEL BIMETALLIC CATALYSTS

Tyler L. Nash, Gary W. Beall

1 Department of Chemistry and Biochemistry, Texas State University- San Marcos, 601 University Dr., San Marcos, TX 78666, USA: tn1055@txstate.edu
2 Physics Department, Faculty of Science, King Abdulaziz University, Jeddah, 21589, Saudi Arabia

Since its discovery, graphene been studied extensively in a variety of applications, but there are other 2-D materials that merit further study. One such family of sheet-like materials is formed when divalent transition metals are reacted with square planar metal cyanides. In this work, the square planar metal cyanide, potassium tetracyanoplatinate(II), was reacted with nickel(II) sulfate to form a square grid-like nanosheet structure. An in-situ process was developed to coat the surface of activated carbon with a layer of this material, and multiple samples were produced with varying concentrations of reactants. In each coated sample, the cyanide linkages were removed and the metals reduced to their elemental state via pyrolysis in a reducing atmosphere. Figure 1 shows scanning electron microscope images of the sheets on the carbon surface before pyrolysis and the reduced metals on the surface after pyrolysis. The resulting Pt-Ni bimetallic catalysts were tested via the hydrogenation of styrene to ethylbenzene, and the testing showed significant catalytic activity and excellent selectivity toward the desired product. Potential applications of this material include hydrogenation catalysts, fuel cell catalysts, and autocatalysts.

Figure 5. SEM Images of nanosheets before and after pyrolysis on the carbon surface.
EFFECT OF CALLOVO-OXFORDIAN CLAY ROCK ON THE DISSOLUTION RATE OF THE SON68 SIMULATED NUCLEAR WASTE GLASS

James Neeway*

Pacific Northwest National Laboratory, PO Box 999, Richland, WA 99352, james.neeway@pnnl.gov

In a high-level nuclear waste repository in a subsurface Callovo-Oxfordian clay rock formation, such as the one proposed in the Paris basin in northeastern France, nuclear waste glass will be corroded once the surrounding ground waters breach the stainless steel canister. The resulting glass corrosion will lead to the mobilization of soluble radionuclides with a release governed by the glass dissolution rate. To simulate this scenario in the laboratory, several tests were constructed to measure glass dissolution rates of the simulated nuclear waste glass, SON68, in the presence of the near-field materials Callovo-Oxfordian clayrock and P235GH stainless steel. Experiments consisted of placing glass and stainless steel between two Callovo-Oxfordian claystone cores in a reactor assembly. Simulated clay pore water was passed by an HPLC pump through the reactor at pressure of 120 bars. Experiments were run for up to 600 days. The effluent solution was collected and analyzed by ICP-MS for glass dissolution tracer elements (Si, B, Cs, Li, Mo) at regular time intervals. One experiment involved a 32Si-doped glass sample to study the diffusion of Si in the Callovo-Oxfordian claystone. Si concentrations at the outlet were similar in experiments with and without glass present (~4 mg/L at 25°C and ~15 mg/L at 90 °C) while the pH of the effluent was measured to be from 7.5-8.5. It was seen that SON68 dissolution rates in the presence of clay and steel using this assembly were similar to calculated results from experiments performed in silica-saturated solutions at the same temperature and similar pH for the bulk glass. However, the side of the glass coupons in direct contact with the claystone was seen to have a corrosion thickness 2.5× larger than the side in contact with the bulk glass powder not in direct contact with the claystone. Results also suggest that the movement of Si through the claystone is controlled through a dynamic dissolution/precipitation mechanism.
OVERVIEW OF GAPS IN HIGH-LEVEL NUCLEAR WASTE FORM/CLAY INTERACTIONS

James Neeway*

Pacific Northwest National Laboratory, PO Box 999, Richland, WA 99352, james.neeway@pnnl.gov

Nuclear waste has been generated from the production of energy from nuclear reactors as well as from past activities of nuclear weapons production. The safe disposal of this waste generally involves direct disposal of the spent nuclear fuel (SNF) from the reactor or reprocessing the SNF to create a radioactive waste form, generally an insoluble mineral or glass. The final high-level waste (HLW) form(s) would then be packaged and sent to a deep-surface geologic repository. In order for the design and management of a secure disposal site, the HLW materials must limit the release of radioactive materials to the surrounding environment for very long time periods. This stability is dependent on the waste form itself as well as the physical and chemical characteristics imposed by the surrounding geology. The present paper gives an overview of the literature available on the interactions of high-level waste forms and the surrounding environment (engineered barriers and geological materials), as well as suggestions on overcoming existing uncertainties that may aid in more robust performance assessment models. There will be a focus on interactions with clay that are often used as a buffering material or, in some countries, as the host rock. We will also give a brief description of low-level radioactive waste (LLW) form storage and how the near field may interact with these materials.
RECOVERY OF SOIL MICROBIAL POPULATIONS, FUNCTION, AND COMMUNITY COMPOSITION FOLLOWING RECLAMATION OF A LIGNITE SURFACE MINE

Justin Ng\textsuperscript{1,2}, Terry Gentry\textsuperscript{2*}, Frank Hons\textsuperscript{2}, and Jizhong Zhou\textsuperscript{3}

\textsuperscript{1}School of Agriculture and Natural Resources, Abraham Baldwin Agricultural College, Tifton, GA 31793, USA;  
\textsuperscript{2}Department of Soil and Crop Sciences, Texas A&M University, College Station, TX 77843-2474, USA: tngentry@ag.tamu.edu  
\textsuperscript{3}Institute for Environmental Genomics, University of Oklahoma, Norman, OK 73019, USA.

Lignite surface mines are typically reclaimed by backfilling with previously removed soil; however, this process destroys the original soil structure thus disrupting its biological properties. A study was conducted to determine the amount of time required for microbial abundance, function, and community composition to recover in a 40-year chronosequence (0, 5, 10, 15, 20, 30, and 40 years) of reclaimed mine soils in Texas, USA. Microbial abundance was determined by measuring microbial biomass levels and using qPCR targeting bacteria (16S rRNA) and fungi (ITS). Microbial functional activity was determined by measuring C and N mineralization rates. Microbial community composition was determined using 16S rRNA gene pyrosequencing and GeoChip functional gene microarrays. Soil microbial biomass levels and C and N mineralization required 15 to 20 years, following reclamation, to equal levels in a nearby, un-mined reference soil (UM). Likewise, numbers of bacteria and fungi (as determined with qPCR) recovered within 20 years. The soil bacterial communities at all sites were dominated by \textit{Actinobacteria}, \textit{Acidobacteria}, and \textit{Proteobacteria}. However, community composition in the reclaimed sites did not match the UM site even after 40 years of reclamation. Interestingly, the communities in the 10- and 15-year reclamation sites were more similar to the UM site than the 30- and 40-year post-reclamation sites were. This indicates that the communities initially became more similar to the UM site, up to around 15 years, and then deviated into different communities. Since this corresponded with the recovery of major soil processes, this suggests that the functional redundancy of the microbial community contributed to the recovery of soil ecosystem functions, even though the community did not return to its original composition.
POSSIBLE ROLE OF CLAY MINERALS IN PHOTOCATALYST

Makoto Ogawa*1,2

1 Graduate School of Science and Engineering, Waseda University;  
2 Department of Earth Sciences, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan: makoto@waseda.jp

The utilization of smectite group of clay minerals as scaffolds for designing functional nanostructures has extensively been conducted.1,2 Surface modification of smectites with organoammonium ions has given hydrophobic and microporous nature to uptake nonionic organic contaminants from environments.3,4 The states of the adsorbed nonionic organic compounds have been altered and varied by the modification of smectites as shown by the controlled release and specific catalytic reactions. Cationic species have been easily concentrated on smectites from aqueous phase and the states (orientation and distribution) have been controlled by the co-adsorption of both cationic and nonionic species. The functions of smectite-organic intercalation compounds derived from the precisely controlled nanostructures have been discussed extensively.

The application of clay minerals in designing photofunctional materials is one of the topics of interdisciplinary area of research in photochemistry, surface chemistry, materials chemistry and so on.5,6 In this paper, application of clay minerals for photocatalytic reaction will be discussed.5-8 One of the role of clay minerals is the scaffold to immobilize photocatalytically active species such as noble metal nanoparticles, semiconductor nanoparticles, dyes, and organometallic complexes. More recently, we utilized clay mineral suspension as reaction media for photocatalytic reactions of organic compounds by titania.8 Photosensitizing dyes have been immobilized on a smectite and the intercalation compound was further complexed with titania nanoparticle for visible light driven photocatalytic reactions.7

INTERACTION BETWEEN ANIONIC CLAYS AND BLOOD COMPONENTS

Jae-Min Oh*, Hyoung-Mi Kim

Department of Chemistry and Medical Chemistry, College of Science and Technology, Yonsei University, Wonju, Gangwondo, 220-710, Korea: jaemin.oh@yonsei.ac.kr

Anionic clay, also known as layered double hydroxide (LDH), is attracting interests as intravenously injectable drug delivery carrier due to its high accommodation ability for anionic drugs and cellular uptake efficiency. We have evaluated the interaction between anionic clays and blood components according to their physicochemical properties such as particle size and surface charge. Anionic clays with chemical formula Mg₂Al(OH)₂(CO₃)₀.₅ was prepared to have controlled size and surface charge by properly regulating synthetic condition like temperature and metal ratio. Powder X-ray diffraction patterns showed that all the anionic clays possess hydrotalcite-like structure. Scanning electron microscopic analyses on anionic clays prepared by controlled temperature showed the average particle sizes of ~40, ~150, ~350, and ~2000 nm. According to zeta potential measurement, the surface charges of metal ratio controlled anionic clays were determined to be 32.9, 28.8 and 19.0 mV. In order to evaluate the interaction between anionic clays and human blood components depending on particle size and surface charge, we carried out hemolysis and protein fluorescence quenching assay. It was shown that the hemolysis increase with larger particle size and low positive surface charge. The surface interaction between anionic clays and blood cells was visualized by both optical and electron microscopy, suggesting possible non-covalent attachment of anionic clay particles on red blood cells.
ASSESSMENT OF KAOLINITES ORDER-DISORDER FOR SOILS AND SEDIMENTS FROM DOCE RIVER BASIN, MINAS GERAIS–BRAZIL

Anderson A. Pacheco¹, Mauricio P.F. Fontes¹, Juan S. Lezama-Pacheco² and Scott Fendorf²

¹Department of Soil, Universidade Federal de Viçosa, Viçosa, MG 36570-000, BRAZIL: andersonpacheco@ymail.com
²Department of Environmental Earth System Science, Stanford University, Stanford, CA 94305-4216, USA.

Soils of Doce river basin are developed from orthogneiss and granitic-granodioritic rocks subjected to strong weathering process. The presence of kaolinite and gibbsite is conditioned primarily by dissolved silica concentrations, resulting from pedogenetic evolution. With slight to moderate desilication, and resulting lower silicate concentrations, kaolinite formation is the favored. The objective of this study was to evaluate the degree of structural disorder of kaolinite in different compartments of the Doce river basin. Samples were collected along the main channel of the river and they were classified as stable upland soils, alluvial soils (present in floodplains), and fluvial soils (from the river bed).

Clay fractions were separated and iron oxides were removed by the DCB method (Mehra & Jackson, 1960) in samples of 58 fluvial soils (sediments), 37 alluvial soils and 22 stable upland soils. These samples were examined by powder x-ray diffraction (XRD) in a multifunctional Panalytical X’Pert Pro PW 3040/60 diffractometer.

Kaolinite was characterized structurally using indices described in Hughes & Brown (1979) and Liètard (1977). The full width at half maximum (FWHH) (°2θ) were measured for peaks positions of the (001) and (002) planes of kaolinite. It was not possible to measure the crystallinity of kaolinite using multiple indices as was done in Hinckley (Hinckley, 1962); Range and Weiss (Range and Weiss, 1969); Aparicio - Galán- Ferrell (Aparicio et al., 2006); Stoch (Stoch, 1974) and Plançon and Zacharie (Plançon and Zacharie, 1990), due to the high degree of structural disorder of kaolinites of this study. As a comparison, all indices of crystallinity calculated were compared with the indices of standard kaolinite (KGa 1b - well crystallinity with HBI: ∞; R2: 1.01 and KGa 2 - poor crystallinity with HBI: 40.4; R2: 0.84) and also with a kaolinite (well crystallinity) of Amazonia (Brazil) with HBI: ∞; R2: 1.2. The indices of Hughes and Brown (1979) for well crystallized kaolinite were assigned as the upper limit of crystallinity and denoted as infinity within our rating procedure.

The crystallinity of the soil derived kaolinite from the Doce river basin have a high structural disorder, as noted by the standard kaolinite indices (Tables 1 and 2). Under formation conditions of humid tropical climates, kaolinite often has a low degree of crystallinity (Hughes and Brown, 1979; Singh and Gilkes, 1992), which depends on chemical and morphological characteristics of soil as influenced by climate factors. Similar values were found by Pacheco (2011) for soils of the river Alegre basin (Brazil).

A linear correlation study (<5%) of the crystallinity indices for upland, fluvial, and alluvial soils was conducted. The correlation found between the HBI and R2 was $r = 0.48$, $r =$
Everything is big: From nanoparticles to planets

0.03 and \( r = 0.31 \), respectively. The poor correlation is not unexpected given the wide variety of chemical and physical weathering processes within the tropical soils. These and other parameters (e.g. CEC, sampling depth, clay content) are in agreement with literature values, although they have been conducted with kaolinite ranging from regular to good crystallinity (Murray and Lyons, 1959; Varajão et al., 2001; Aparicio and Galán, 1999).

Table 1. Average crystallinity indices for soils.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HBI</th>
<th>R2</th>
<th>FWHM 001</th>
<th>FWHM 002</th>
<th>Sample</th>
<th>HBI</th>
<th>R2</th>
<th>FWHM 001</th>
<th>FWHM 002</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>16.09</td>
<td>0.83</td>
<td>0.48</td>
<td>0.45</td>
<td>P12</td>
<td>26.69</td>
<td>0.84</td>
<td>0.41</td>
<td>0.42</td>
</tr>
<tr>
<td>P2</td>
<td>20.53</td>
<td>0.74</td>
<td>0.44</td>
<td>0.43</td>
<td>P13</td>
<td>18.58</td>
<td>-</td>
<td>0.43</td>
<td>0.45</td>
</tr>
<tr>
<td>P3</td>
<td>23.50</td>
<td>0.75</td>
<td>0.43</td>
<td>0.44</td>
<td>P14</td>
<td>23.56</td>
<td>0.69</td>
<td>0.39</td>
<td>0.37</td>
</tr>
<tr>
<td>P4</td>
<td>21.76</td>
<td>0.79</td>
<td>0.44</td>
<td>0.43</td>
<td>P15</td>
<td>19.18</td>
<td>-</td>
<td>0.44</td>
<td>0.45</td>
</tr>
<tr>
<td>P5</td>
<td>16.09</td>
<td>0.79</td>
<td>0.44</td>
<td>0.43</td>
<td>P16</td>
<td>-</td>
<td>-</td>
<td>0.53</td>
<td>0.67</td>
</tr>
<tr>
<td>P6</td>
<td>20.84</td>
<td>0.73</td>
<td>0.45</td>
<td>0.44</td>
<td>P17</td>
<td>20.95</td>
<td>0.64</td>
<td>0.49</td>
<td>0.50</td>
</tr>
<tr>
<td>P7</td>
<td>24.49</td>
<td>0.81</td>
<td>0.44</td>
<td>0.40</td>
<td>P18</td>
<td>34.42</td>
<td>0.79</td>
<td>0.36</td>
<td>0.37</td>
</tr>
<tr>
<td>P8</td>
<td>24.24</td>
<td>0.76</td>
<td>0.48</td>
<td>0.48</td>
<td>P19</td>
<td>183.26</td>
<td>0.86</td>
<td>0.34</td>
<td>0.33</td>
</tr>
<tr>
<td>P9</td>
<td>25.05</td>
<td>0.74</td>
<td>0.47</td>
<td>0.47</td>
<td>P20</td>
<td>13.82</td>
<td>-</td>
<td>0.72</td>
<td>0.91</td>
</tr>
<tr>
<td>P10</td>
<td>22.86</td>
<td>0.75</td>
<td>0.50</td>
<td>0.46</td>
<td>P21</td>
<td>29.71</td>
<td>0.76</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>P11</td>
<td>23.54</td>
<td>0.78</td>
<td>0.49</td>
<td>0.47</td>
<td>P22</td>
<td>19.27</td>
<td>0.51</td>
<td>0.68</td>
<td>0.79</td>
</tr>
</tbody>
</table>

HBI: Hughes and Brown Index; R2: Liètard Index; WHMH: Full width at half maximum. P1-P11 are alluvial soils. P12-P22 are upland soils.

Table 2. Average crystallinity indices for fluvial soils (sediments)

<table>
<thead>
<tr>
<th>Sample</th>
<th>HBI</th>
<th>R2</th>
<th>FWHM 001</th>
<th>FWHM 002</th>
<th>Sample</th>
<th>HBI</th>
<th>R2</th>
<th>FWHM 001</th>
<th>FWHM 002</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>18.89</td>
<td>0.73</td>
<td>0.44</td>
<td>0.43</td>
<td>S7</td>
<td>24.15</td>
<td>0.80</td>
<td>0.45</td>
<td>0.46</td>
</tr>
<tr>
<td>S2</td>
<td>18.06</td>
<td>0.78</td>
<td>0.42</td>
<td>0.42</td>
<td>S8</td>
<td>22.34</td>
<td>0.77</td>
<td>0.46</td>
<td>0.45</td>
</tr>
<tr>
<td>S3</td>
<td>19.11</td>
<td>0.80</td>
<td>0.44</td>
<td>0.44</td>
<td>S9</td>
<td>24.09</td>
<td>0.78</td>
<td>0.46</td>
<td>0.44</td>
</tr>
<tr>
<td>S4</td>
<td>18.63</td>
<td>0.72</td>
<td>0.46</td>
<td>0.44</td>
<td>S10</td>
<td>17.23</td>
<td>0.73</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>S5</td>
<td>18.65</td>
<td>0.75</td>
<td>0.44</td>
<td>0.45</td>
<td>S11</td>
<td>25.24</td>
<td>0.78</td>
<td>0.47</td>
<td>0.48</td>
</tr>
<tr>
<td>S6</td>
<td>19.66</td>
<td>0.76</td>
<td>0.44</td>
<td>0.45</td>
<td>S12</td>
<td>27.61</td>
<td>0.76</td>
<td>0.48</td>
<td>0.48</td>
</tr>
</tbody>
</table>

HBI: Hughes and Brown Index; R2: Liètard Index; WHMH: Full width at half maximum.

Linear correlation between crystallinity indices and levels of heavy metals was undertaken. The values ranged from \( r = -0.33 \) to \( r = 0.50 \). Heavy metal sorption involves a variety of processes, including inner and outer-sphere adsorption complexes (Yuan et al., 2013; Fontes, 2013), and thus we would not expect a high correlation with crystallinity values or CEC.

Therefore, we conclude that kaolinite within the Doce River Basin of Brazil are poorly crystalline owing to the strong weathering conditions of this tropical environment. Further, the indices used in this study can be considered to estimate the crystallinity of poorly ordered kaolinites.

AVATAR DNA@CLAY NANOSHELL HYBRID SYSTEM

Dae-Hwan Park*, Jin-Ho Choy

1Center for Intelligent Nano-Bio Materials (CINBM), Department of Chemistry and Nano Science and Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Republic of Korea: parkdh@ewha.ac.kr

Long admired for informational role and recognition function in multidisciplinary science, DNA nanohybrids have been emerging as ideal materials for molecular nanotechnology and genetic information code. Here, we designed an optical machine-readable DNA icon on microarray, Avatar DNA, for automatic identification and data capture such as Quick Response and ColorZip codes. Avatar icon is made of telepathic DNA-DNA hybrids inscribed on chips, which can be identified by camera of smartphone with application software. Information encoded in base-sequences can be accessed by connecting an off-line icon to an on-line web-server network to provide message, index, or URL from database library. Avatar DNA is then converged with nano-bio-info-cogno science: each building block stands for inorganic clay nanosheets, nucleotides, digits, and pixels. Chemically well-defined bio core@inorganic clay shell nanohybrid, which consists of rational DNA molecules core with a size of ≈100 nm and spherical hydrotalcite nanoshell with wall thickness of ≈10 nm reassembled with exfoliated layered double hydroxide (LDH nanosheets), is prepared. The encapsulation of information DNA and its release, due to the pH dependent solubility of LDH nanoshell, plays a crucial role in maximizing the stability of base sequence-manipulated and probes-functionalized DNA molecules with designed information. This convergence could address item-level identification that strengthens supply-chain security for drug counterfeits. It can, therefore, provide molecular-level vision through mobile network to coordinate and integrate data management channels for visual detection and recording.
ALTERATION OF BASALTIC GLASS TO Mg/Fe-SMECTITE UNDER ACIDIC CONDITIONS: A POTENTIAL SMECTITE FORMATION MECHANISM ON MARS

Tanya Peretyazhko*1, Brad Sutter2, and Douglas W. Ming3

1Lunar and Planetary Institute, Houston, TX 77058; tanya.peretyazhko@nasa.gov.
2Jacobs, NASA Johnson Space Center, Houston, TX 77058, USA.
3NASA Johnson Space Center, Houston, TX 77058, USA.

Phyllosilicates of the smectite group including Mg- and Fe-saponite and Fe(III)-rich nontronite have been identified on Mars. Smectites are believed to be formed under neutral to alkaline conditions that prevailed on early Mars. This hypothesis is supported by the observation of smectite and carbonate deposits in Noachian terrain on Mars. However, smectite may have formed under mildly acidic conditions. Abundant smectite formations have been detected as layered deposits hundreds of meters thick in intracrater depositional fans and plains sediments, while no large deposits of carbonates are found. Development of mildly acidic conditions at early Mars might allow formation of smectite but inhibit widespread carbonate precipitation. Little is known regarding the mechanisms of smectite formation from basaltic glass under acidic conditions. The objective of this study was to test a hypothesis that Mars-analogue basaltic glass alters to smectite minerals under acidic conditions (pH 4). The effects of Mg and Fe concentrations and temperature on smectite formation from basaltic glass were evaluated.

Phyllosilicate synthesis was performed in batch reactors (Parr acid digestion vessel) under reducing hydrothermal conditions at 200°C and 100°C. Synthetic basaltic glass with a composition similar to that of the Gusev crater rock Adirondack (Ground surface APXS measurement) was used in these experiments. Basaltic glass was prepared by melting and quenching procedures. X-ray diffraction (XRD) analysis indicated that the synthesized glass was composed of olivine, magnetite and X-ray amorphous phase. Samples were prepared by mixing 250 mg Adirondack with 0.1 M acetic acid (final pH 4). In order to study influence of Mg concentration on smectite formation, experiments were performed with addition of 0, 1 and 10 mM MgCl2. After 1, 7 and 14 day incubations the solution composition was analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and the altered glass and formed phyllosilicates were examined by XRD analysis. Mineralogical changes were significant in Adirondack incubated with 10 mM MgCl2 at pH 4 and heated at 200°C. X-ray diffraction analysis revealed formation of phyllosilicate during 14 day incubation (Figure 1). Smectite was confirmed as the phyllosilicate after treatments with glycerol and KCl and heating to 550°C. The position of 02l (4.60 Å) and 060 (1.54 Å) diffraction bands were indicative of trioctahedral smectite such as saponite. Analysis of solution composition demonstrated that aqueous concentration of Mg decreased from 10 mM to ~4 mM after 7 day incubation likely due to saponite formation. Smectite also formed in Adirondack incubated with 0 mM MgCl2 at pH 4 and heated at 200°C. However, diffraction peak positions of 02l (4.52 Å) and 060 (1.51 Å) suggested formation of dioctahedral nontronite. The 100°C Mg and Fe(II) treated basaltic glass experiments are ongoing and results will be presented.

We demonstrate here the first reported synthesis of saponite from a basaltic precursor under mildly acidic conditions. Saponite and smectite minerals in general have thought to have
formed under neutral to alkaline conditions during the Noachian era followed by acid sulfate alteration. Our results provided a new plausible mechanism of smectite formation under acidic conditions on early Mars. The lack of the carbonate detection in Noachian materials also supports a non-alkaline environment during this era.

Figure 1. X-ray powder diffraction patterns of synthetic Adirondack basaltic glass treated with 10 mM MgCl₂, at pH 4 heated at 200°C for varying times. Olivine and magnetite are present in initial non-altered basaltic glass while saponite forms during basaltic glass alteration. Identified peaks indicate saponite while all other peaks are associated with magnetite and olivine. The broad hump from 20 to 40° 2θ indicates X-ray amorphous basaltic glass.
IMACS: AN INTERNATIONAL MASTER PROGRAMME ENTIRELY DEVOTED TO CLAY MINERALS

S. Petit1, P. Patriér Mas1, G. Christidis2, F. Rocha3, C. Detellier4, and A. Mexias5

1Université de Poitiers, UMR 7285 CNRS IC2MP, France; 2 Technical University of Crete, Chania, Greece; 3 University of Aveiro, Portugal; 4 University of Ottawa, Canada; 5 Federal University of Rio Grande Do Sul, Porto Alegre, Brazil: sabine.petit@univ-poitiers.fr

Most existing Masters Courses dealing with clays focus on a single discipline or domain in which Clay Science does not necessarily constitute the main part of the course (Earth Sciences, Civil and Geotechnical Engineering, Materials Science, Environmental and Life Science, Chemistry and Chemical Engineering). However, Clay Science is a multidisciplinary endeavour, combining geology, mineralogy, crystallography, with physics, geotechnology, and soil mechanics together with inorganic, organic, physical and colloid chemistry and biochemistry. The IMACS (International Master in Advanced Clay Science) is the first multidisciplinary programme that brings together the widely-distributed knowledge of clay science.

IMACS is an integrated 2 years master programme developed by five Universities: the University of Poitiers (France), the Technical University of Crete (Chania - Greece), the University of Aveiro (Portugal), the University of Ottawa (Canada) and the Federal University of Rio Grande Do Sul (Porto Alegre – Brazil). AIPEA is an associated member of this consortium. The French Clay Group (GFA) also supports IMACS.

The teaching language is English. During the first year, basic knowledge on clays is provided, followed by a four month master project, which completes the first year programme. The second year incorporates two elective specialization options in the following fields: 1) Environment, soil and geological systems, 2) Geomaterials and civil engineering – Assessment and processing, 3) Advanced clay – nanomaterials, and 4) Healing minerals. The master thesis (6 months) completes this second year and can be carried out at any of the partner research laboratories. The completion of the curriculum is rewarded by a multiple Master Degree.

The IMACS programme was approved by the European Commission under a very competitive application scheme as an Erasmus Mundus Joint Master programme in July 2009 and it opened in September 2010. Erasmus Mundus is a cooperation and mobility programme in the field of higher education supported by the European Commission. This programme offers financial support for high-quality joint master courses, attractive scholarships/fellowships for both Non European and European student candidates and short-term scholarships for Non European and European academics to carry out research or teaching assignments as part of the joint masters project.

Free language training in the local languages is offered by the five higher education institutions. Moreover, the programme makes available a range of services and facilities (e.g. visa request, accommodation, insurance, bank account opening, social and cultural activities among many others…) to the students.
This Masters Course is open to students holding a BSc (or a degree equivalent to 180 ECTS) or an academic equivalence based on professional experience, and a fluent understanding of the English language.

IMACS website: http://www.master-imacs.org
CONTRIBUTION OF IR SPECTROSCOPY TO CLAY MINERALS STUDIES

S. Petit*1

1 Université de Poitiers, CNRS UMR 7285 IC2MP, HydrASA, 6 rue Michel Brunet, 86022 Poitiers Cedex, France : sabine.petit@univ-poitiers.fr

Spectroscopies offer powerful toolboxes to attain the short range order of compounds. Infrared (IR) spectroscopy is based on vibrations of atoms and molecular groups. The IR spectrum of a clay mineral is then sensitive to its chemical composition, atomic distributions, and structural modifications. Both the complexity and the positions of the absorption bands in the spectra give information on functional groups present and thus on the sample. Among the others, this makes IR spectroscopy a very informative technique to characterize clay minerals and their crystal-chemistry as well as to study their surface properties via organic molecules interactions. It is also an appropriate technique to study poorly crystallized clay minerals, some of them sometimes behaving as XRD amorphous.

Although the relationship between clay structure and IR spectrum is complex and has been only partially rationalized up to now, it is possible to attain informations with this spectroscopy that could not be reached easily by other techniques. Theory alone gives only limited support, and the interpretation of IR spectra is generally done by empirically assigning the observed bands to vibrational modes. Careful studies of well-characterized families of natural and synthetic minerals and the coupling of several IR ranges played an essential role in giving concrete structural significance to spectral features. Detailed interpretation of the IR spectra of clay minerals measured in traditional MIR but also in the more and more used NIR region, supported by well designed advanced accessories guarantees that IR spectroscopy will remain one of the most important experimental methods for clay mineral investigation in the future.

This lecture aims to indicate the benefit to use infrared spectroscopy for clay mineral studies through some case studies.
THE PERSON WHO INTRODUCED ME TO CLAYS SYNTHESIS AND INFRARED SPECTROSCOPY

S. Petit*1

1Université de Poitiers, CNRS UMR 7285 IC2MP, HydrASA, 6 rue Michel Brunet, 86022 Poitiers Cedex, France : sabine.petit@univ-poitiers.fr

I would like to pay tribute to Alain Decarreau who was my PhD supervisor and who introduced me into the clay world.

Alain Decarreau was a Professor at the university of Poitiers till 2007. He was the President of the GFA (French Clay Group) from 1994 - 1997, after having been its Vice-President (1990-1993). He was a pioneer in clay synthesis, with a particular interest towards crystal growth process and element partitioning.

We worked together for more than 20 years. We continue to have stimulating discussions and this lecture will show what discussing with people can produce.
RESULTS OF THE SEVENTH REYNOLDS CUP CONTEST IN QUANTITATIVE MINERAL ANALYSIS

M. Ploetze

1Institute for Geotechnical Engineering, ClayLab, ETH Zurich, CH-8093 Zurich, Switzerland: ploetzel@ethz.ch

Results of the seventh Reynolds Cup contest in quantitative mineral analysis will be presented. The biennial competition is supported by the Clay Minerals Society CMS, the German clay group DTTG and the Clay Minerals Group of the Mineralogical Society of UK. The main goal of the Reynolds Cup is to promote and improve quantitative mineral analysis but in a sportive spirit. Unlike other round-robins, the Reynolds Cup competition utilizes mixtures of pure standards that represent realistic sedimentary rock compositions giving a free choice of analytical methods to the participants [1].

Also in the seventh round the popularity of the Reynolds Cup contest is still increasing (Fig. 1). Eighty sets of three samples were shipped at the request of individuals in 21 countries. Participants were allowed approximately ten weeks to submit their results.

The presentation will report the specialties of the provided mixtures and details of their preparation. Furthermore, the analytical approaches used by the participants and the methodology of the analytical techniques used by the top three contestants will be explained. Following the presentation the prizes will be awarded to the top three finishers.

EVIDENCE FOR LOCAL-SCALE CATION-EXCHANGE REACTIONS IN PHYLLOSILICATES AT GALE CRATER, MARS


1 NASA Johnson Space Center, Houston, TX 77058, USA: elizabeth.b.rampe@nasa.gov; 2 Planetary Science Institute, Tucson, AZ 85719, USA; 3 NASA Ames Research Center, Moffett Field, CA 94035, USA; 4 Department of Geological Sciences, Indiana University, Bloomington, IN 47405, USA; 5 Chesapeake Energy, Oklahoma City, OK 73154, USA; 6 SETI Institute, Mountain View, CA 94043, USA; 7 School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA; 8 Lunar and Planetary Institute, Houston, TX 77058, USA; 9 Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA; 10 Department of Geosciences, University of Arizona, Tucson, AZ 85721, USA.

The Mars Science Laboratory rover, Curiosity, landed in Gale crater on August 5, 2012. A primary mission science objective is to search for past habitable environments, and, in particular, to assess the role of past water. The identification of phyllosilicates in Gale crater from orbital visible to near-infrared spectrometers suggests the presence of aqueous environments in the distant past and helped guide the selection of Gale crater as the landing site. Phyllosilicates were first discovered by Curiosity within the Sheepbed mudstone with the CheMin X-ray diffraction instrument. The Sheepbed mudstone contains diagenetic features that occur locally, including Mg-enriched raised ridges (interpreted as synaeresis cracks) and Ca-sulfate veins, indicating several stages of aqueous alteration. CheMin analyzed two samples from the mudstone, named John Klein and Cumberland, and these samples were acquired within ~3 m laterally from one another and ~30 cm stratigraphically. FULLPAT models of CheMin data from John Klein and Cumberland show that the mudstone is made up of ~20% phyllosilicate, and the position of the phyllosilicate 02l peaks at 23.1° Co-Kα in both samples suggests that the mudstone contains a 2:1 trioctahedral clay mineral (e.g., saponite). Although the similarity in 02l peak positions in the John Klein and Cumberland samples indicates similarity in the phyllosilicate crystal structure, there is a striking difference in the position of their 001 peaks. The 001 peak in John Klein has a spacing of 10 Å, indicating that the phyllosilicate structure is collapsed, as might be expected on the dry martian surface. However, the 001 peak in Cumberland has a spacing of ~13.2 Å (Lorentz-polarization corrected), indicating that the phyllosilicate structure is expanded. Mg-rich raised ridges and Ca-sulfate veins suggest that fluids with different compositions may have altered this mudstone. We hypothesize that these fluids caused local-scale cation-exchange reactions in the clay minerals, and variation in interlayer cation composition can explain the differences in 001 peak position between John Klein and Cumberland. We tested this hypothesis by measuring XRD patterns of cation-saturated swelling clay minerals in a dry environment in a laboratory version of CheMin.
A variety of swelling clay minerals were selected for cation saturation: saponite (SapCa-1), ferroan saponite (Griffith Park, CA), nontronite (NAu-1), montmorillonite (SWy-1), and trioctahedral vermiculite (Libby, MT). The <2 m size fractions of these materials were Mg-, Ca-, and K-saturated, then measured in the laboratory version of CheMin (CheMin IV) at the NASA Johnson Space Center. Dry N$_2$(g) (~0.2% relative humidity; ~100 ppm H$_2$O) flowed into the sample chamber to mimic the dry environment on the martian surface and desiccate the clay minerals. Measurements were made periodically for up to one week until no shift in the 001 peak was observed.

Results from the Mg- and Ca-saturated phyllosilicates show that their structures remained expanded, even under very dry conditions. The Mg-saturated samples of each phyllosilicate were generally more expanded than the Ca-saturated samples (Table), and their 001 peak positions were more consistent with that of the phyllosilicate in Cumberland. Variations in the 001 spacings within the Mg-saturated samples and the Ca-saturated samples may be attributed to different layer charges in each phyllosilicate because layer charge affects the ability to absorb H$_2$O. Measurements of the K-saturated phyllosilicates are ongoing; however, we hypothesize that the K-saturated phyllosilicates will fully collapse because K$^+$ has a low hydration energy and does not retain H$_2$O in the interlayer site when exposed to such dry conditions.

Based on our laboratory measurements of cation-saturated swelling clay minerals, we suggest that variations in interlayer cation composition of the phyllosilicates in the Sheepbed mudstone can explain the differences in 001 peak positions of the phyllosilicates in the John Klein and Cumberland samples. A cation with a low hydration energy (e.g., K$^+$) in the phyllosilicate interlayer site in John Klein would cause the full collapse of its structure, and a cation with a high hydration energy (Mg$^{2+}$) in the phyllosilicate interlayer site in Cumberland would cause the structure to retain H$_2$O and remain expanded. Variations in interlayer cation composition between the two martian mudstone samples measured only a few meters apart would suggest that aqueous alteration and cation exchange occurred on a very local scale. Diagenetic features and differences in the swelling characteristics of the clay minerals in the Sheepbed mudstone indicate a complex history of aqueous alteration at this site.

### Table. Spacings of the 001 peaks (not Lorentz-polarization corrected) of Mg-saturated and Ca-saturated phyllosilicates measured on the CheMin IV under dry N$_2$(g).

<table>
<thead>
<tr>
<th>Phyllosilicate</th>
<th>Mg-sat 001 position</th>
<th>Ca-sat 001 position</th>
<th>untreated 001$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SapCa-1</td>
<td>12.0 Å</td>
<td>11.9 Å</td>
<td>11.4 Å</td>
</tr>
<tr>
<td>NAu-1</td>
<td>13.0 Å</td>
<td>12.1 Å</td>
<td>12.2 Å</td>
</tr>
<tr>
<td>SWy-1</td>
<td>12.2 Å</td>
<td>11.0 Å</td>
<td>10.0 Å</td>
</tr>
<tr>
<td>Ferroan saponite</td>
<td>13.7 Å$^b$</td>
<td>in progress</td>
<td>11.9 Å$^c$</td>
</tr>
<tr>
<td>Libby vermiculite</td>
<td>13.9 Å</td>
<td>10.9 Å</td>
<td>10.5 Å</td>
</tr>
</tbody>
</table>

$^a$Values for the unsaturated parent clay minerals are given for reference.

$^b$Measured from <150 m size fraction of altered basalt.

$^c$Measured from <45 m size fraction of altered basalt.
MOLECULAR SIMULATIONS OF WATER-METHANE AND WATER-CARBON DIOXIDE FLUIDS BETWEEN NA-MONTMORILLONITE CLAY SURFACES

Qi Rao¹, Yuan Xiang¹, and Yongsheng Leng*¹

¹ Department of Mechanical & Aerospace Engineering, The George Washington University, Washington, DC 20052, USA: leng@gwu.edu

Water-methane (CH₄) and water-carbon dioxide (CO₂) fluids are two common binary mixtures in geological fluids. The thermodynamic properties of these two fluid mixtures in clay minerals are of considerable interest and importance in petroleum industry and CO₂ capture and storage (CCS). These properties are directly relevant to many practical issues during the oil and gas recovery and CO₂ sequestration, such as the location and migration of methane or carbon dioxide and their effects on the stability of clay hydrate. The composition, structure, and dynamics of water-CH₄ or water-CO₂ fluids in clay interlayer are investigated through a combination of the equation of state (EOS) theory, the grand canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulations. The chemical potentials of each species at the temperatures and pressures corresponding to different burial depths are calculated. These chemical potentials are used in the GCMC simulations to determine the contents of each species in the clay interlayer at specific temperature and pressure. The results are used as initial inputs for further MD simulations to investigate the structural and dynamic properties of the confined fluids. The swelling behavior of Na-montmorillonite in water-CH₄ / water-CO₂ fluids is investigated through GCMC simulations.

It is found that the initial clay swelling in water-methane fluid mixture is dominated by water adsorption into clay interlayer, followed by the formation of methane hydrates as the basal spacing increases. Simulation results show that at burial depth of 6 km, corresponding to 460 K and 900 bar pressure, methane can penetrate into clay interlayer even at one hydration layer. As clay continues to swell, significant amount of methane hydrates will form in Na-montmorillonite clay. Methane content in clay is found to increase in a step fashion, from initial inner-sphere complex to both inner- and outer-sphere structures. Further, methane is not fully coordinated by water molecules due to the low density of water content in Na-montmorillonite clay. Simulation results show that at geological conditions at sub-surface level (300 K, 30 bar or 50 bar), there is a competition of surface sorption between water and methane molecules. Both relative humidity (RH) and pressure have strong influence on this competition. Higher relative humidity may facilitate water molecules entering clay interlayer region and inhibit the intercalation of methane molecules. Stable methane hydrates may occur at relatively higher temperature and lower pressure (300 K, 50 bar), with a relatively lower humidity (20 % humidity).

A special case of clay mineral at the basal spacing of 12.55 Å has been studied in water-CO₂ fluid mixture. The temperature is set at 35°C and the pressure varies from 10 ~ 150 bar. This situation corresponds to the experimental condition (Rother et al.) of sub-single hydration layer equilibrated with CO₂. Two values of humidity (40% and 50%) are considered in the simulations. The EOS and GCMC simulation results show that the pore density of CO₂ in clay interlayer, as a function of CO₂ bulk density, compares reasonably well with the experimental
data. The discrepancy between simulation and experimental results occurs in the CO₂ bulk density between 0.2 ~ 0.4 g/ml. This discrepancy could be attributed to several factors, such as large humidity variations in the experiment, the assumption used in the experiment to calculate adsorption amount, the sensitivity of bulk CO₂ density to the pressure in this density region, which corresponds to the transition from CO₂ gas phase to scCO₂.
ELECTRON MICROSCOPY STUDIES OF CLAYS AND CLAY-BASED COMPOSITES

Oren Regev*1,2, Jaime C. Grunlan2

1Department of Chemical Engineering, Ben-Gurion University of the Negev, 84105 Beer Sheva, Israel: oregev@bgu.ac.il
2Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843-2474, USA.

Clay is a useful filler in gas barrier and flame retardant applications. High performances of both have been reported for thin films consisting of clay-polymer nano-composites, prepared using layer-by-layer (LbL) technique. The internal structure of such LbL film is, however, less explored.

During my talk, I will demonstrate a few transmission electron microscopy (TEM) studies of clay-polymer composites in LbL structure. The internal structure of the dry film is explored using microtomy followed by imaging in high resolution TEM at nanometer resolution. I will discuss the clay-polymer interaction within the film, full and partial clay coverage, and the importance of clay exfoliation (Figure 1). The determination of clay size distribution in liquid is presented using cryogenic-TEM technique.

Figure 1: TEM cross-sectional micrograph of five clay-polymer layers.
ADSORPTION OF OLIVE OIL ON CLAY MINERALS AND NANOCOMPOSITES

Giora Rytwo1,3*, Roy Lavi3, Yelena Konovalova1, and Roee Gutman2

1Department of Environmental Sciences, Tel Hai College, Upper Galilee 12210 Israel: rytwo@telhai.ac.il
2Department of Nutrition Sciences, Tel Hai College, Upper Galilee 12210 Israel
3Environmental Physical Chemistry Group, MIGAL Galilee Research Institute, Kiryat Shmona, 11016, Israel.

Oil–clay interactions have attracted interest mainly from an environmental point of view, seeking efficient sorbents for marine oil spills. Natural clays are considered ineffective sorbents for hydrophobic organic compounds however sorptive capabilities can be modified by replacing the inorganic interlayer cations with organic cations. The use of a bentonite–sawdust mixture was suggested, however, efficient sorption was obtained only upon hydrophobic modification of the clay. Zadaka et al. (2013) showed that even though montmorillonite, talc and kaolinite do not have a large affinity for oils, sepiolite is unusual and adsorbs up to 6 g/g.

This study tested adsorption of olive oil on two fibrous clays (palygorskite and sepiolite), two smectites (montmorillonite and hectorite) and two non-charged nanocomposites (montmorillonite with poly-DADMAC and sepiolite with chitosan). Adsorbed amounts were tested by separating oil, water and clay by their density, and evaluating the amount of oil on the clay by peak rations of ATR-FTIR measurements (Rytwo et al., 2013). Fibrous clays exhibited 5-8 fold more adsorption than smectites. Neutralization of the clay surface by preparing neutral nanocomposites does not improve significantly oil sorption on montmorillonite, and reduces considerably the adsorption on sepiolite.

Hydrophobicity of the acicular clays-oil complexes was confirmed by NMR relaxation times: while relaxation rates of oil-hectorite complexes increase with concentration of the solid particles in suspension, as it is in most cases, oil-palygorskite complexes exhibited a very unusual behavior where relaxation rates decreased with increasing concentration of particles in suspension. Such behavior can only be explained by the increased hydrophobicity of the particles that hinder the relaxation of the protons.

Influence of fibrous and smectite clay minerals on oil emulsions prepared with a non-ionic surfactant was also tested by means of a dispersion analyzer. Acicular clays de-emulsify oil-surfactant stable emulsion, and separate whereas smectites don’t affect the emulsion. This effect is emphasized in Fig. 1: 6h after preparation, it can still be seen that the original emulsion ("none") and the montmorillonite treated samples ("SWy-2") remain still as stable dispersion, whereas the S9 treated emulsion ("S9") clarifies completely, with some free oil observed at the top of the test tube ("creaming" effect).

Based on those results we assumed that efficiency of fibrous minerals is due to the silanol neutral sites that have proven efficient at adsorbing non-polar molecules (Rytwo et al., 1998). This hypothesis is indeed confirmed by ATR-FTIR measurements. Fig. 2 shows a clear alteration of the OH deformation doublet at app. 750-800 cm⁻¹, and a bathochromic shift of about 10 cm⁻¹ on
the Si-O-H stretch at app. 3700 cm$^{-1}$. Both effects were ascribed in previous studies to adsorption on neutral sites of sepiolite (Rytwo et al., 2002; König et al., 2012).


**Fig.1:** Influence of clay on an olive oil- non ionic surfactant emulsion in water. The left test tube ("none") contains pure emulsion, "S9" and "SWy-2" are emulsions with 1.5 g L$^{-1}$ sepiolite or montmorillonite, respectively.

**Fig.2:** ATR-FTIR spectra of raw sepiolite (solid line), and sepiolite with olive oil added at 1:1(dashed line) and 5:1 g oil g$^{-1}$ clay (dash-dot line). The 750-820 cm$^{-1}$ region exhibits deformation vibrations of the OH bonds of the silanol group whereas absorption bands at app. 3680 cm$^{-1}$ are ascribed to the Si-O-H vibration.
INTERCALATION OF PHYTOCHEMICAL FROM JABORANDI LEAVES INTO SYNTHETIC BEIDELLITE CLAYS

Vanessa Yumi Sakai*, Leiz Maria Costa Véras, Maria Adelaide Guimarães, Filipe Camargo Dalmatti Alves Lima, José Roberto de Souza de Almeida Leite, Helena Maria Petrilli, Jocelyne Miehé-Brendlé, and Vera Regina Leopoldo Constantino

1Instituto de Química, Universidade de São Paulo, São Paulo - SP, Brazil: *vanessa.sakai@usp.br
2Núcleo de Pesquisa em Biodiversidade e Biotecnologia, Universidade Federal do Piauí, Parnaíba - PI, Brazil;
3Instituto de Física, Universidade de São Paulo, São Paulo - SP, Brazil;
4Pôle Matériaux à Porosité Contrôlée, Institut de Science des Matériaux de Mulhouse, UMR CNRS 7361, Université de Haute Alsace, Mulhouse, France.

Many substances of pharmaceutical interest can be extracted from leaves of Jaborandi tree (*Pilocarpus microphyllus*), which is frequent in the Brazilian flora, especially in the region of Maranhão state.[1] One of these substances is pilocarpine (Figure 1), an imidazole alkaloid that is commercialized in the form of eye drops for lowering intraocular pressure in patients with glaucoma[2] and it is also used in the treatment of xerostomia, a disease also known as “dry mouth”. Its oral administration has side effects, as nausea, shakes and sweats.[3] Besides, it is not recommended to people suffering from peptic ulcer and gastrointestinal spasm.[4]

The stability of pilocarpine in solution depends on the pH: it is stable in pH region between 4 and 6.[5] Above and below this range, pilocarpine can be degraded by epimerization or by hydrolysis of the lactone ring, forming products that don’t have the same pharmacologic and therapeutic effects of the alkaloid.[2]

In order to evaluate the possibility of increase the performance of pilocarpine (Pilo) for oral administration, the protonated phytochemical was intercalated by ion-exchange into synthetic beidellite clays of different cation exchange capacities. The theoretical formula of beidellite is \( \text{Na}_x(\text{Al}_2)(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH,F})_2\cdot n\text{H}_2\text{O} \), which \( x \) can be 0.28 (BNa0.28), 0.58 (BNa0.58) or 0.78 (BNa0.78).[6] The hybrid materials were characterized by elemental analysis, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and thermal analysis (TGA). Vibrational spectrum of pilocarpine hydrochloride was simulated by Density Functional Theory (DFT) in order to assign the data obtained for the beidellite intercalated samples.

The elemental analysis show that the material BNa0.28_Pilo has 6.5 wt% of carbon while BNa0.58_Pilo and BNa0.78_Pilo present 8.9 wt% and 8.5 wt%, respectively, resulting in 10.2%, 14.1% and 13.5% (wt/wt) of pilocarpine in the clay hybrid samples. X-ray diffraction data reveal that the basal spacing of BNa0.28, BNa0.58 and BNa0.78 samples after pilocarpine intercalation is

![Figure 1. Structure of pilocarpine hydrochloride.](image-url)
1.46 nm, 1.48 nm and 1.53 nm, respectively. The (001) reflections of all hybrid samples are shape; (003) reflections are observed for BNₐ₀.₅₈_Pilo and BNₐ₀.₇₈_Pilo samples whereas (002) reflection is present for BNₐ₀.₂₈_Pilo. Considering the alkaloid dimensions calculated by DFT in a distorted configuration (0.96 x 0.75 x 0.62 nm), it is possible to suggest a parallel orientation of the organic species between the layers.

Some characteristics bands of pilocarpine are present in FTIR spectra as follow: 3150 – 2940 cm⁻¹ (νCH₂), 1767 cm⁻¹ (νCN), 1614 cm⁻¹ (δCH₂) and 1460 cm⁻¹ (δNH). The broad band at around 1050 cm⁻¹ is attributed to Si-O of the beidellite clays. Besides pilocarpine bands, two strong clay bands are also observed in Raman spectra (Figure 2). The band at 209 cm⁻¹ is attributed to AlO₆ vibrational mode of beidellite, while the band at 707 cm⁻¹ is assigned to distortion of SiO₄ tetrahedron. According to DFT calculation, the band at 767 cm⁻¹ in Raman spectrum of BNₐ₀.₇₈_Pilo sample is related with a distorted pilocarpine configuration between the layers. Spectroscopic results suggest that pilocarpine was not degraded in the intercalation process into beidellites.

According to DSC and TGA curves, pilocarpine hydrochloride melts at 207°C; above this temperature (up to 650°C), the organic compound is decomposed releasing CO₂ (m/z = 44) and H₂O (m/z = 18). In the clay hybrid materials, the thermal stability of pilocarpine increased approximately 50°C in comparison to its related chloride salt and the decomposition process is observed up to higher temperatures. Next studies comprise the pilocarpine release profile from hybrid beidellites in intestine simulated media.

ACKNOWLEDGMENTS: Fapesp, CNPq, Nanobiomed Network (Capes), Vegoextrações do Nordeste LTDA.

![Figure 2. FTIR and Raman spectra of BNₐ₀.₇₈_Pilo sample. Bands of beidellite are indicated with asterisks.](image_url)
URANIUM(VI) AND NEPTUNIUM(V) RETENTION BY CLAY MINERALS AND NATURAL CLAY ROCK—INFLUENCE OF CLAY ORGANICS, TEMPERATURE AND PORE WATER SALINITY

Katja Schmeide*1, Claudia Joseph1,2, and Katharina Fritsch1

1Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstr. 400, 01328 Dresden, Germany: k.schmeide@hzdr.de;
2present address: Glenn T. Seaborg Institute, Physical & Life Sciences Directorate, Lawrence Livermore National Laboratory, L-231, P.O. Box 808, Livermore, CA 94550, USA.

The long-term disposal of high-level nuclear waste in deep geological formations is discussed worldwide as main strategy for nuclear waste management. In addition to salt and crystalline rock, argillaceous rock has been proposed as potential host rock and backfill material for nuclear waste repositories. This is due to favorable characteristics of clay minerals such as their swelling properties and their large surface areas leading to a low permeability and high retention efficiency toward radionuclides. Sorption and diffusion of safety relevant radionuclides on/in clay rock are important physicochemical processes that have to be studied to contribute to a reliable long-term safety assessment for future nuclear waste repositories.

Clay rock is closely associated with natural organic matter. Low molecular weight organic acids such as acetate, lactate, propionate and formate as well as fulvic and humic acid-like substances can be released from the clay under certain conditions [1]. These organics can influence the migration of radionuclides in the environment by forming soluble complexes or stable colloids. In addition, for the disposal of high-level nuclear waste in clay formations, elevated temperatures of up to 100 °C are expected close to the waste containers resulting from the radioactive decay of the stored radionuclides. Besides that, pore waters of North German clay deposits, considered for underground nuclear waste repositories, show relatively high salinities (2 to 3.5 M). Thus, effects of organic matter, temperature and salinity have to be taken into account for a reliable prediction of radionuclide migration in the geosphere.

Batch sorption studies with clay minerals revealed that the U(VI) sorption onto kaolinite [2] is much higher than the Np(V) sorption [3] in 0.1 M NaClO4. In the presence of humic acid, the actinide sorption is increased in the acidic pH range and decreased in the near-neutral pH range. The influence of ionic strength was studied for U(VI) sorption onto montmorillonite by applying 0.1 to 3 M NaCl and CaCl2 as background electrolytes. It was observed that the ionic strength effect on U(VI) sorption on montmorillonite is very small. In NaCl, a decrease of U(VI) sorption with ionic strength is only observed below pH 6 and up to an ionic strength of 2 M. In CaCl2, U(VI) sorption is at least partly governed by secondary phase formation.

The retention behavior of the natural clay rock Opalinus Clay (Mont Terri, Switzerland) toward U(VI) was studied by means of batch sorption and diffusion experiments. Opalinus Clay is considered as representative host rock of a potential nuclear waste repository in argillaceous rock. For the U(VI) sorption onto Opalinus Clay in synthetic Opalinus Clay pore water (pH = 7.6, I = 0.36 M) at 25 °C, the distribution coefficient, Kd, was determined with 22.2 ± 0.4 L/kg [4]. This shows that the U(VI) sorption is relatively weak under pore water
conditions. It is comparable to the Np(V) sorption onto Opalinus Clay \( (25 \pm 5 \text{ L/kg} [5]) \). This can be attributed to the predominance of the weakly sorbing \( \text{Ca}_2\text{UO}_2\text{(CO}_3\text{)}_3\text{(aq)} \) complex in the Opalinus Clay pore water.

The U(VI) sorption onto Opalinus Clay was also studied in 0.1 M NaClO$_4$ in the pH range 3 to 10. Results of surface complexation modelling [6], applied for blind prediction of pH-dependent U(VI) sorption onto Opalinus Clay, showed that U(VI) may predominantly sorb onto illite and montmorillonite. In addition, U(VI) sorption onto Fe(III) minerals was predicted. U(VI) sorption onto further minerals of the clay (kaolinite, chlorite, quartz, feldspars) is negligible.

With increasing concentration of low molecular weight organic acids \( (10^{-5} \text{ to } 10^{-2} \text{ M}) \), the U(VI) sorption onto Opalinus Clay in pore water decreases due to complex formation in solution. The mobilizing effect of the organics on U(VI) increases in the following sequence: formate \( \leq \text{lactate} < \text{acetate} < \text{propionate} < \text{tartrate} < \text{citrate} \). In the presence of \( 1 \times 10^{-2} \text{ M} \) citrate, which has been identified as important ligand in radioactive waste problems, the \( K_d \) value for U(VI) amounts to only \( (1.1 \pm 0.3) \text{ L/kg} \). The influence of the organic ligands on the U(VI) sorption onto Opalinus Clay correlates with the stability of the respective U(VI) complexes. In contrast, humic acid \( (\leq 50 \text{ mg/L}) \) does not affect U(VI) sorption [4]. With increasing temperature up to 60 °C, the U(VI) sorption increases both in the absence and in the presence of clay organics.

The U(VI) diffusion in compacted Opalinus Clay was studied in the absence and presence of humic acid at 25 and 60 °C under anaerobic conditions using Opalinus Clay pore water [7]. The effective diffusion and distribution coefficients \( (D_e \text{ and } K_d) \) determined for U(VI) and humic acid at 25 and 60 °C show that humic acid has no significant influence on the U(VI) diffusion. The diffusion profiles obtained for humic acid in Opalinus Clay at 25 and 60 °C show contributions of at least two different humic acid particle size fractions \( (< 1 \text{ kDa and } 10^{-100} \text{ kDa}) \). The smaller humic acid fraction diffused through the whole clay samples at both temperatures within three months whereas the larger humic acid fraction diffused only about 500 µm into the clay. This shows the filtration effect of the compacted clay and also a different sorption affinity of the humic acid size fractions toward Opalinus Clay. At 60 °C, the diffusion profiles of two U(VI) species were observed, which were attributed to a colloidal and an aquatic U(VI) species. The \( D_e \) and \( K_d \) value of the aquatic U(VI) species increased with increasing temperature. However, these changes compensated each other, thus, an increase of the temperature to 60 °C did not accelerate the migration of U(VI) through Opalinus Clay.

Under environmentally relevant conditions \( (\text{pH} > 7) \), U(VI) is only weakly sorbed by the natural clay rock Opalinus Clay. However, since molecular diffusion is the decisive retardation process in clay rock, Opalinus Clay has a good retention potential toward U(VI).

STUDENT LEARNING FROM THE REYNOLDS CUP COMPETITION

Paul A. Schroeder*1

1Department of Geology, University of Georgia Athens, GA 30602-2501, USA; schroe@uga.edu

The Reynolds Cup (RC) competition is a round-robin contest that uses naturally occurring materials combined in known proportions. Each participating group receives a set of threes mixtures. No information is provided about what phases are present in each sample and their abundances. Ranking for success is determined by a “bias” that uses the sum of differences between the quantitative estimate for each phase measured by the participant and the correspondingly known quantitative value for each phase. The winning bias total for three samples per competition is usually less than 50. The larger bias sums range up to 400.

A graduate class in clay mineralogy at the University of Georgia (UGA) has participated each year the RC competition has been held. Students are presented with the samples and tasked to perform mineral characterization and quantification according to the rules of the competition. A major benefit of the RC competition has been to bring focus not only to the importance of quantifying complex mineral assemblages but the challenge of working with materials in limited supply and producing results in a timely fashion (i.e., a “real world” experience). Student awareness of competing against experienced and well-equipped national and industry labs builds an added esprit-de-corp that creates a motivation difficult to instill otherwise. The RC competition helps to emphasize the need for integration of multiple characterization techniques, such as X-ray diffraction, X-ray fluorescence, thermal gravimetric, infrared spectroscopy, and electron microscopy. The theory behind each methodology is presented in lecture, however the data analysis is pursued collectively during lab as open discussions with peer evaluation of interpretations. Students gain an appreciation of error, including unintentional mistakes that have included the extreme of dropping a sample on the floor and sweeping it up to continue study.

The potential for meaningful student learning from the RC competition is high and it offers an opportunity for expanded teaching in clay science. To make pedagogical use of the competition, some considerations include: 1) keeping the RC competition synchronous with the academic calendar, i.e., Spring semester, 2) creating a sub-competition for student groups only, 3) producing extra sets of mixtures that can be later used for teaching purposes, and 4) continuing to post the winning accounts of “how we did it” to give students ideas for their approach this complex challenge.

The true prize for students, as Bob Reynolds would have liked, is more than the bragging right for winning the competition. It is the opportunity to kinesthetically learn. Bragging rights now reside amongst the previous six UGA classes that have taken on the challenge. The UGA student biases have ranged from 192 to 332, with the 2006 class currently holding the lowest and hence greatest claim to fame. Deep appreciation is expressed to all the organizers who work extremely hard to make the RC competition a success and who create (what was perhaps, originally an unintended consequence) the opportunity for practical student learning in clay science.
WEATHERING OF GLAUCONITE IN A LUVISOL PROFILE FROM GORA PULAWSKA, POLAND

Michał Skiba¹*, Katarzyna Maj-Szeliga¹, Wojciech Szymański², and Artur Błachowski³

¹Institute of Geological Sciences, Jagiellonian University, Kraków, 30-063, Poland: michal.skiba@uj.edu.pl
²Institute of Geography and Spatial Management, Jagiellonian University, 30-387 Kraków, Poland
³Institute of Physics, Pedagogical University, 30-084 Kraków, Poland.

Glaconite is an iron-rich, dioctahedral, interlayer cation deficient mica commonly occurring in soils developed from sediments and sedimentary rocks. Generally in the course of soil weathering glauconite releases potassium and iron and transforms into other phyllosilicates. However, the exact mechanism of glauconite weathering appears to be poorly understood and only a few papers dealing with the issue are available. The aim of the research reported herein was to study the weathering of glauconite taking place in a Luvisol profile developed on quartz-glaconite sand in Góra Puławska near Puławy (eastern Poland).

Basic soil properties were determined for the collected samples. Bulk soil material (i.e. <2 mm fraction), separated clay fractions (<2 µm and <0.2 µm), and glauconite pellets were analysed by X-ray diffractometry. The pellets and the fine clays were also analysed using Fourier transform infrared spectrometry and Mössbauer spectroscopy. Thin sections prepared from undisturbed soil materials were examined using optical microscope. Chemical composition of the fine clay and the pellets was analysed by energy dispersive spectrometry under scanning electron microscope.

The bulk soil material contains quartz, glauconite, glauconite-smectite mixed-layered minerals rich in smectite layers, and traces of feldspars. When compared with the parent material (the C horizon), the Bt1 and Bt2 horizons are enriched in clay minerals while the Ap, AEg, and E horizons are depleted in clays. The observed mineral distribution is most likely controlled by the weathering of clay minerals in the uppermost part of the profile and translocation of clay fractions down the profile (lessivage). However contamination with glaciofluvial and/or aeolian material has to be taken into consideration. According to the microscopic observations of the thin sections clay is present in the B/C and C horizons in the form of clay coatings and clay infilings. This indicates that initially the parent sand did not contain clay fraction. The fraction was formed most likely somewhere in the upper part of the soil profile and was deposited in the lower horizons by percolating atmospheric waters. Green pellets separated from all the soil horizons are composed of glauconite showing more or less uniform chemical composition, while clay fractions from all the horizons contain glauconite and glauconite-smectite. Fine clay fractions separated from Ap and AEg horizons are enriched in glauconite-smectite in relation to the fractions separated from the lower horizons. The presence of glauconite and glauconite-smectite minerals in the clay fractions studied indicates that glauconite weathering in the soil studied involves formation of glauconite clay by the pellets disintegration and glauconite smectitization. Ferrous iron constitutes only 6-7% of the total iron in the primary glauconite. This indicates that ferrous iron oxidation is not the main mechanism leading to the glauconite smectitization.
Because the smectite appears to be depleted in magnesium and total iron and enriched in aluminum and silicon when compared with primary glauconite, leaching of magnesium and iron together with possible reorganization of the structure appear to be the likely mechanisms for the glauconite smectitization.
MICROBIAL COMMUNITY DYNAMICS AND ARSENIC CHEMISTRY OF IRON-OXIDE RICH ROOT-PLAQUE IN RICE RHIZOSPHERE UNDER WATER MANAGEMENT PRACTICES

Anil Somenahally*1, Wengui Yan2, Richard Loeppert1, and Terry Gentry1

1Department of Soil and Crop Sciences, Texas A&M University, College Station, TX 77843-2474, USA: ASomenahally@tamu.edu
2 USDA-ARS, Dale Bumpers National Rice Research Center, Stuttgart, Arkansas 72160, USA

Rice rhizosphere under continuous submergence can compartmentalize to two distinct zones of rhizosphere soil and root-plaque due to radial oxygen diffusion along the roots. Dissolved FeII from the anoxic bulk soil can diffuse, oxidize, and subsequently precipitate as iron oxides on the oxidized root surface. Major form of iron oxide comprising these plaques is reportedly poorly-crystalline ferrihydrate, that can provide binding sites for metals such as arsenic and reduce immediate bioavailability to roots. However, whether root-plaque is a sink or a source of As for the rice plant depends on localized clay-microbe interactions as microbial activity can impact the dissolution/precipitation of iron oxide and speciation of arsenic. We conducted a field experiment to study the impact of two water management practices on arsenic chemistry and microbial populations in the root-plaque and rhizosphere. Arsenic speciation was measured using HPLC-ICP-MS, microbial populations were characterized with 454 pyrosequencing of 16S rRNA gene, quantitative-PCR and microbial functional gene composition by Geochip 4.0 array.

The root-plaque had significantly higher As concentrations compared to the adjacent rhizosphere soil, with relatively higher As:Fe ratios in continuously flooded compared to the intermittently flooded plots. Results also indicated that soil-As speciation, specifically the occurrence of methyl-As species in the root plaque, had a greater impact than water management on grain-DMAsV concentrations. Microbial population and functional gene diversity were different between rhizosphere and root-plaque area. Microbial arsenic reduction and methylation genes were detected, implying that bacterial iAsV reduction and iAsIII efflux and arsenic methylation can be prevalent on root-plaque. Iron reducing and sulfate reducing bacteria were prevalent on root-plaque suggesting that dissimilatory Fe(III) reduction and subsequent release of associated As could also be occurring on root-plaque, given appropriate localized redox conditions. Results of this study showed that unique biogeocomplex at root-plaque can significantly affect arsenic bioavailability to the rice plant.
MOLECULAR INVESTIGATION OF CO2 ADSORPTION AND SWELLING STRAIN IN NA-EXCHANGED WYOMING MONTMORILLONITE

Paul Spiering1,2, Rick Wentinck2, Andreas Busch2, Johannes G.E.M. Fraaije1, and Tim J. Tambach*2

1Leiden Institute of Chemistry, University of Leiden, Einsteinweg 55, 2333 CC Leiden, The Netherlands;
2Shell Global Solutions International BV, Kesslerpark 1, 2288 GS Rijswijk, The Netherlands: tim.tambach@shell.com

Injection of CO2 into geological reservoirs is considered to permanently store CO2 or to enhance production of hydrocarbons. Most of these reservoirs are sealed by tight, argillaceous rocks with high clay content (e.g. kaolinite, illite, smectite), ensuring containment of fluids and gases. Buoyancy of injected CO2 causes upwards migration in the reservoir until it reaches the clay-rich seal. Aqueous diffusion through the caprock is the dominant transport mechanism as viscous flow through the seal is prevented by high capillary forces. The seal could contain swelling clays, such as montmorillonite, which are able to significantly adsorb CO2. (Giesting et al., 2012). This can cause clay swelling and build-up of swelling pressures, which we consider as an important aspect for the long-term containment of injected CO2. Experimental data on the influence of CO2 in swelling clays is challenging to interpret due to the lack of a validated molecular model. The goal of this work is to use molecular simulations for gaining better insights in molecular configurations and mechanisms present in Na-exchanged Wyoming montmorillonite exposed to CO2 and H2O.

We carried out our simulations using Culgi and used a hybrid scheme of molecular dynamics (MD) – Monte Carlo (MC) simulations to reproduce the H2O and CO2 equations of state (EOS) as well as to model CO2 adsorption in Na-montmorillonite. Translation of molecules is done with MD, while volume expansion and contraction at constant pressure perpendicular to the clay layers (Pz) is done using MC. Hence the NPzT ensemble is used, together with the ClayFF force field (Cygan et al., 2004). The simulations are benchmarked with earlier work (Cygan et al., 2012; Tambach, 2005) and demonstrate step-wise swelling in layers, with increasing basal spacing as a function of water content.

We further focused our work on simulating the swelling strain of CO2 adsorption in montmorillonite, which is experimentally measured at elevated temperature and pressure (Giesting et al., 2012). At these conditions, the domain of the dehydrated state to the one layer hydrate is dominant in geological reservoirs of interest. The experiments indicate limited swelling at discrete dehydrated and one-layer hydrate states, but up to 9% swelling strain for swelling states between those. This is qualitatively reproduced with molecular simulations. We analyzed the associated molecular configurations using radial distribution functions (RDFs) and density profiles, pointing to significant changes in coordination of H2O and CO2 to the Na cations. These observations potentially cause observed changes in swelling strain.
References


INTERLAYER IN-SITU REACTION PREPARATION METHOD OF NANOSTRUCTURED TiO$_2$/MONTMORILLONITE MATERIALS

Hongjuan Sun$^{1,2}$, Tongjiang Peng$^1$, Hailiang Dong$^{3,4}$, and Chaojian Gu$^1$

$^1$Institute of Mineral Materials & Application, Southwest University of Science and Technology, Mianyang, Sichuan, 621010, PR China;
$^2$Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510460, PR China: sunhongjuan@swust.edu.cn
$^3$State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing, 100083, China;
$^4$Department of Geology and Environmental Earth Science, Miami University, OH 45056, USA.

Nanostructured TiO$_2$/Montmorillonite materials have wide applications in plastic degradation, photocatalysis, antibacterial agent development and water purification. However, the synthesis method for its nanoparticles is not easy. In order to homogeneously disperse TiO$_2$ nanoparticles (anatase phase) within the interlayer space of montmorillonite, in-situ interlayer reaction method was introduced to prepare nanostructured TiO$_2$/Montmorillonite materials. In this method, Cetyl trimethyl ammonium cation (CTA$^+$) was firstly intercalated into the interlayer space of montmorillonite structure. Then tetrabutyl orthotitanate (TBOT) was entered into the interlayer space of CTA$^+$-montmorillonite heterostructure through solvation. TBOT in the heterostructure underwent in-situ hydrolysis and de-hydroxylation. Upon heating to 300$^\circ$C, CTA$^+$ was burned off and anatase was formed in the interlayer space of montmorillonite structure. Various intermediate and final products were characterized by X-ray diffraction, infrared spectroscopy and transmission electron microscopy. The characterization results showed that TBOT successfully entered the interlayer space of montmorillonite that was pre-exchanged with CTA$^+$. The structure of (CTA$^+$, TBOT)-montmorillonite composite was poorly ordered, and the montmorillonite layers were not delaminated. In addition, the final structure of anatase-montmorillonite heterostructure was disordered along the [001] direction.

**Keywords:** Montmorillonite, Interlayer space, In-situ reaction, TiO$_2$/montmorillonite heterostructure
CLAY-ASSISTED DISPERSION OF NANOPARTICLES IN POLYMER MATRICES

D. Sun*, X. Zhang, C.C. Chu, W.N. Everett, and H.-J. Sue

Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843-3123, USA

Achieving good dispersion of nanoparticles in polymer matrices is a non-trivial task. It usually requires significant efforts to functionalize the nanoparticle surfaces using appropriate compatibilizers and/or suitable processing equipment. In many cases, utilization of compatibilizers is not desirable due to its potential negative impact to the matrix properties. Effective processing tools typically involve high shear, which can lead to breakage or damage to the nanoparticles. Consequently, new approaches for achieving good dispersion of nanoparticles in polymer matrices are needed.

In this talk, two examples of clay-assisted dispersion of nanoparticles in polymer matrices will be presented. The first example involves the utilization of a synthetic clay, alpha-zirconium phosphate (ZrP) to disperse zinc oxide (ZnO) quantum dots in epoxy and in polymethylmethacrylate (PMMA). Highly stable and fully dispersed ZnO in epoxy using ZrP as an inorganic dispersant can be readily achieved (Fig. 1). The second example involves the usage of ZrP to exfoliate and disperse single-walled carbon nanotubes (SWCNTs) in epoxy. The degree to which the SWCNTs can be dispersed depends on the weight ratio between SWCNT and ZrP (Figure 2). The fundamental mechanisms responsible for the above clay-assisted dispersion processes are discussed.
THE STRUCTURE, DYNAMICS AND FUNCTION OF SYNTHETIC AND BIOLOGICAL POLYMERS AT THE CLAY MINERAL SURFACE FROM MOLECULAR DYNAMICS SIMULATION

Jacob B. Swadling¹, James L. Suter¹, Derek Groën¹, David W. Wright², and Peter V. Coveney¹*

¹Centre for Computational Science, Department of Chemistry, University College London, WC1H 0AJ, UK. *Email: p.v.coveney@ucl.ac.uk; ²Department of Structural and Molecular Biology, University College London, WC1E 6BT.

Our work illustrates various facets of the interaction between charged mineral surfaces and an array of ionic species and polymers with applications as vast as novel drilling fluids in the petrochemical industry to probing the chemical origins of life¹–³.

Compared to proteins the relationship between structure, dynamics and function in RNA enzymes (known as ribozymes) is far less understood despite the fact that such entities are found in a wide range of organisms and have been proposed as "molecular fossils" of the very first self replicating molecules. Through large-scale replica exchange molecular dynamics we have demonstrated the ability of clay minerals to radically alter the kinetics of physico-chemical processes such as nucleic acid folding, and elucidate how prevailing geochemical environments alter the ribozymal catalytic function of naturally occurring ribozymes. To investigate how ribozymal function is governed by structure and dynamics, we study the hammerhead ribozyme in bulk water and in a clay mineral environment by computer simulation using replica exchange molecular dynamics. The hammerhead ribozyme serves as a prototype for understanding the structure and function of the wider class of ribozyme molecules. Through extensive sampling of the major conformational states of the hammerhead ribozyme, we are able to elucidate both the tertiary structure and that of the active site, thereby reconciling conflicts between proposed reaction mechanisms and accounting for the differences reported experimentally in the catalytic activity of hammerhead ribozyme structures in different environments.

Figure 5. Simulation snap-shot of the hammerhead ribozyme from 50 ns of replica exchange molecular dynamics. The surface bound ribozyme shows a significantly altered conformation compared to the ribozyme in bulk water. The ribozyme is tethered to the mineral surface via a terminal planar base.
However, the simulation of layered nano-minerals is challenging; the microscopic structure and mechanisms operate over many different length scales, ranging from nanometers to microns. One of the key challenges in the simulation of such systems is efficiently sampling these scales to understand how the microscopic structure affects the macroscopic properties. To this end, we have constructed a multiscale simulation scheme to scan across length scales from atoms to microns for charged mineral surfaces and polymer molecules. This scheme varies from the electronic structure (to capture the polymer-clay interactions, especially those of the reactive clay edges) through classical atomistic molecular dynamics to coarse-grained models (to capture the long length scale structure).

![Image](image_url)

Figure 2. Snapshot taken from 200 ns of simulation of poly(vinyl) alcohol (PVA) polymer and montmorillonite clay.

We will show how we constructed the important polymer-polymer and polymer-clay interfacial interactions at each level. We present our current simulations: systems containing discrete clay mineral tactoids at both the atomistic and coarse-grained level. The latter system is of unprecedented size and allows us to observe the structural details and properties of the clay-polymer system on the sub micron level, which can be related to experimental results. We will discuss how the results and our multiscale simulation scheme can be used in the future for predictive modeling of these and related systems.

MOLECULAR MODELING OF THE EFFECT OF 40Ar RECOIL IN ILLITE PARTICLES ON THE K-Ar ISOTOPE DATING OF THEIR HOST ROCKS

Marek Szczerba*1, Arkadiusz Derkowski1, Andrey Kalinichev2, and Jan Środoń1

1 Institute of Geological Sciences, Polish Academy of Sciences, Kraków, Poland: ndszczer@cyf-kr.edu.pl
2 Laboratoire SUBATECH, Ecole des Mines de Nantes, Nantes, France.

The 40K decay to 40Ar is the basis of isotope age determination of micaceous clay minerals in the zone of diagenesis. The difference in K-Ar ages between fine and coarse grained illite particles has been interpreted using detrital-authigenic components system and its crystallization history (Środoń et al., 2002). This approach assumes that the dated mineral remained a closed system since crystallization. On the other hand, Lerman and Clauer (2005) and Lerman et al. (2007) have suggested post-crystallization diffusion as a mechanism responsible for lower K-Ar isotope age estimates of finer particles. Yet another feasible mechanism is also possible: natural 40Ar recoil. The aim of this research was to check if the latter mechanism can result in 40Ar loss that is significant enough to provide observable decrease of K-Ar age of the finest illite crystallites in diagenetic temperatures.

The study is based on molecular dynamics simulations. The energy and velocity of 40Ar atoms after recoil were calculated on the basis of the energy of emitted gamma ray after the 40K - 40Ar electron capture transition: 28.66 eV. The simulations were performed for two force fields REAXFF (van Duin et al., 2001; Pitman and van Duin, 2012) and CLAYFF (Cygan et al., 2004) using the LAMMPS computer program (Plimpton, 1995). All the simulations were performed for the same initial velocity (kinetic energy) but for varying the recoil angles that cover the whole range of their possible values.

The results show that 40Ar recoil can lead to different deformations of the structure, often connected with the displacement of OH groups or breaking of the Si-O bonds. At the end of the simulation, there are four possible final positions of 40Ar, with respect to the 2:1 layer. For high recoil angles relative to the surface normal, the most common effect observed is that 40Ar bounces back from the basal oxygen surface and remains in the interlayer space. For lower angles (close to the surface normal), 40Ar enters into the tetrahedral sheet and remains there. 40Ar can also enter the octahedral sheet upon recoil, but with very low probability. Under certain recoil angles pointed approximately in the direction of the vacancy in the octahedral sheet, the 40Ar can pass through the octahedral vacancy and then stop in the tetrahedral sheet on the opposite side of the 2:1 layer. The maximum recoil distance of 40Ar along the interlayer depends on the filling of the interlayer with potassium or water. If there is void space in the interlayer, 40Ar can jump maximally to the second after the neighboring position. If all interlayer positions are fully filled, 40Ar bounces back to the initial position independent of the initial recoil angle.

The energy barrier for 40Ar passing through the hexagonal cavity of the tetrahedral sheet was calculated to be equal to 17 kcal/mol. This reaction is strongly exothermic (ΔE = -26 kcal/mol), therefore there is almost no possibility for 40Ar to remain inside the 2:1 layer during geological time. The deformation of the 2:1 structure caused by the 40Ar recoil and associated
with the re-positioning or removal of OH groups will be annealed during geological time, as it can be assumed by analogy with the dehydroxylation reactions.

In order to apply the results of the MD simulations to the calculation of the potential effect of $^{40}$Ar recoil on the K-Ar dating of illite, the illite crystallites were built with small integer number of 2:1 layers containing $^{40}$Ar atoms distributed randomly within the structure. $^{40}$Ar can be lost due to recoil if its position before recoil is close enough to the crystallite side edges. $^{40}$Ar can escape from the structure also due to the thermal motion over geological time periods.

It was found that $^{40}$Ar loss shows substantial dependency on the crystallite diameter and the number of 2:1 layers it contains. The $^{40}$Ar loss can vary from 13% for the finest crystallites (2 layers and 0.01 m diameter) to close to zero for the thickest and largest (in the ab plane) ones. A virtual removal of the interlayer potassium ions closest to the edges of an illite crystallite, results in a significant correction of the total $^{40}$Ar loss, which drops by a factor of 2-4, or even more. Because the decrease of the K-Ar estimated age is proportional to the $^{40}$Ar loss, the finer crystallites show lower apparent age than the coarser ones, although the age of crystallization is assumed equal for all the crystallites. From the model it is also clear that the lack of K removal from illite fringes (potentially Ar-free) strongly increases the apparent age differences among crystallites.

LITERATURE


Lerman A., Ray B.M. and Clauer N., 2007, Radioactive production and diffusional loss of radiogenic $^{40}$Ar in clays in relation to its flux to the atmosphere, Chemical Geology, 243, 205-224


Środoń J., Clauer N. and Eberl D.D., 2002, Interpretation of K-Ar dates of illitic clays from sedimentary rocks aided by modelling, American Mineralogist, 87, 1528-1535
DESIGN AND CHARACTERIZATION OF HYBRID MATERIALS FROM NATURAL INORGANIC NANOTUBE “HALLOYSITE”

Atsushi Takahara*1,2,3, Wei Ma2, Hui Wu3, Di Tao1, and Weng-On Yah1

1Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 819-0395, Japan;
2WPI-I2CNER, Kyushu University, Fukuoka 819-0395, Japan;
3JST Takahara Soft Interfaces Project, CE80, Kyushu University, Fukuoka 819-0395, Japan:
takahara@cstf.kyushu-u.ac.jp

Organic/inorganic nanohybrids by surface functionalization of inorganic nanostructures are attracting a great deal of research interest. Halloysite is naturally occurring aluminosilicate clay mineral with a hollow nanotube structure. It has a 1:1 Al:Si ratio and a stoichiometry of Al2Si2O5(OH)4.nH2O, with siloxane groups in the outside and aluminol groups in the inside of the tube. In this study, the authors propose several techniques for surface modification of halloysite nanotubes and demonstrate some potential applications.

The selective hydrophobization of the inner surface of tubular halloysite was developed.1 Aqueous phosphonic acid was found to bind on aluminol sites at the tube lumen and did not bind the tube’s outer siloxane surface. The bonding was characterized with solid state nuclear magnetic resonance (29Si, 13C, 31P NMR), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). NMR and FTIR spectroscopy of selectively modified tubes proved binding of octadecyl phosphonic acid within halloysite lumen through bidentate and tridentate P-O-Al linkage. Selective modification of the halloysite clay lumen creates inorganic micelle-like architecture with hydrophobic aliphatic chain core and hydrophilic silicate shell. An enhanced adsorption capacity of the modified halloysite toward hydrophobic derivatives of ferrocene was shown. This demonstrates that different inner and outer surface chemistry of clay nanotubes can be used for selective modification, enabling different applications, from water purification to drug immobilization and controlled release.

We also demonstrate the use of a catecholic anchor (DOPA) for selective modification of inner surface of halloysite nanotube.2 Aqueous DOPA can bind to the aluminol groups at the tube lumen while does not bind the siloxane external surface under the same condition. Selectivity of surface modification was evidenced using XPS and 13C solid state NMR spectroscopy. Surface-initiated atom transfer radical polymerization (SI-ATRP) was performed through selectively adsorbed DOPA to graft a layer of polymer brush into the nanotube lumen.

Furthermore, by using halloysite nanotube, we prepared fluorine-free liquid marbles.3 Halloysite was modified with octadecyltrimethoxysilane. The surface-modified halloysite formed pincushion agglomerates on the surface of the liquid droplets, which create superhydrophobic surface similar to that of the plant gall surface prepared by aphids. As a result, the liquid marbles showed high mechanical strength upon impact without the use of low surface energy fluoroalkyl or fluorine-modified materials. Our results suggest a new strategy for designing novel materials for liquid marbles inspired by nature.


AFLATOXIN SORPTION ON VOLCANIC ASH DERIVED SOILS

Maria Guadalupe Tenorio Arvide*1, Yolanda P. Silva Uribe2, Youjun Deng3, Ricardo Munguía P.4, and Miguel A. Valera P5.

1Departamento de Investigación en Ciencias Agrícolas, Instituto de Cienciencias, Benemérita Universidad Autónoma de Puebla, Av. 14 Sur 6301, Fracc. Jardines de San Manuel, Puebla, Puebla, México: tenorio.arvide@correo.buap.mx
2Colegio de Ing. Ambiental, Benemérita Universidad Autónoma de Puebla;
3Department of Soil and Crop Sciences, Texas A&M University, College Station, TX 77843-2474, USA.
4 Laboratorio de Micología, Instituto de Ciencias. BUAP.

A consequence of climate change is reflected quality food, especially when those are contaminated with fungus; such as Aspergillus flavus and parasiticus, and their potential micotoxin, called Aflatoxin B1, and is most potent toxic substance that appear naturally, around the world and could be present in maize, cereals, nuts. Food and feed contaminated with aflatoxins affect animals and humans health. Decontamination process includes physical, and chemical methods, alternative method include natural adsorbents such as, zeolites and bentonites.

It is important to mention that soil derived from volcanic ash has unique chemical and mineralogical properties that affect their agriculture uses, management, and potential applications, those soils has been used in the sorption process of different contaminants, for example atrazine, diuron, 2,4-dichlorophenol and pentachlorophenol; in this this research, the objective is to investigate aflatoxin sorption on volcanic ash derived soils.

The soil samples have been examined on their properties: physical, chemical, biological and mineralogical. The soil sample’s texture is loam, color redish brown; pH 4.5 (1:2; soil:water) and 3.5 (1:2; soil: KCl), delta pH value indicates variable charge soils, another important property of consider in the sorption process. The organic matter is about 11 %, CEC 43.6 cmol/kg. On the soil sample was possible to identify fungus in order of prevalence: Fusarium, Aspergillus and Penicillum, those fungus under stress conditions (humidity and temperature) could produce secondary metabolite called micotoxins. About mineralogical properties was possible to identify by X-ray diffraction (XRD) quartz and kaolinite, it was confirmed by Fourier transform infrared (FTIR) spectroscopy. Finally the isotherm was calculated using Freundlich equation, the maximum sorption capacity calculated was 2·10^{-3}mol g^{-1}, it is a low value in comparison with other kind of aflatoxin sorbents.

In conclusion, the propose material is potentially effective as sorbent of aflatoxin B1, it is important to continue with this research, get details about the stability, desorption process, and potential use as an inhibitor of mold originated by fungus Aspergillus and/or Fusarium.
MARTIAN SMENTITES AND RELATED MATERIALS IN THE NAKHLITE MARTIAN METEORITES.

Allan H. Treiman¹*, John C. Bridges²

¹ Lunar and Planetary Institute, Houston, TX 77058; treiman@lpi.usra.edu. USA.
² Space Research Centre, Department of Physics & Astronomy, University of Leicester, Leicester LE1 7RH, UK. j.bridges@le.ac.uk

The recent discovery of smectite clay minerals on Mars by the CheMin instrument on MSL prompts further study of clay minerals in the martian meteorites. Clay minerals and mineraloids in the nakhlite martian meteorites (pyroxenitic igneous rocks, crystallized at 1300 ma) were recognized in 1975 by Reid and Bunch and by Ashworth and Hutchison, as veinlets of ‘iddingsite’, Figure 1a. The veins were shown to be truncated by fusion crust and therefore pre-terrestrial (i.e. martian) in 1991 by Gooding et al., and to have formed at ~650 ma by Swindle et al. They contain a mixture of phases, including poorly crystalline silicate ‘gel’, siderite, ferromagnesian smectite, Fe-rich serpentine, minor Fe oxy-hydroxides, with gypsum, anhydrite, and halite (Treiman et al. 1993; Changela and Bridges 2010). X-ray Absorption (XANES) analyses indicate that the smectite, serpentine, and gel are all ferric-rich (Bridges et al. 2014). Only Lafayette contains abundant crystalline smectite; its composition (from EMP and XANES) is ~(Ca0.2K0.1)(Fe2+1.3Fe3+1.7Mg2.6Mn0.1)(Si6.7Al0.9Fe3+0.4)O20(OH)4. Crystalline clays are also reported from Nakhla and Y000593, although most of their veins consist only of gel.

There is limited structural data on the Lafayette smectite. 001 interlayer d-spacings range from ~1.5 nm in air (synchrotron XRD) to ~1.0 nm under high vacuum (TEM). The Lafayette smectite shows a peak at 0.459 nm, which is interpreted as its 021 band; that location suggests the smectite is trioctahedral and Fe-rich. The smectite is mixed and interlayered with material of ~0.7 nm spacing, a 1:1 phyllosilicate ferric serpentine. Most serpentine is located in the mesostasis of Lafayette. The Lafayette smectites have not been examined after glycolation or other derivitizations.

The origin of this hydrothermal assemblage in the nakhlites has been explained in relation to the thermal histories of the various nakhlites. Alteration veins from within a few metres of the martian surface (based on igneous cooling rates, e.g., MIL03346) contain only gel, while veins with a deeper origin also contain crystalline phyllosilicates and salt minerals siderite, gypsum). The different cooling rates and mineralogy can be correlated with depth beneath the martian surface, which establishes a physical framework for deposition of alteration materials. Changela and Bridges (2010) suggest that olivine and mesostasis glass in the nakhlites were altered by rising hydrothermal fluids. Nakhlites (e.g., Lafayette) nearer the inferred heat and fluid source are richer in alteration material overall and richer in crystalline clay compared to shallower samples. The sequence of mineral deposition was: siderite, smectite (where present), minor Fe oxy-hydroxide, and gel. The smectite and gel replaced siderite locally; siderite is apparently replaced (in some samples) by a porous mass of iron oxides (Fig. 1a; compare to Fig. 2a of Changela et al. 2010). Bridges and Schwenzer (2012) showed that the nakhlite alteration was associated with near neutral fluids, at low water/rock ratio, that precipitated Ca-siderite at ~150 °C, followed by crystallization of the smectite and gel at ~50 °C. Final evaporation of the residual fluids led to precipitation of the sulfate and halite.
Figure 1. Lafayette martian meteorite, BSE images of thin sections; scale bars 10 µm (Treiman et al. 1993).
Left. Veinlet replacing olivine with classic ‘V’ edge. Crystalline smectite (sm) in radiating sprays, with inner zone of amorphous ‘gel’ (a). Porous oxide material (po) may have replaced original siderite.
Right. ‘Iddingsite’ veinlet (v) traversing olivine (bright). As the veinlet approaches the fusion crust (fc), its internal structure (arrow) disappears and it is turns to vesicular melt and iron oxide (i).

Figure 2. Physical model of nakhlite alteration (Changela & Bridges 2010). “An impact on the Martian surface initiated the melting of buried H2O–CO2 ice (permafrost). The fluid (indicated by curved arrows) flows in the direction from Lafayette to Nakhl through impact-induced fractures. The enlarged region shows the different assemblages associated with the olivine grains of the different nakhlites”

FERRIAN SAPONITE FROM GRIFFITH PARK (LOS ANGELES, CA)–INSIGHT INTO CLAY MINERALS AT YELLOWKNIFE BAY (GALE CRATER, MARS)


1 Lunar and Planetary Institute, Houston, TX 77058. USA. treiman@lpi.usra.edu
2 ARES Directorate, NASA Johnson Space Center, Houston TX 77058. USA.
3 Dept. Physics, University of Alabama at Birmingham, Birmingham, Alabama 35294. USA.
4 Jacobs NASA Johnson Space Center, Houston, Texas 77058. USA.
5 UTC Aerospace Systems – Jacobs JETS Contract, Houston, TX, 77058. USA.
6 Dept. of Geological Sciences, Indiana University, Bloomington, IN 47405. USA.
7 Exobiology Branch, NASA Ames Research Center, Moffett Field, CA 94035. USA.
8 Planetary Science Institute, Tucson, AZ 85719. USA.
9 Chesapeake Energy Corporation, Oklahoma City, OK 73118. USA.
10 Department of Geosciences, University of Arizona, Tucson AZ 85721. USA.

Ferrian saponite from the eastern Santa Monica Mountain, near Griffith Park (Los Angeles, CA), was investigated as a mineralogical analog to smectites discovered on Mars by the CheMin X-ray diffraction instrument onboard the Mars Science Laboratory (MSL) rover Curiosity. The martian smectites occur in sediment of basaltic composition; in CheMin XRD, they show broad 001 peaks at 10-13 Å, and 02\l bands peaking at 4.59 Å, consistent with a trioctahedral phyllosilicate.

The Griffith saponite occurs in basalts as pseudomorphs after olivine and mesostasis glass (Fig. 1) and as fillings of vesicles and cracks; its 02\l bands have the same position and shape as the martian smectite, but its 001 peak is at 15Å (11.8Å desiccated in dry N2) and is sharp. For several samples of Griffith saponite, we obtained electron microprobe chemical data, Mössbauer spectra, X-ray diffraction patterns with a lab version of the CheMin instrument, and visible and near-IR (VNIR) reflectance spectra. The Griffith saponite is magnesian [Mg/(Mg+\Sigma Fe) = 65-70%], ferrian [Fe3+/\Sigma Fe = 65-90%], and lacks significant tetrahedral Fe3+. It is fully a trioctahedral smectite, with interlayer Ca and Na, and no octahedral Al3+: e.g., (Ca0.42Na0.03)(Fe3+1.17Fe2+0.66Mg4.16)(Si6.55Al1.42)O20(OH)4 (Table 1). The abundance of Fe3+ gives a nominal excess charge of +1 to +2 per formula unit, which is likely compensated by substitution of O2– for structural OH–. We hypothesize that the Griffith saponite was initially deposited with all its iron as Fe2+, and was oxidized later.

VNIR spectra of the Griffith saponite (Fig. 2) show distinct absorptions at 1.40 (OH), 1.90 (molecular H2O), 2.29-2.32 μm and 2.40 μm ([Fe3+, Fe2+, Mg2+]OH). The position of the ~2.3 μm spectral feature varies systematically with the redox state of the octahedrally coordinated Fe, from 2.300 μm for (Fe3+/\Sigma Fe)=90%, to 2.318 μm for (Fe3+/\Sigma Fe)=65. This correlation may permit surface oxidation state to be inferred (in some cases) from VNIR spectra of Mars obtained from orbit.
### Table 1. Compositions (electron microprobe) and Structural Formulae of Some Saponites from Griffith Park, CA.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>AMNH Vf-c</th>
<th>AMNH ExOl</th>
<th>AMNH Meso</th>
<th>MU Vf-c</th>
<th>MU ExOl</th>
<th>MU Meso</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>44.63 ±1.3445.95</td>
<td>1.2545.75</td>
<td>1.9543.68</td>
<td>1.7844.20</td>
<td>1.2742.76</td>
<td>±1.96</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.01 ±0.010.03</td>
<td>0.020.10</td>
<td>0.170.02</td>
<td>0.020.09</td>
<td>0.180.51</td>
<td>±0.68</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.36 ±0.757.91</td>
<td>0.567.91</td>
<td>0.447.93</td>
<td>0.437.69</td>
<td>0.217.26</td>
<td>±0.78</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.01 ±0.010.02</td>
<td>0.020.01</td>
<td>0.020.01</td>
<td>0.010.01</td>
<td>0.010.01</td>
<td>±0.03</td>
</tr>
<tr>
<td>FeO</td>
<td>14.87 ±0.5215.60</td>
<td>0.5616.35</td>
<td>0.10216.35</td>
<td>0.4414.80</td>
<td>0.3015.97</td>
<td>±1.95</td>
</tr>
<tr>
<td>NiO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
<td>±0.020.03</td>
</tr>
<tr>
<td>MnO</td>
<td>0.07 ±0.030.08</td>
<td>0.020.12</td>
<td>0.040.56</td>
<td>0.040.70</td>
<td>0.040.68</td>
<td>±0.06</td>
</tr>
<tr>
<td>MgO</td>
<td>19.00 ±0.9119.09</td>
<td>0.5918.18</td>
<td>0.8818.87</td>
<td>0.9619.45</td>
<td>1.0516.86</td>
<td>±2.85</td>
</tr>
<tr>
<td>CaO</td>
<td>2.66 ±0.1221.3</td>
<td>0.452.33</td>
<td>0.303.02</td>
<td>0.103.28</td>
<td>0.084.23</td>
<td>±1.36</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.09 ±0.020.07</td>
<td>0.030.08</td>
<td>0.050.13</td>
<td>0.030.12</td>
<td>0.030.44</td>
<td>±0.47</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.03 ±0.020.03</td>
<td>0.010.03</td>
<td>0.010.03</td>
<td>0.020.01</td>
<td>0.010.23</td>
<td>±0.47</td>
</tr>
<tr>
<td>total</td>
<td>89.74 ±2.1090.90</td>
<td>2.1890.86</td>
<td>1.4588.98</td>
<td>2.4490.37</td>
<td>0.9188.98</td>
<td>±2.23</td>
</tr>
<tr>
<td>Mg# %</td>
<td>69</td>
<td>69</td>
<td>67</td>
<td>70</td>
<td>70</td>
<td>65</td>
</tr>
<tr>
<td>Fe³⁺/Fe⁴⁺</td>
<td>64</td>
<td>67</td>
<td>67</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>IVSi</td>
<td>6.55 ±0.0966.65</td>
<td>0.0866.65</td>
<td>0.106.59</td>
<td>0.046.64</td>
<td>0.046.66</td>
<td>±0.19</td>
</tr>
<tr>
<td>IVAl</td>
<td>1.42 ±0.0913.5</td>
<td>0.081.35</td>
<td>0.101.41</td>
<td>0.041.36</td>
<td>0.041.34</td>
<td>±0.19</td>
</tr>
<tr>
<td>IVFe³⁺</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>VIAl</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>VIFe³⁺</td>
<td>1.17 ±0.0513.2</td>
<td>0.041.85</td>
<td>0.161.67</td>
<td>0.001.67</td>
<td>0.151.87</td>
<td>±0.25</td>
</tr>
<tr>
<td>VI Cr</td>
<td>0.00 ±0.0000.2</td>
<td>0.000.00</td>
<td>0.000.00</td>
<td>0.090.00</td>
<td>0.000.00</td>
<td>±0.00</td>
</tr>
<tr>
<td>VI Ti</td>
<td>0.00 ±0.0000.00</td>
<td>0.000.01</td>
<td>0.020.00</td>
<td>0.000.01</td>
<td>0.020.06</td>
<td>±0.08</td>
</tr>
<tr>
<td>VIFe²⁺</td>
<td>0.66 ±0.030.57</td>
<td>0.030.14</td>
<td>0.010.19</td>
<td>0.010.19</td>
<td>0.020.21</td>
<td>±0.03</td>
</tr>
<tr>
<td>VI Ni</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.00</td>
<td>±0.000.00</td>
</tr>
<tr>
<td>VI Mn</td>
<td>0.01 ±0.000.01</td>
<td>0.000.01</td>
<td>0.010.07</td>
<td>0.010.09</td>
<td>0.010.09</td>
<td>±0.01</td>
</tr>
<tr>
<td>VI Mg</td>
<td>4.16 ±0.264.12</td>
<td>0.113.94</td>
<td>0.264.25</td>
<td>0.284.35</td>
<td>0.393.92</td>
<td>±0.65</td>
</tr>
<tr>
<td>Σ VI M</td>
<td>6.00 ±0.286.02</td>
<td>0.145.95</td>
<td>0.396.18</td>
<td>0.346.32</td>
<td>0.356.15</td>
<td>±0.44</td>
</tr>
<tr>
<td>XII Ca</td>
<td>0.42 ±0.020.33</td>
<td>0.070.48</td>
<td>0.050.68</td>
<td>0.030.74</td>
<td>0.030.98</td>
<td>±0.33</td>
</tr>
<tr>
<td>XII Na</td>
<td>0.03 ±0.010.02</td>
<td>0.010.03</td>
<td>0.030.04</td>
<td>0.010.03</td>
<td>0.010.13</td>
<td>±0.14</td>
</tr>
<tr>
<td>XII K</td>
<td>0.01 ±0.000.01</td>
<td>0.000.01</td>
<td>0.000.01</td>
<td>0.000.00</td>
<td>0.000.05</td>
<td>±0.09</td>
</tr>
<tr>
<td>Σ Charge</td>
<td>+0.91 ±0.67+0.71</td>
<td>±0.35+1.17</td>
<td>±0.84+2.02+0.82+2.06+0.76+3.11+1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interlayer Charge</td>
<td>+0.88 ±0.06+0.69</td>
<td>±0.15+1.00</td>
<td>±0.05+1.41+0.06+1.51+0.06+2.14+0.88</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. BSE image, thin section (sample AMNH 89172). Saponite (sp) pseudomorph after olivine euhedron in center. Arrows denote saponite flakes (cleavages) perpendicular to large cracks, which represent cleavage fractures on \{001\} & \{010\} in the original olivine crystal. Other materials.

Figure 2. VNIR unpolarized reflectance spectra of several Griffith saponite samples (names in top frame). Top: Full spectrum, note strong absorptions from X-OH groups, and variable strength of Fe^{2+}-Fe^{3+} bands. Bottom: Detail of MOH region, continuum normalized. The location of the ~2.3 µm band varies with oxidation state: the AMNH sample (blue) has the lowest Fe^{3+}/ΣFe = 0.64, while the CAS samples have Fe^{3+}/ΣFe = 0.9.
MOLECULAR SIMULATION OF THE INITIAL STAGE OF SILICATE GROWTH

Thuat T. Trinh¹, A. Pavlova², Rutger A. van Santen², and Evert Jan Meijer¹*

¹ Van ’t Hoff Institute for Molecular Sciences and Amsterdam Center for Multiscale Modeling, Faculty of Science, University of Amsterdam, The Netherlands
² Schuit Institute of Catalysis Laboratory of Inorganic Chemistry and Catalysis Eindhoven University of Technology, Eindhoven, The Netherlands

The silica condensation reaction is an essential elementary reaction step in the growth of silicate minerals. Understanding how silicate minerals nucleate and grow is of fundamental scientific interest and of technological importance.

Numerous experimental and theoretical studies have addressed the physical chemistry of aqueous silicate oligomers in the pre-nucleation stage of siliceous mineral formation. In this initial stage, monosilicic acid condensates to form silicate oligomers. The oligomers include dimers, trimers, tetramers, 3-rings, 4-rings, double 3-rings, double 4-rings or other larger oligomer. The dominant species depends sensitively on reaction conditions, the type of solvent, and the presence or absence of structure directing agents (SDAs).

Theoretical modeling has been an attractive tool to reveal the molecular picture of the initial stage of silica growth. The general picture that has emerged is that the reaction proceeds in two stages, with an initial SiO-Si bond formation, followed by a water removal step. Most previous theoretical studies have focused on the thermodynamic properties of silica condensation reaction using gas-phase cluster models supplemented by a continuum model to address the role of the solvent.

In the present contribution we aim to provide a more realistic picture by incorporating an explicit molecular representation of the aqueous solvent. Using ab initio density-functional theory based molecular dynamics simulation we focus on the role of the water molecules and of a selected set of counter ions, i.e. Li⁺, NH₃⁺, and Na⁺.
EXPOSURES OF 3-D STRUCTURES OF BENTONITE INTERCALATED WITH SURFACTANTS BY TRANSMISSION X-RAY MICROSCOPY (TXM)

Yu-Min Tzou*, Ya T. Chan

Department of Soil and Environmental Sciences, National Chung Hsing University, 250 Kuo Kuang Road, Taichung 40227, Taiwan; ymtzou@nchu.edu.tw

Bentonite, one of important clay minerals, has various applications, including drilling mud, absorbent, and groundwater barrier. To serve as an efficient adsorbent for organic pollutants, it is a common strategy to modify bentonite toward more hydrophobic surfaces using surfactants. The intercalations of surfactants would lead to clay swelling, and in the past the internal structures of the organo-clays were usually hypothetically evaluated based on the changes in the interlayer space. In the study, we used Transmission X-ray Microscopy (TXM), with a spatial resolution of 50 nm, to observe directly the 3-D tomographic reconstruction imagines of the organo-clay composites upon intercalating the surfactants. Besides, the changes in the structural arrangements and the internal structures of the organo-clay before and after adding organic pollutants were also examined by the new technique. This approach can provide a good insight into the reactive mechanisms of organic pollutants with organo-clay, and facilitate the understanding of the structural changes accompanied with the accommodation of foreign organic compounds.
THE FIRST X-RAY DIFFRACTION ANALYSES OF CLAY MINERALS ON MARS


¹Planetary Science Institute, Tucson, AZ 85719, USA: dvaniman@psi.edu;
²SETI Institute, Mountain View, CA 94043, USA;
³Department of Geological Sciences, Indiana University, Bloomington, IN 47405, USA;
⁴NASA Johnson Space Center, Houston, TX 77058, USA;
⁵NASA Ames Research Center, Moffett Field, CA 94035, USA;
⁶Chesapeake Energy, Oklahoma City, OK 73154, USA;
⁷Lunar and Planetary Institute, Houston, TX 77058, USA;
⁸Department of Geosciences, University of Arizona, Tucson, AZ 85721, USA;
⁹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA;
¹⁰Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA;
¹¹Division of Geologic and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA.

Since the Viking missions of 1976, data from orbit and from the martian surface have increasingly supported a significant role for clay minerals on the planet. Clay minerals have also been confirmed as minor alteration phases within martian meteorites. In the past decade, visible and near-infrared spectroscopy from orbit has been used to map phyllosilicate occurrences, with results suggesting that clay minerals are widespread in the oldest martian terrains. A current model for clay mineral occurrences on Mars relates them principally to the southern highlands, where they remain as vestiges of a wet environment that ended ~4 Gy ago as a drier system evolved, dominated by sulfate rather than clay mineral alteration products. Such a transition lends significance to the study of clay minerals on Mars and the evidence they may hold for a major environmental shift. To obtain detailed mineralogy, including phyllosilicate types and abundances, the Mars Science Laboratory rover in Gale crater, Curiosity, carries CheMin, the first X-ray diffraction (XRD) instrument used on a planet other than Earth. With CheMin we have obtained the first direct sampling and characterization of clay minerals on Mars.

CheMin uses a Co tube and a CCD detector, with powder samples and piezo-driven vibrating sample cells in transmission geometry. The detector is an E2V CCD-224 with an array of 600 x 582, 40 µm pixels in the active collection area. The CCD is cooled during operation and is energy-selective, with a quick read cycle that allows single-photon recognition and energy discrimination of ~225 eV, sufficient to resolve diffracted Co Kα and Kβ. The CCD produces 2D diffraction patterns that can be processed into 1D Co Kα patterns with ~0.3° 2θ resolution.

At the time of this abstract, CheMin has collected XRD data from three powder samples: a scoop sample from an eolian deposit named Rocknest and two drill samples from a mudstone, named John Klein and Cumberland. The mudstone is informally named as the Sheepbed member of the Yellowknife Bay formation and is overlain by sandstones of the Gillespie Lake and
Glenelg members. No phyllosilicates were detected in the Rocknest eolian deposit, but clay minerals comprise ~20% of the John Klein and Cumberland mudstone samples. Otherwise both the eolian and mudstone locales carry similar detrital minerals from basaltic sources, along with a significant X-ray amorphous component. Minor phases include Ca-sulfates and, in the mudstone, Fe-sulfides and secondary oxides. The mudstone has a surprisingly high abundance of magnetite for a fine-grained sediment. The high magnetite content and notable dearth of Fe-forsterite, relative to other mafic minerals from basaltic sources, has led to a model suggesting formation of clay minerals and magnetite as products of Fe-forsterite alteration.

Typical XRD analysis of clay minerals on Earth can include preparation of oriented mounts, control of relative humidity, cation-exchange treatments, glycolation, and heat treatment that are not possible for CheMin on Mars. Moreover, the upper 2θ limit in CheMin is ~53°, precluding measurement of the 06l diffraction band (above 70° Co Kα) for determination of trioctahedral or dioctahedral character. However, the less-commonly used position of the maximum in the 02l two-dimensional diffraction band is similarly related to the b unit-cell parameter and can be used to distinguish trioctahedral (~ 22.5° Co Kα; 4.59 Å) from dioctahedral (~23.1° Co Kα; 4.47 Å) minerals (Fig. 1). The 02l bands in both mudstone samples suggest turbostratic stacking and we interpret these clay minerals as smectites. The 02l diffraction band maximum is very similar in John Klein and Cumberland and indicates a trioctahedral clay mineral such as saponite or Fe-saponite. The similarity of John Klein and Cumberland suggests a common origin, not unexpected because the two samples are from the same horizon and are only ~3 m apart.

The XRD pattern of John Klein has a broad 001 peak at ~10 Å, corresponding with smectite or illite (Fig. 1). The broad 001 peak and the lack of other well-defined peaks, such as an 002 peak at 5 Å, argue against the presence of well-crystallized phyllosilicates such as mica or illite. In addition, peaks for kaolinite or chlorite-group minerals at 7 Å are absent. The low-angle region of the Cumberland XRD pattern has a second 001 peak at ~13.2 Å (corrected for Lorentz polarization). This larger interlayer spacing in the Cumberland sample is of considerable interest because complete collapse of a smectite would be expected in the very dry conditions within CheMin (<1% RH at midday). Possible explanations include H₂O retention in the interlayers by high hydration-energy cations, such as Mg or Ca, and partial pillaring via incipient chloritization. These possibilities are being addressed in the lab and will be addressed in the field as more samples are analyzed at Gale crater. In several months, Curiosity will be at the base of the central mound of Gale crater where abundant clay minerals have been recognized from orbit; our plan is to traverse through the phyllosilicate stratigraphy and into overlying “drier” sulfate strata. The record of a major shift in ancient Mars environments, recorded in part by clay mineralogy, might be found at Gale crater.
FINE-GRAINED REGULARLY INTERSTRATIFIED SERPENTINE-TOCHILINITE INTERGROWTH IN THE MIGHEI-TYPE CARBONACEOUS CHONDRITE QUEEN ALEXANDRA RANGE 93005: IMPLICATIONS FOR EXTENT OF PARENT-BODY AQUEOUS ALTERATION

Michael A. Velbel

1Department of Geological Sciences, Michigan State University, East Lansing, MI 48824-1115: velbel@msu.edu

Meteorites are naturally delivered samples from a variety of parent bodies throughout the solar system. In their chemical compositions, minerals, and textures, they preserve direct evidence of the processes by which our solar system’s planets and small bodies originated, were modified, and evolved to their present state. Carbonaceous chondrites are primitive (undifferentiated) meteorites whose parent bodies are outer-Main-Belt asteroids. The two groups of carbonaceous chondrites with the greatest abundances of hydrous minerals (phyllosilicates) are the compositionally primitive (solar composition) and rare CI (Ivuna) group, and the much more abundant CM (Mighei) group. Other than naturally delivered interplanetary dust particles and similarly small mission-returned samples (e.g., comet dust returned from comet 81P/Wild 2 by NASA’s Stardust mission; mineral fragments recently returned from asteroid 25143 Itokawa by the ISAS Hayabusa mission), CI, CM, and other undifferentiated meteorites are our only direct and abundant samples of materials formed and modified during the earliest stages of solar system evolution.

Studies of meteorites contribute to the knowledge base for interpreting the composition and history (including aqueous alteration) of asteroids and comets by both remote (fly-by) missions (e.g. NASA Deep Impact, EPOXI/Deep Impact Extended Mission, Stardust NExT, and Dawn; ESA Rosetta) and robotic sample-return missions (e.g., NASA Stardust, OSIRIS-REx; ISAS Hayabusa, Hayabusa-2). Destinations for the next generation of future asteroid sample-return missions (Hayabusa-2 and OSIRIS-REx) were selected in part on the basis of the expected presence of volatiles, including hydrated silicates and associated reduced carbon compounds. At the group level, CM carbonaceous chondrites (referred to as CM chondrites or CMs) are the best spectroscopic matches to the target asteroid of the upcoming OSIRIS-REx sample-return mission ((101955) 1999 RQ36).

Queen Alexandra Range 93005 (hereinafter, QUE 93005) is a CM2 Antarctic find. QUE 93005 has been previously studied for a variety of aqueous alteration phenomena (e.g., paragenesis and compositions of serpentine-group and carbonate minerals) and is one of the most highly altered CM2 chondrites known. Ion-beam milled transmission electron microscope (TEM) grids of its fine-grained constituents were analyzed by using a JEOL 2200FS TEM at the Center for Advanced Microscopy at Michigan State University.

Fine-grained materials of QUE 93005 include abundant serpentine as is common in CM2s, and sparse but widely distributed occurrences of a layer-structured mineral with basal spacings of $1.77 \text{ nm} < d_{001} < 1.82 \text{ nm}$ (from selected area electron diffraction (SAED) patterns and TEM images). The basal spacing of the ideal 1:1 serpentine-tochilinite interstratification as
reported from other CM2 chondrites is $d_{001} = 1.81$ nm. The observed occurrences of layer-structured material in QUE 93005 are consequently interpreted as regularly interstratified 1:1 serpentine-tochilinite. A general formula for 1:1 regularly interstratified serpentine-tochilinite is

$$1.67(\text{Fe, Mg})_3\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 6(\text{Fe, Ni, Cu})\text{S} \cdot 10(\text{Fe, Mg})(\text{OH})_2$$

Although other interstratifications are known from previous studies of CM2s, 1:1 interstratified serpentine-tochilinite is the mostly widely documented serpentine-tochilinite interstratification in CM2 chondrites. As previously reported from some other CM2 chondrites, all SAED patterns of this material showed much greater diffracted intensity for (003) and higher-order (004), (005) and (007) Bragg diffraction spots relative to (001) and (002). In some SAED patterns, streaking along c* indicates slight rotational stacking disorder perpendicular to the image plane.

Previous work based on other CM2 chondrites presented a model linking the observed alteration of several phases with progressive aqueous alteration. Discrete tochilinite forms early by reaction of S-bearing solutions with kamacite (Fe,Ni metal). Primary anhydrous chondritic phases are altered to phyllosilicates (most commonly of the serpentine group). Continued reactions of aqueous solutions with olivine and pyroxene release Si that reacts with earlier-formed tochilinite to form interstratified serpentine-tochilinite. The exhaustion of interstratified tochilinite marks advanced alteration. The most extensively aqueously altered CM chondrites lack tochilinite, all of which has been consumed by either serpentine-forming reactions or by partitioning of Fe and S into sulfides at either peak temperatures >120°C and/or oxidizing conditions.

Previous work on QUE 93005 reported absence of tochilinite and drew inferences of advanced alteration from the supposed absence. The observations of tochilinite in QUE 93005 reported here require reconsideration of the aqueous alteration history of this meteorite. Preservation of 1:1 regularly interstratified serpentine-tochilinite in QUE 93005 indicates

- an intermediate degree of aqueous alteration that did not result in complete depletion of tochilinite as previous proposed for this meteorite,
- that aqueous-alteration conditions after formation of the 1:1 interstratified serpentine-tochilinite were not oxidizing and
- the ~120°C threshold temperature for the destruction of tochilinite in the interstratified phase was not exceeded during or after aqueous alteration of this meteorite.

While still among the most altered CM2s known, QUE 93005 may not be as extensively altered as previously thought.
THE SMECTITE TO CORRENSITE TRANSITION: PRELIMINARY RESULTS FROM THE MH-2 CORE, WESTERN SNAKE RIVER PLAIN, IDAHO

Jeffrey R. Walker*, Joseph Wheeler, Alexandra Boersma, and Katie Ewan

Department of Earth Science and Geography, Vassar College, Poughkeepsie, NY  12604: jewalker@vassar.edu

The MH-2 hole, one of three holes completed as a part of HOTSPOT: The Continental Scientific Drilling Project, was drilled to a depth of 1821m on the Mountain Home Air Force Base southeast of Boise, Idaho to evaluate the potential for development for geothermal energy on the base. Hot water (140°C) under artesian pressure was encountered at a depth of 1745 m. The stratigraphy of the well consists of Pleistocene basalt flows to 200m depth, then mixed lacustrine sediments with several interbedded basalt flows to 950m depth, then basaltic flows and hyaloclastic material with one major interbed of lacustrine sediment to the bottom of the well.

Initial bulk rock XRD analyses indicate the presence of smectite throughout the well. Detailed clay mineral analysis identified a restricted zone of corrensite formation between 1750m and 1793m. Below 1790m smectite was again dominant. Within the corrensite zone, smectite co-existed with corrensite except in the deepest sample (1793m) which was pure corrensite. The upper boundary of the corrensite zone corresponded roughly to the occurrence of hot (140°C) artesian water that has been equilibrated with basaltic rocks, but the entire corrensite zone extended well below the artesian flow into a region of low porosity with fractures filled with clay minerals.

The transition from smectite to corrensite in the MH-2B hole appears to be discontinuous or stepwise with no intermediate R0 phases with no C:S proportions significantly different from 50:50. Since the zone of corrensite is restricted in occurrence, the system is an ideal place to study the physical controls on the discontinuous smectite to corrensite transition. The presence of hot artesian fluid in this zone supports that assertion that high fluid/rock ratios are associated with discontinuous transition from smectite to corrensite. However, the occurrence of smectite + corrensite in the zone of high fluid flow, and corrensite where fractures have been sealed suggests that some recrystallization may have occurred once fluid flow was restricted by fracture sealing.

The timing of, and specific controls on, the smectite to corrensite transition in drill hole MH-2B are still unclear, and will be the focus of detailed textural and compositional studies of the different clay minerals.
TECHNETIUM INTERACTIONS WITH HUMIC SUBSTANCES

Nathalie A. Wall* 

Chemistry Department, Washington State University, Pullman WA 99164-4630, USA: nawall@wsu.edu

Humic substances are known to bind metals and promote contaminant transports in the subsurface. Meanwhile, large amount of $^{99}$Tc have been stored underground at different sites in U.S. (e.g. 30,000 Ci at Hanford Site (WA)\(^1\)) and Tc can now be found in soils and waters in the vicinity of these sites (an estimated 30 Ci of technetium could reach the Columbia River (WA) in the near future\(^2\)). While the mostly non-absorptive and anionic Tc(VII) is predominant in the environment, Tc(IV) can be found under reductive conditions in soils. Although it is thought that Tc(IV) will form the insoluble TcO$_2$·1.6 H$_2$O\(_{am}\) and will remain relatively immobile, our work have shown that humic substances, ubiquitous in clays, can bind to Tc(IV) and increase its solubility\(^3,4\). Moreover, humic substances size fractionation will vary with solution conditions (e.g. pH, ionic strength), and therefore could influence the amount of Tc bound to each humic size fraction. This presentation will describe the quantification of the binding constant for the Tc(IV)–humic substances moieties, the effect of humic acids on Tc(IV) solubility, and the effect of solution conditions on humic properties and their interactions with Tc(IV).

Literature Cited
DIAGENESIS AND ANCHIMETAMORPHISM OF THE MESO-NEOPROTEROZOIC AND THE LOWER PALEOZOIC ALONG PROFILE YANGJIAPING IN NORTH HUNAN PROVINCE, CHINA

Heijing Wang*1, Jian Zhou2, Ling Wang1, Zhao Zhou1, and Lei Yuan1

1School of Earth and Space Sciences, Peking University, 5# Yiheyuan Road, Haidian District, Beijing 100871, P. R. China: hjwang@pku.edu.cn
2Chinese Academy of Geological Sciences, 26# Baiwanzhuang Road, Xicheng District, Beijing 100037, P. R. China.

Low temperature metamorphic indicators, such as illite crystallinity, cell dimension of K-white micas, polytype, lattice strain, crystal size distribution and mineral assemblage were employed in the study of diagenesis and metamorphism for the Meso-Neoproterozoic and the Lower Paleozoic along profile Yangjiaping in north Hunan Province, China.

Illite crystallinity (IC) of the <2 μm fractions ranges from 0.21-0.24°Δ2θ for the Meso-Neoproterozoic to 0.28-0.67°Δ2θ for the Lower Paleozoic (calibrated with Kisch IC set 1991). This indicates that the Meso-Neoproterozoic was overprinted by high anchimetamorphism whilst the Lower Paleozoic overprinted by geological processes from diagenesis to low anchimetamorphism. According to anchizonal boundaries (0.21-0.38°Δ2θ, CuKα), the profile was classified into a northern anchizone and a southern diagenetic zone. The peak anchimetamorphic temperature of the Meso-Neoproterozoic and the Lower Paleozoic was roughly evaluated by chemical geothermometer of chlorite at ca. 262°C. The illites (K-mica) b₀ values in anchizone range from 0.9000 to 0.9045 (nm) and, on average 0.9017 nm, implying roughly a low to intermediate pressure condition. Illites occur as the 2M₁ polytype in anchizone (most of the Meso-newproterozoic) and as a mixture of 2M₁+1M types in the lower Paleozoic.

The product of logarithms mean particle size and logarithms frequency of illite, here called “general logarithms ripening” (GLR), is well separated into two groups, in which these GLRs less than 1.88 belong to diagenetic while those larger than 1.88 belong to anchimetamorphic. This is a new observation. Post-anchimetamorphic structural stress not only forms a series of faults but also induces the lattice strain in minerals and hence impacts the illite crystallinity and causes the Kübler Index to increase in width and result in an unusual value.

Comparing with the cases in the near south (Changsha-Liling-Liuyang, Huangtudian-Xianxi and Yuanuping), the rocks of the Meso-Neoproterozoic and the Lower Paleozoic in the profile underwent diagenesis and anchimetamorphism with a low to intermediate pressure condition. This result is different from the greenschist or subgreenschist facies of the Banxi Group or from the lower-greenschist facies or sedimentary cover of the Sinian to the Lower Paleozoic, of which most previous researchers thought.
CLAY SWELLING IN ANHYDRITIC CLAYSTONE

Timothy P. Wangler*1, Amir R. Shahab1, and Robert J. Flatt1

1Institute for Building Materials, Department of Civil, Environmental and Geotechnical Engineering, ETH Zürich, 8093 Zürich, Switzerland; wangler@ifb.baug.ethz.ch

Anhydritic claystones, rocks with relatively high proportions of anhydrite and clays, are susceptible to expansion from exposure to water due to the anhydrite-to-gypsum transformation and the swelling of the clay fraction. One finds this rock in the troublesome Gipskeuper, and tunnels through this formation in Switzerland and southwestern Germany have experienced repeated floor heave events over many years, leading to expensive repairs1. Despite numerous studies that have spanned the past few decades2–4, the relative contributions of the crystallization pressure due to the anhydrite-to-gypsum transformation and the swelling pressure of the swelling clays are still unknown due to the highly coupled nature of the problem.

Above a temperature of approximately 40 °C, anhydrite becomes more stable than gypsum in the presence of water5, and the anhydrite-to-gypsum transformation is effectively shut off. This has been demonstrated on actual samples of anhydritic claystone taken from the Chienberg Tunnel in Switzerland. By performing swelling experiments above this temperature, we are able to effectively decouple the two swelling phenomena and study clay swelling in isolation, enabling us to better quantify the contribution of clay swelling to this problem.

EFFECT OF SURFACE MODIFIER AND ASPECT RATIO ON RHEOLOGY OF MODEL NANOPlateLETS IN EPOXY

Kevin L. White*1,2, Peng Li3, Spencer Hawkins3, Haiqing Yao3, Atsushi Takahara1,2, and HJ Sue3

1International Institute for Carbon-Neutral Energy Research, Kyushu University, Fukuoka, 819-0395, Japan: kevinwhite@ms.ifoc.kyushu-u.ac.jp;  
2Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, 819-0395, Japan;  
3Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843, USA.

The flow behavior and viscoelasticity of colloidal suspensions are macroscale consequences of properties and processes that occur on length and time scales governed by the individual suspended particles. Suspension rheology thereby provide a valuable microscopic probe to interrogate the particle-level structure and interactions. To unambiguously identify the mechanisms responsible for macroscale properties in fluids, model particles with well-defined shape, size, polydispersity, and inter-particle potential are needed.

We have recently investigated the linear and non-linear viscoelasticity of model 2-dimensional nanoparticles over a range of concentrations1-5. The model particles are α-zirconium phosphate (ZrP) nanoplatelets, which are inorganic metal phosphates that crystallize in stacks consisting of individual plate-like crystals. The shape, size, and exfoliation state of the nanoplatelets can be easily controlled based on reaction conditions and surface modifier6.

The influence of inter-particle interactions was investigated by exfoliating the nanoplatelets to individual sheets (aspect ratio of 160) with monodisperse thickness (~ 0.7 nm) using three different surface modifiers (Figure 1). Suspensions containing nanoplatelets exfoliated with a low molecular weight quaternary ammonium cation (tetra-n-butylammonium hydroxide, TBA), show “hard plate”-like behavior expected for rigid, non-interacting sheets at low concentration. At higher concentrations, the suspensions show pronounced viscoelasticity at intermediate frequency and transition to purely viscous (dissipative) flow behavior on long time scales. Suspensions containing nanoplatelets exfoliated with M1000, a hydrophilic polyetheramine oligomer, show similar behavior to the ZrP-TBA system, albeit on a more rapid time scale. The densely packed oligomers form a brush layer that sterically stabilizes the nanoplatelets and contributes to “hard plate”-like response. Suspensions containing nanoplatelets exfoliated with M600, a lower molecular weight, hydrophobic polyetheramine, show drastically different rheological response that suggests permanent local microstructure resulting from interactions between the surface groups.
The effect of particle size was investigated by synthesizing ZrP with lateral diameter ranging from 100 nm to 1 μm. The magnitude and concentration-dependence of viscous response increase with aspect ratio, and the relative elastic response diminishes. The behavior is attributed to the competition between excluded volume, particle rotation, and particle mobility, (Figure 2). The steady shear response of the smaller nanoplatelets is consistent with the behavior of rigid Brownian plates. As aspect ratio increases, the steady shear response shifts to a region dominated by hydrodynamic effects. For systems with large aspect ratio, more complex behaviors are also observed and discussed based on the effects of excluded volume interactions on particle tumbling and the change in nanoplatelet mobility and microstructure due to shear-induced deformation.

Figure 2. Particle size effect studied by synthesizing nanoplatelets with range of diameters. Figure shows calculations of real volume and maximum volume (defined by minimum enclosing sphere) of isolated oblate spheroid, and theoretical predictions for intrinsic viscosity at zero shear rate and rotary diffusion coefficient, which defines time scale of particle motion.

The use of model nanoparticles with tunable shape and surface interactions allows a broad range of behaviors to be probed and meaningfully connected to the motion and interaction of individual particles. These studies are anticipated to provide insights into the origins of the complex non-equilibrium behavior observed in some systems, which will be discussed. Further theoretical and numerical work is being pursued to quantitatively describe bulk flow properties in terms of the mobility, inter-particle interactions, flexibility, and phase transitions of high aspect ratio, disk-like particles.
ROD-LIKE KAOLINITE COATED WITH METAL OXIDES: MICROSTRUCTURE AND FUNCTIONS

Huaming Yang *, Peiwei Hu

School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China. hmyang@csu.edu.cn

Natural minerals have been compounded with the functional matrix to produce the advanced composites, usually via the surface deposition route. Kaolinite (Al₂Si₂O₅(OH)₄), a 1:1 dioctahedral aluminosilicate clay mineral, has two different basal cleavages faces of tetrahedral siloxane (Si-O-Si) surface and octahedral gibbsite (Al₂O₃) sheet, while octahedral alumina and silica tetrahedral sheets exposed reactive functional moieties at the edges of kaolinite particles, including Al-OH and Si-OH groups. Actually, the composites, prepared via assembling metal oxides on the surface of kaolinite, showed the enhanced performance and the reducing cost. Antimony-doped tin oxide (ATO) was a well-known transparent semiconductor with a large band gap (>3.6 eV), providing transparency in the visible range and high n-type electric conductivity, which made it a valuable alternative to the expensive indium tin oxide. This paper reported the synthesis of ATO/kaolinite composites via depositing the chemically co-precipitated antimony/tin(IV) oxides on the surface of rod-like kaolinite substrate. The samples were characterized using X-ray diffraction (XRD), X-ray photoelectron spectrum (XPS), scanning electronic microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), ultraviolet-visible (UV-vis) and photoluminescence (PL) spectra. The effect of the heat-treatment of kaolinite substrate on the microstructure and photoelectric properties of the composites were systematically investigated. The results indicated that the color, coating morphology and conductivity of ATO coatings varied with the surface characteristic of substrate. XPS analysis demonstrated that the doping level and oxidation state of Sb of ATO nanoparticles changed after they deposited on the different substrate surfaces. The ATO nanoparticles coated onto the kaolinite substrate by heat-treatment at 1000 °C had the minimum resistivity of 5.9 Ω·cm, so it was the potential substrate for preparing ATO/kaolinite conductive composites with low cost. The amount and the valence state of doped antimony showed an obvious effect on the conductivity of the composites. PL properties analysis of Sb-SnO₂ nanoparticles indicated that the peaks appeared at 430-530 nm blue luminescences could be attributed to the singly charged oxygen vacancies or crystal defects which were formed during the growth of the particles. We believe that the as-synthesized ATO/kaolinite composites could have potential application in the optoelectronic fields.
TRANSFORMATION OF ZINC/GALLIUM-LAYERED DOUBLE HYDROXIDE TO GALLIUM ZINC OXYNITRIDE VIA UREA PYROLYSIS

Jae-Hun Yang*, Yirong Pei, and Jin-Ho Choy

Center for Intelligent Nano-Bio Materials (CINBM), Department of Chemistry and Nano Science, and Department of Bioinspired Science Ewha Womans University, Seoul 120-750, Republic of Korea: ohsik@ewha.ac.kr

Visible-light harvesting photocatalyst for energy and environmental application has attracted a great attention. Ga/Zn-oxinitride solid solution \((\text{GaN})_{1-x}(\text{ZnO})_x\) is one of the promising visible-light harvesting photocatalysts for overall water-splitting. Layered double hydroxides (LDHs; known as anionic clays) are the solid solution of divalent- and trivalent-metal hydroxides with 2-dimensional structure, which could be used as precursors for mixed metal oxides and oxynitrides.

Recently, we found the novel synthetic route to \((\text{GaN})_{1-x}(\text{ZnO})_x\) from Zn/Ga-LDH by using urea as nitrogen source of nitridation reaction at high temperature. At first, Zn/Ga-LDH with carbonate anion in gallery space was prepared via conventional coprecipitation method at pH 9, which was confirm with series of X-ray diffraction (XRD) peaks with a basal spacing of 0.74 nm. \((\text{GaN})_{1-x}(\text{ZnO})_x\) with yellow color has been successfully synthesized via calcining the mixture of \(\text{Zn}_2\text{Ga-LDH}\) and urea at 1123 K under nitrogen gas-flow depending on mixing ratio of urea to LDH. According to XRD analysis, \((\text{GaN})_{1-x}(\text{ZnO})_x\) was found to be successfully prepared without any impurity, and intermediates were amorphous phase and zinc cyanide \((\text{ZnCN}_2)\). By using urea instead of ammonia, the reaction time was shortened to 2 hour, and the bandgap energy and Zn content of thus prepared \((\text{GaN})_{1-x}(\text{ZnO})_x\) was determined to be 2.8 eV and \(x = 0.09\), respectively. Furthermore, the bandgap energy of \((\text{GaN})_{1-x}(\text{ZnO})_x\) could be adjusted via two-step calcining process; firstly calcining the mixture of LDH and urea at 673 K to be amorphous, and then secondly calcining the pelletized amorphous material at 1123 K under nitrogen gas flow. The bandgap energy and Zn content of \((\text{GaN})_{1-x}(\text{ZnO})_x\) prepared via two-step pyrolysis was determined to be 2.42 eV and \(x = 0.52\), respectively, which could absorb larger range of visible-light energy than the sample prepared via one-step urea pyrolysis. This urea pyrolysis method could be applied to synthesizing various metal oxynitrides and controlling their bandgap.
WELL-ORDERED POROUS TITANIA-PILLARED CLAYS FROM MODIFIED LAYERED SILICATES

Jae-Hun Yang*, Huiyan Piao, and Jin-Ho Choy

Center for Intelligent Nano-Bio Materials (CINBM), Department of Chemistry and Nano Science, and Department of Bioinspired Science Ewha Womans University, Seoul 120-750, Republic of Korea: ohsik@ewha.ac.kr

Layered silicates, known as clays, are good support for stabilizing metal oxide nanoparticles including TiO$_2$, Al$_2$O$_3$, etc. without any aggregation between silicate layers to form the porous metal oxide pillared structure. TiO$_2$ is the representative UV-light harvesting photocatalyst with high photocatalytic activity and photo-stability. The photocatalytic activity is affected by the crystallinity, particle size, the specific surface area etc.. TiO$_2$ nanohybrid with high specific surface area could be synthesized by pillaring TiO$_2$ nanoparticles between silicate layers. However, it is difficult to prepare porous TiO$_2$ pillared layered silicates with well-ordered (00l) x-ray diffraction (XRD) peaks since a part of Mg$^{2+}$ or Al$^{3+}$ ions in octahedral sites of layered silicates are dissolved in the strong acidic condition during TiO$_2$ pillaring reaction, and the silicate layers are slightly disordered.

Recently, we have successfully prepared well-ordered porous TiO$_2$ pillared layered silicates by using the layered silicates with controlled layer charge density prepared by incorporating metal cations such as Mg$^{2+}$, Ni$^{2+}$, Fe$^{2+}$, Cu$^{2+}$, Mn$^{2+}$ and Cr$^{3+}$ into a part of the octahedral empty sites of the silicate layers. TiO$_2$ pillared layered silicates have been successfully synthesized by incorporating TiO$_2$ nano-sol particles into silicate layers via ion-exchange reaction and the consequent calcination. XRD profiles of thus prepared TiO$_2$ pillared layered silicates show well-ordered (00l) peaks and their basal spacing are determined to be ~ 2.5 nm, indicating that TiO$_2$ nanoparticles with ~ 1.5 nm were successfully incorporated into the silicate layers to form the nanopore structure. From the nitrogen adsorption-desorption isotherms, those TiO$_2$ pillared layered silicates calcined at 773 K show the enhanced porosity such as specific surface area (320 ~ 380 m$^2$/g) and pore volume (0.27 ~ 0.31 mL/g) compared to that of pristine layered silicate (10 m$^2$/g) and its TiO$_2$ pillared layered silicate (242 m$^2$/g and 0.21 mL/g). The diffuse reflectance UV-visible spectra show that the absorption edges of TiO$_2$ pillared layered silicates are blue-shifted compared to that of bulk anatase TiO$_2$ due to the quantum size effect of TiO$_2$ particles. The photocatalytic activity of TiO$_2$ pillared layered silicates for the photodecomposition of methyliorange in the aqueous suspensions under UV irradiation would be systematically discussed with the porosity and the composition of silicate layers.
INFLUENCE OF ANIONIC SURFACE MODIFIER ON THERMAL STABILITY AND MECHANICAL STRENGTH OF POLYPROPYLENE/LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES

Jae-Hun Yang*1, Wei Zhang1, Joung-Yoon Choi2, and Jin-Ho Choy1

1Center for Intelligent Nano-Bio Materials (CINBM), Department of Chemistry and Nano Science, and Department of Bioinspired Science Ewha Womans University, Seoul 120-750, Republic of Korea: ohsik@ewha.ac.kr ;
2Fire Safety Evaluation Team, Department of Built Environment, Korea Conformity Laboratories, Chungbuk, Republic of Korea

Polypropylene/organo-layered double hydroxide nanocomposites (PP/O-LDH) were successfully synthesized via solution blending method. In order to change the surface property of layered double hydroxide to be hydrophobic for improving the compatibility with hydrophobic polymer, we modified LDH surface by incorporating anionic surfactants such as lauric acid, palmitic acid, stearic acid, dodecylsulfate and dodecylbenzene sulfonate, etc. depending on aliphatic carbon chain length and anionic functional groups (-COO-, -OPO3−, -OSO3−, -C6H4SO3−) into LDH layers with electrostatic interaction. In PP nanocomposites containing organo-LDH obtained from solution blending method, the (00l) x-ray diffraction peaks originated from organo-LDH were not observed, indicating that organo-LDH were exfoliated and homogeneously dispersed in PP matrix. According to the thermogravimetric analysis, PP/O-LDH nanocomposites showed the significantly improved thermal stability by up to 60 K in terms of the 50% weight loss temperature (ΔT0.5) compared to pristine PP. And the well dispersed rigid LDH sheet with high aspect ratio in PP matrix give rises to the enhancement of elastic modulus. This orgno-LDH could play a role of inorganic nanofiller in polymer for flame-retarding.
FORMATION OF CLAY MINERALS IN DEEP SUBSEA FLOOR SEDIMENT, SOUTH PACIFIC GYRE: IODP EXPEDITION 329

Kiho Yang*1, Kogure Toshihiro2, Bryce Hoppie3, Robert Harris4, Hionsuck Baik5, IODP Expedition 329 shipboard scientists6, and Jinwook Kim1**

1Department of Earth System Sciences, Yonsei University, Seoul, Korea:
2Department of Earth and Planetary Sciences, University of Tokyo, Japan;
3Department of Chemistry and Geology, Minnesota State University, Mankato, USA;
4College of Oceanic and Atmospheric Sciences, Oregon State University, USA;
5Korea Basic Science Institute (KBSI), Seoul, Korea;
6IODP Expedition 329 shipboard scientists

*khyang@yonsei.ac.kr ; **Correspondence to jinwook@yonsei.ac.kr

Subsea floor sediment in the South Pacific Gyre (SPG) was recovered for the first time by Integrated Ocean Drilling Program (IODP) Expedition 329 (2010.10.10-2010.12.13). Clay mineralogy from two sites (U1369 and U1365) was investigated. The comparisons of clay mineralogy and formation from the sites U1365 (margin of SPG), and site U1369 (center of SPG close to the East Pacific Rise). The sediment at the site U1369 has a young crustal age of 13.5 Ma compared with the site U1365 (84-120 Ma).

Fine clay fractions less than 1 m were analyzed by x-ray diffractometer (XRD), transmission electron microscope (TEM) with the selected area electron diffraction (SAED) pattern, and electron dispersive spectrometer (EDS). Saturation index (SI) with respect to smectite was modeled based on the pore water chemistry.

Smectite was a dominantly phase at the site U1365 compared with the various clay minerals of smectite, mica, and chlorite at the site U1369. Difference in the clay mineral assemblages between two sites may indicate that there were difference environmental conditions concerned to clay minerals formation. Observation of various mica polytypism may suggest the influence of temperature in the clay mineral formation at two sites. For example, the disordered 1Md mica was dominantly observed at site U1365 whereas the high order of polytypes such as 1M, 2M1, and 3T at site U1369. The presence of high-ordered mica, chlorite at U1369 indicates that the formation of smectite was likely to be inherited from the reaction of hydrothermal fluid and basaltic crust. The heat-flow analysis as well as the formation of gypsum confirms the hydrothermal alteration at the site U1369. On the contrary, the presence of iron rich smectite, with abundant of RSO (red-brown to yellow-brown semiopaque oxide) at the basalt-sediment contact (U1365) may indicate that the formation of prototype of smectite was originated from alteration of basalt with seawater at ambient temperature. The RSO minerals and mixture with smectite were frequently observed at near the basaltic crust at the site U1365. By adapting EDS, high content of iron in smectite was confirmed at the basalt-sediment contact. Furthermore, the direct TEM observation of smectite formation in the alteration of basalt was detected and SI for smectite in this region confirmed the formation of smectite in this condition.
SORPTION-DESORPTION OF CARBOXYLIC AND AMINO ACIDS ON PURE CLAY MINERALS

Sabina Yeasmin*1, Balwant Singh1, Rai Kookana2, Mark Farrell2, Donald Sparks3, and Cliff T. Johnston4

1 Department of Environmental Sciences, Faculty of Agriculture and Environment, The University of Sydney, Sydney, NSW 2006, Australia: sabina.yeasmin@sydney.edu.au
2 CSIRO Land and Water / Sustainable Agriculture Flagship, PMB 2, Glen Osmond, SA 5064, Australia;
3 S Hallock du Pont Chair, Plant and Soil Sciences, University of Delaware, Newark, DE 19716, USA;
4 Crop, Soil and Environmental Sciences, Purdue University, West Lafayette, IN 47907, USA.

Although low molecular weight organic compounds (LMWOC) (e.g., carbohydrates, carboxylic acids and amino acids) represent a small portion of soil organic carbon, they are considered key contributors of a number of soil processes. LMWOCs are labile form of soil organic carbon that are easily utilized by microbes and also highly susceptible to leaching losses. Sorption is an imperative process that influences fate, concentration, and bioavailability of these organic substances in soils. The sorption of LMWOCs on minerals is a foremost process for their preservation in soils and this process is influenced by both the properties of soil minerals and the organic compounds. Therefore, characterization of mineral-specific sorption behavior of definite LMWOC group is must to understand the stabilization of soil organic carbon at mineral surface. The objective of this study was to test the hypothesis that sorption-desorption behavior of LMWOC on soil minerals is influenced by properties of both the mineralogy and organic compounds.

Batch experiments were conducted to evaluate the sorption-desorption behavior of 14C-labelled LMWOCs on pure clay minerals. Two carboxylic acids (oxalic and citric) and four amino acids (glutamic, lysine, alanine and phenylalanine) were used in this experiments. Minerals selected to represent common soil minerals, and differing charge characteristics and crystallinity were kaolinite (KGa-2), illite (IMt-2), montmorillonite (SWy-2), ferrihydrite and goethite. Organic acid-mineral interaction mechanisms were evaluated by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). Sorption data were described well with the non-linear form of the Freundlich equation. The results showed that sorption of carboxylic and glutamic acid was higher on both phyllosilicates and Fe oxides compared to other compounds (except basic lysine), indicating the significance of carboxylic groups in the sorption of LMWOCs. Minerals interacted with these acids mostly via the carboxylate group through both inner- (mainly Fe oxides and kaolinite) and outer-sphere (2:1 phyllosilicates) complexation. This was supported by desorption data, with lower proportions of desorption observed for Fe oxides and kaolinite than the 2:1 phyllosilicates. Cationic lysine showed a stronger affinity to permanently charged phyllosilicates than Fe oxides, which possessed overall positive charge under the experimental conditions. The sorption of aliphatic alanine and aromatic phenylalanine was consistently low for all minerals, with a relatively higher sorption (and a lower desorption) of phenylalanine than alanine. These amino acids interacted mostly via carboxylate with Fe...
oxides and via amino groups with 2:1 phyllosilicates. These interactions were mediated by electrostatic interactions, H-bonding and van der Waals interactions.

Overall, Fe oxides were found to be more potent sorbents for both carboxylic and amino acids (except lysine) than phyllosilicates. However, the desorption of amino acids (except glutamic acid) was lower from permanent charged minerals than the variable charged minerals. ATR-FTIR spectra indicated the role of carboxylic groups in the sorption and retention of the organic compounds on Fe oxides (and kaolinite) and of amino groups on 2:1 phyllosilicates. The differences in sorption-desorption pattern and their interaction mechanisms were apparently mediated by the mineral properties (surface charge and specific surface area) and the chemistry of LMWOCs. The results of this study allow an understanding of the effects of mineralogical and chemical factors that affect the sorption of organic compounds under field conditions.
SPATIAL VARIATION OF ZINC SPECIES IN PEAT SOILS: AN X-RAY ABSORPTION STUDY

Soh-joung Yoon*1,2, Carmen Enid Martinez1,3

1Department of Crop and Soil Sciences, Pennsylvania State University, University Park, PA 16802-3504, USA;
2Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon 305-350, South Korea:
syoon@kigam.re.kr
3Department of Crop and Soil Sciences, Cornell University, Ithaca, NY 14853, USA.

Peatlands, characterized by their high contents of organic matter accumulated under reducing conditions, can effectively retain heavy metals. Metal enrichment in peatlands is considered to be the result of complex biogeochemical processes and the disturbance of metalliferous peatlands can have negative environmental effects. Peat soils in our study site near Manning, NY are naturally enriched with zinc. The study site used to be a natural wetland with no reported phytotoxicity. Since 1940s, the site has been artificially drained for agricultural production, leaving part of the soil barren. Zinc contents of the barren soils are several thousand mg kg⁻¹ at the surface and even higher in the deep, up to several percent. The spatial variation of zinc contents in the soil can be related with the variation of local environmental conditions, especially of local redox conditions, and so can that of zinc species. Exposure of the organic soil to an oxidizing environment by drainage could have affected the zinc species in the soil, more likely near the surface. A location with conspicuously high zinc contents in the deep soil was observed to be in contact with an impermeable clay lens, which could have provided local reducing conditions. In the previous study of the deep soil samples with the highest zinc contents, we found zinc sulfide nanoparticles formed by bacteria capable of reducing oxidized forms of sulfur. Here we examine zinc species in the peat soil at the surface and at depth using Zn K-edge X-ray absorption fine structure (EXAFS) spectroscopy. Deep soil samples, more enriched with zinc than surface soils, showed higher reduced sulfur contents as revealed by sulfur K-edge X-ray absorption near edge structure (XANES) spectroscopy. EXAFS analyses of deep soil samples showed significant zinc-sulfur coordination, indicating the existence of zinc sulfide. EXAFS analysis results on zinc-oxygen coordination will also be presented to show their spatial variation including the location with the clay lens.
TAILORING THE THIRD DIMENSION IN LAYERED MATERIALS

Jingfang Yu,1 Lichen Xiang,2 Benjamin R. Martin,2 Jingjing Liu,1 Abraham Clearfield,3 Zhiping Luo,4 and Luyi Sun1,*

1Department of Chemical & Biomolecular Engineering and Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, United States
2Department of Chemistry and Biochemistry & Materials Science, Engineering, and Commercialization Program, Texas State University, San Macros, TX 78666, United States
3Department of Chemistry, Texas A&M University, College Station, TX 77842, United States
4Department of Chemistry and Physics, Fayetteville State University, Fayetteville, North Carolina 28301, United States

*Author to whom correspondence should be addressed:
Dr. Luyi Sun, Tel: (860) 486-6895; Fax: (860) 486-4745; Email: luyi.sun@uconn.edu

Layered materials have been well investigated and have found widespread application. Traditionally, one can only alter the lateral dimension of layered compounds. The layer thickness or composition is hard to be finely controlled. Herein we demonstrate that by introducing a layer growth coordinator or inhibitor, one can directly synthesize layered intercalation compounds or single layered nanosheets, respectively. The key strategy is to introduce a third component, which helps tailor the interaction between neighboring layers, and in turn help guide the interlayer growth. Such a new capability allows one to design and synthesize unique layered intercalation compounds and single layer nanosheets for designated applications.
HYDRATION AND MOBILITY OF INTERLAYER IONS OF (NAX, CAY)-MONTMORILLONITE: A MOLECULAR DYNAMICS STUDY

Lihu Zhang*, Xiancai Lu, Xiandong Liu, Kan Yang, Huiqun Zhou, and Rucheng Wang

State Key Lab for Ore Deposit Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing Jiangsu, 210093, P. R. China: zhanglihu1987@163.com

Molecular dynamics simulations were performed to investigate the swelling behavior of (Na\textsubscript{x}, Ca\textsubscript{y})-montmorillonite, the mobility of Na\textsuperscript{+} and Ca\textsuperscript{2+}, and the stability of their hydrate complexes. Two-layer hydrate is thermodynamically the most predominaTed state. The change from inner-sphere complexes to outer-sphere complexes of Ca\textsuperscript{2+}/Na\textsuperscript{+} occurs at about 170 mg\textsubscript{water}/g\textsubscript{clay}. The mobility of Na\textsuperscript{+} is greater than that of Ca\textsuperscript{2+} and the hydration complexes of Ca\textsuperscript{2+} are much stable than that of Na\textsuperscript{+}.

Fig. 1. Snapshot of (Na\textsubscript{0.3750}, Ca\textsubscript{0.3125})-montmorillonite at water content of 243 mg\textsubscript{water}/g\textsubscript{clay}. Cation Na=violet, Ca=blue, atom O=red, H=white, Si=light grey, Al=light pink, Mg=green
FACILE PREPARATION OF MnFe₂O₄/HALLOYSITE NANOTUBULAR ENCAPSULATES WITH ENHANCED MAGNETIC AND ELECTROMAGNETIC PERFORMANCES

Ao-Bo Zhang*¹, Ying Ye¹, and Xue-Gang Chen¹

¹Ocean College, Zhejiang University, Hangzhou 310058, P. R. China: 1988aobo@163.com.

Nanotubular encapsulate is a novel nano-structure which may present superior performance than traditional nanocomposites. In this study, we present a facile one-step method to fabricate MnFe₂O₄/Halloysite nano-encapsulates using metal oleate as ferrite precursor and modification for HNTs. The TEM images proved that ferrite nanoparticles successfully embedded into the inner channels of halloysite nanotubes (Fig. 1 (a)). Ferrite nanoparticles are attached on both the inner and outer surface of HNTs, with most particles are embedded in the inner channels. HRTEM images revealed that the \( d \) spacings of nanoparticles are 0.30 nm (Fig. 1 (b)) for the inner particles and 0.49 nm for the outer particle, which are corresponding to the (220) and (111) planes of MnFe₂O₄ (Jacobsite, JCPDF#74-2403), respectively. This result indicates that the constriction of HNTs will shift the exposure facets of ferrite nanoparticles to with narrow spacings, which may resulted in distinctive physicochemical properties. The construction of nano-encapsulates was attributed to the surface modification of metal oleates. Previous study revealed that octadecyl-phosphonic acid [1] and catecholic anchor (Dopa) [2] would selective modified halloysite nanotubes. Our works revealed that metal oleate have similar selective modification for HNTs, result in HNTs with hydrophobic core and hydrophilic shell, metal oleate complex favorably entered into the inner surface and then ferrite nanoparticles were in-situ formed during subsequently heat treatment.

Fig. 1 (a) TEM image of MnFe₂O₄/Halloysite nano-encapsulates; (b) HRTEM figure of MnFe₂O₄ nanoparticles located on the inner surfaces of halloysite.
Fig. 2 Frequency dependence of reflection loss (RL) of microwaves by natural halloysite (HNTs), MnFe$_2$O$_4$/HNTs nano-encapsulates (HF-1), and the sample with ferrite particles totally outside the HNTs (HF-2).

The obtained MnFe$_2$O$_4$/halloysite nano-encapsulates (HF-1) present different magnetic and EM performances than the sample with ferrite particles totally outside the HNTs (HF-2). The magnetization curves shows that HF-1 sample show threefold higher saturation magnetization (Ms) value (4.21 emu g$^{-1}$) than that of HF-2 (1.09 emu g$^{-1}$), maybe due to the constraint of HNTs which changed the exposure facets and particle sizes of ferrite particles. We further compared the EM wave absorption performance of HNTs, HF-1, and HF-2 by calculating their reflection loss (RL) values for microwaves. At measured thickness of 2 mm, HNTs and HF-2 show similar poor RL values of > -2 dB at all frequencies. HF-1 shows much improved EM wave absorption with maximum RL of -5.4 dB and bandwidths of RL<-5 dB at 14.0-14.5 GHz (Fig. 2). The variations of RL as functions of frequency and thickness indicate that HF-1 is a potential microwave absorber at frequency of 10-18 GHz and thickness of >7.5 mm. This study opens a new way to fabricate magnetic-halloysite nanocomposites and further studies on the preparation and application of other halloysite nanotubular encapsulates are now in progress.

HYDRATION STUDY OF PALLYGORSKITE AND SEPIOLITE USING MOLECULAR SIMULATION

Jinhong Zhou¹, Xiancai Lu*¹

¹ State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, P.R. China: xcljun@nju.edu.cn

Palygorskite and sepiolite are applied widely in industry because of their fibrous structures. They are commonly used in industrial products for adsorption applications. Here we use molecular simulation method to study the hydration properties of palygorskite and sepiolite. Even though they both have similar fibrous morphology, but the difference between them (i.e. fibrous pore size) could has influence on the hydration properties.
THE REMOVAL OF DDT IN AQUEOUS SOLUTION BASED ON THE ADSORPTION BY NANOSCALE ZERO-VALENT IRON

Rongbing Zhou¹, Weihong Wu¹, Junhong Tang¹, Zhengmiao Xie¹, Zuliang Chen², Mallavarapu Megharaj², and Ravendra Naidu²

¹ Institute of Environ Sci & Engineering, Hangzhou Dianzi University, Hangzhou, Zhejiang 310018, China: brz3000@163.com
² Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes, SA 5095, Australia

In this study, nanoscale zero-valent iron (nZVI) was used to remove DDT from aqueous solution, where the new findings included the formation of iron oxide after nZVI corrosion in DDT aqueous solution and following the DDT adsorbed onto the iron oxide rather than that of dechlorination since not degraded products were observed by gas chromatography-mass spectrometry (GC-MS) analysis, and the formation of iron oxide was confirmed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transforms infrared spectra (FTIR). To further confirm the adsorption of DDT onto the iron oxide, different adsorption kinetics were employed to examine the adsorption of DDT, where the pseudo-second-order model was well fitted for adsorption, as well as isotherm and thermodynamic studies shows that removal of DDT by nZVI was adsorption step. Finally, the mechanism of DDT onto the iron oxide was proposed. This study provides a new insight of removal of DDT from solution by the adsorption.

Fig. 1. Effect of nZVI on removal of DDT (Fe addition, 2 g/L; initial concentration of DDT, 1 mg/L; temperature, 293 k; stirring rate, 250 rpm)
**51st Annual Meeting of CMS**  
Abstracts  
*Everything is big: From nanoparticles to planets*

---

**Fig. 2.** SEM images. A: Before reaction; B: After reaction

**Fig. 3.** XRD pattern. A: nZVI before reaction with DDT; B: nZVI after reaction with DDT

**Fig. 4.** FTIR result

**Fig. 5.** GC-MS result
EFFECT OF CLAYS ON ORGANIC MATTERS OCCURRENCE IN ARGILLACEOUS SOURCE ROCKS

Xiaojun Zhu*, Jingong Cai

State Key Laboratory of Marine Geology, Tongji University, Shanghai 200092, China: superb.zxj@gmail.com

Clays as a most important constituent of argillaceous source rock, its specific physicochemical property (e.g. fine particle, expansiveness, etc.) plays a key role in organic matter preservation. However, there exist many of morphological compositions of organic matter in source rock (e.g. amorphous organic matter, structural organic matter, etc.) (Li and Batten, 2005; Ercegovac and Kostić, 2006), which vary in content and surface properties. Therefore, great concern should be paid to the effect of clays on the correlations with organic components and organic matter occurrence in the study of source rocks.

Argillaceous source rock formed in different members (belonged to different sedimentary environments) were used to perform the measurements of X-ray diffraction (XRD), specific surface area (SSA), pyrolysis and palynofacies, respectively, so as to obtain the parameters of mineralogy and organic matter, etc. of the sample. Studies finds that the content of clays in different members (or different sedimentary environments) varied obviously, which was higher in member Es2 with 45.7% of average content (river-delta deposition) than in Es1 (lake deposition) or Es3 (deep-half deep lake facies), and the SSA in Es2 also was the largest; organic matter of argillaceous source rocks, total content of which was ranged from 0.12% to 4.01% which in Es2 was 2~3 folds lower than that in Es1 or Es3, was composed of amorphous organic matter (AOM) and morphological organic matter (MOM), and organic matter in Es2 was dominated with MOM while which in Es1 and/or Es3 was dominated with AOM. For the correlations between clays and different organic components in different members, it is positive in Es1 and/or Es3 but negative in Es2; organic matter with MOM-dominant is negatively correlated with external, inner and total surface area, while organic matter with AOM-dominant is negatively correlated with external surface area and positively correlated with inner and total surface area. Predecessors have recommended the mechanisms of organic matter preservation of sulfuration, polymerization and aggregation as well as selective preservation (Burdige, 2007; Hedges and Keil, 1995; Zonneveld et al., 2010), synthesizing above analysis, it reveals that organic matter in argillaceous source rock with AOM-dominant is mainly occurred on clay surfaces (particularly inner surface), indicating the mechanism of adsorption preservation which clay makes is much more important; but the clay gives a smaller contribution to the occurrence of organic matter with MOM-dominant, which is also evidenced from the correlations of each SSA with organic matters in Es2, suggesting that the preservation of these organic matters may be ascribe to their own properties (e.g. selective preservation, sulfication, polymerization), this result indicates that the organic matter preservation in argillaceous source rock is a coexistence of multi-mechanism of preservation.

Therefore, it is important to pay attention to the occurrence of organic matter in argillaceous source rock, especially make sense of the variation in the content of organic component in different occurrence modes of different sedimentary environments, which is of
great significance for understanding the evolution and difference of hydrocarbon generation of organic matter and organic-inorganic interactions.

This work was supported by National Natural Science Foundation of China Program (Grant No. 41072089; 41372130).

References:


AL13-PILLARED MONTMORILLONITE MODIFIED BY INTERCALATION OF CATIONIC AND ZWITTERIONIC SURFACTANTS

Jianxi Zhu*1, Lingya Ma1,2, Jingming Wei1, Runliang Zhu1, and Hongping He1

1CAS Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, P.R. China: zhujx@gig.ac.cn
2University of Chinese Academy of Sciences, Beijing 100049, P.R. China.

Inorganic-organic montmorillonites (IOMt), obtained by intercalating cationic metal complexes and organic cations, are capable of removing a wide range of inorganic and organic contaminants. IOMt can also serve as novel sorbents of volatile organic compounds, and as catalysts in the degradation of adsorbed organic compounds. Little information, however, is available regarding the interlayer microstructure of IOMt which holds the key to understanding their interactions with pollutants, and to developing novel industrial applications. Previous studies have shown that the type of organic modifier used can markedly influence the structural characteristics and sorptive behavior of OMt. Thus, modifiers containing special functional groups, such as zwitterionic surfactants, can significantly improve the sorption capacity of OMt. Sulfobetaine, containing both positively charged (quaternary ammonium) and negatively charged (sulfonate) groups is an example of a zwitterionic surfactant. Besides being highly water-soluble, biodegradable, and biologically safe, sulfobetaine can readily intercalate into the interlayer space of montmorillonite. We might therefore expect that IOMt, intercalated with both a zwitterionic surfactant and a cationic metal complex, has properties and interlayer microstructures that are different from those found in organoclays. Likewise, the capacity of these materials for adsorbing charged organic and inorganic pollutants would differ from that of OMt. Previous studies have also shown that the interlayer structure and properties of OMt and pillared interlayered clays (PILC) are strongly dependent on surfactant configuration and dosage as well as pretreatment conditions. By analogy, this observation would also apply to IOMt.

Here we report on the properties of a series of IOMt prepared by modifying Al13-pillared montmorillonite (AIPMt) with different concentrations of a cationic (C16) and a zwitterionic (Z16) surfactant. Al13 denotes the polyhydroxy-aluminum (Keggin) cation ([Al13V12O40(OH)24(H2O)12])7+. The basal spacing, chemical composition, thermal stability, and microstructure of the IOMt were determined by X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TG), and C, H, and N elemental analysis.

The results show that the structure of the IOMt was strongly influenced by surfactant type. In the case of C16-modified AIPMt (C-AIPMt), the surfactant molecules entered and expanded the interlayer space, leading to the partial release of pre-intercalated Al13 cations. At high surfactant concentrations (> 2.0 CEC), the basal spacing of C-AIPMt showed no further expansion although the gauche/trans conformer ratio of the intercalated surfactant decreased. In the case of Z16-modified AIPMt (Z-AIPMt), however, the amount of Z16 intercalated did not increase when the surfactant concentration exceeded 1.0 CEC, while the basal spacing was identical with that measured for the unmodified AIPMt. This observation may be attributed to a difference in the capacity of AIPMt for intercalating C16 and Z16. The capacity of AIPMt for
intercalating C16 is much greater than that for Z16. We propose that C16 is intercalated through both cation exchange (with Al$_{13}$) and physisorption, while the intercalation of Z16 is primarily mediated by electrostatic attraction between the interlayer Al$_{13}$ cation in AlPMt and the negatively charged group of Z16. As a result, the microstructure of C-AlPMt is markedly different from that of Z-AlPMt.
MOLECULAR MODELING STUDY THE ADSORPTION OF FULLERENE ON CLAY MINERAL SURFACE

Runliang Zhu*, Qing Zhou, Jianxi Zhu, and Hongping He

1Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China; *zhurl@gig.ac.cn

Buckminsterfullerene (C60) as one of the most important carbon-based nanoparticles has potential applications in various fields. Although the toxicity of C60 to organisms is still debated, the potential adverse effects of C60 on human health and the environment require serious attention to their environmental fate, as most C60 will eventually end up in the environment. As such, interactions between C60 and geosorbents are drawing increasing concerns from various scientific communities. Clay minerals as one type of most common inorganic geosorbents are ubiquitous in the environment. Interactions between clay minerals and environmental contaminants (e.g., heavy metals, hydrophobic organic contaminants) have been extensively studied during the past decades, and the obtained results showed that clay minerals can significantly adsorb, and even sequester, many types of contaminants. However, interactions between C60 and clay minerals have not drawn too much attention yet, possibly because of the difficulty in determining the involved interaction information by experimental method. As we know, C60 has extremely low solubility in water and it can very easily form aggregates.

Molecular modeling recently has proven to be a powerful tool in studying the adsorptive characteristics of various contaminants to clay minerals. The obtained results can provide atomic-level insights into the microstructure, and the dynamics and thermal dynamics information, of the adsorption system. Here molecular dynamics (MD) simulations were employed to study the adsorption of C60 on kaolinite, one of the most common clay minerals in soils and sediment, with typical hydrophobic siloxane surface and hydrophilic –OH containing surface. The adsorption free energy of C60 to these surfaces were calculated, which were further compared with that of C60-C60 aggregation energy. The obtained results show that the adsorption free energy of C60 on the hydrophobic surface and hydrophilic surface of kaolinite were -0.25 eV and -0.14 eV, respectively; while the aggregation free energy of two C60 molecules was -0.19 eV. As such, C60 prefer to be adsorbed to siloxane surface than aggregate with each other. However, it less likely to be adsorbed on the hydrophilic –OH surface.
## AUTHOR INDEX

### A

<table>
<thead>
<tr>
<th>Author</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Achilles, C. N.</td>
<td>10, 18, 30, 194, 222, 227</td>
</tr>
<tr>
<td>Adolphe, D.</td>
<td>9, 176</td>
</tr>
<tr>
<td>Agha, M.</td>
<td>11, 89</td>
</tr>
<tr>
<td>Agnew, S. F.</td>
<td>126</td>
</tr>
<tr>
<td>Agresti, D. G.</td>
<td>10, 222</td>
</tr>
<tr>
<td>Akin, I. D.</td>
<td>10, 32</td>
</tr>
<tr>
<td>Alam, S. S.</td>
<td>12, 34</td>
</tr>
<tr>
<td>Andrejkovičová, S.</td>
<td>23, 36</td>
</tr>
<tr>
<td>Archer, Jr, P. D.</td>
<td>11, 38</td>
</tr>
<tr>
<td>Archer, P. D.</td>
<td>18, 164</td>
</tr>
<tr>
<td>Arteaga, S.</td>
<td>12, 40</td>
</tr>
<tr>
<td>Arvidson, R. E.</td>
<td>15, 42</td>
</tr>
<tr>
<td>Atreya, S. K.</td>
<td>18, 164</td>
</tr>
<tr>
<td>Baik, H.</td>
<td>16, 18, 132, 241</td>
</tr>
<tr>
<td>Barré, L.</td>
<td>9, 134</td>
</tr>
<tr>
<td>Barrientos Velázquez, A. L.</td>
<td>12, 24, 25, 40, 44, 81</td>
</tr>
<tr>
<td>Bartlett, S. A.</td>
<td>19, 46</td>
</tr>
<tr>
<td>Beall, G.</td>
<td>25, 82</td>
</tr>
<tr>
<td>Beall, G. W.</td>
<td>24, 25, 101, 107, 178</td>
</tr>
<tr>
<td>Bernardino, N. D.</td>
<td>25, 48</td>
</tr>
<tr>
<td>Bish, D. L.</td>
<td>10, 18, 30, 92, 164, 194, 222, 227</td>
</tr>
<tr>
<td>Blachowski, A.</td>
<td>11, 206</td>
</tr>
<tr>
<td>Blake, D. F.</td>
<td>10, 18, 194, 222, 227</td>
</tr>
<tr>
<td>Boersma, A.</td>
<td>10, 231</td>
</tr>
<tr>
<td>Bonne, M.</td>
<td>9, 176</td>
</tr>
<tr>
<td>Bourg, I. C.</td>
<td>5, 50, 51</td>
</tr>
<tr>
<td>Brendlé, J.</td>
<td>9, 176</td>
</tr>
<tr>
<td>Bridges, J. C.</td>
<td>220</td>
</tr>
<tr>
<td>Bristow, T. F.</td>
<td>10, 18, 194, 222, 227</td>
</tr>
<tr>
<td>Brunner, A. E.</td>
<td>18, 164</td>
</tr>
<tr>
<td>Busch, A.</td>
<td>21, 209</td>
</tr>
<tr>
<td>Butler, S. K.</td>
<td>10, 25, 52, 53</td>
</tr>
</tbody>
</table>

### B

<table>
<thead>
<tr>
<th>Author</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cai, J.</td>
<td>19, 24, 143, 252</td>
</tr>
<tr>
<td>Cain, A. A.</td>
<td>23, 54</td>
</tr>
</tbody>
</table>

### C

<table>
<thead>
<tr>
<th>Author</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caporuscio, F. A.</td>
<td>5, 65</td>
</tr>
<tr>
<td>Cashion, J. D.</td>
<td>23, 98</td>
</tr>
<tr>
<td>Cervini-Silva, J.</td>
<td>13, 19, 55, 57</td>
</tr>
<tr>
<td>Chan, Y. T.</td>
<td>10, 12, 58, 226</td>
</tr>
<tr>
<td>Chang, C.-F.</td>
<td>19, 112</td>
</tr>
<tr>
<td>Chang, P. H.</td>
<td>59</td>
</tr>
<tr>
<td>Chang, P.-H.</td>
<td>20</td>
</tr>
<tr>
<td>Chávez-Balderas, X.</td>
<td>13, 55</td>
</tr>
<tr>
<td>Chemeda, Y. C.</td>
<td>23, 61</td>
</tr>
<tr>
<td>Chen, X.-G.</td>
<td>9, 16, 149, 247</td>
</tr>
<tr>
<td>Chen, Z.</td>
<td>16, 250</td>
</tr>
<tr>
<td>Cheng, H.</td>
<td>9, 12, 63, 147</td>
</tr>
<tr>
<td>Cheng, J.</td>
<td>10, 151</td>
</tr>
<tr>
<td>Cheshire, M. C.</td>
<td>5, 65</td>
</tr>
<tr>
<td>Chipera, S. J.</td>
<td>10, 18, 194, 222, 227</td>
</tr>
<tr>
<td>Cho, H. G.</td>
<td>67</td>
</tr>
<tr>
<td>Cho, H.-G.</td>
<td>13</td>
</tr>
<tr>
<td>Choi, J.-Y.</td>
<td>13, 240</td>
</tr>
<tr>
<td>Chon, C. M.</td>
<td>68</td>
</tr>
<tr>
<td>Chon, C.-M.</td>
<td>13</td>
</tr>
<tr>
<td>Choy, J.-H.</td>
<td>13, 15, 16, 19, 69, 186, 238, 239, 240</td>
</tr>
<tr>
<td>Christidis, G.</td>
<td>13, 189</td>
</tr>
<tr>
<td>Chryssikos, G. D.</td>
<td>10, 23, 79, 141</td>
</tr>
<tr>
<td>Chu, C. C.</td>
<td>16, 212</td>
</tr>
<tr>
<td>Clearfield, A.</td>
<td>7, 70, 245</td>
</tr>
<tr>
<td>Coll, P.</td>
<td>18, 71</td>
</tr>
<tr>
<td>Constantino, V. R. L.</td>
<td>12, 25, 28, 48, 74, 201</td>
</tr>
<tr>
<td>Coveney, P. V.</td>
<td>8, 213</td>
</tr>
<tr>
<td>Craig, P. I.</td>
<td>18, 72</td>
</tr>
<tr>
<td>Crisp, J. A.</td>
<td>18, 194, 227</td>
</tr>
<tr>
<td>Cunha, V. R. R.</td>
<td>28, 74</td>
</tr>
</tbody>
</table>

### D

<table>
<thead>
<tr>
<th>Author</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Das, K.</td>
<td>11, 76</td>
</tr>
<tr>
<td>Davis, J.</td>
<td>5, 50</td>
</tr>
<tr>
<td>Davis, R.</td>
<td>23, 54</td>
</tr>
<tr>
<td>del Angel, P.</td>
<td>13, 55</td>
</tr>
<tr>
<td>Delarmelinda, E. A.</td>
<td>25, 77</td>
</tr>
<tr>
<td>Deligianni, A.</td>
<td>10, 79</td>
</tr>
<tr>
<td>Deneele, D.</td>
<td>23, 61</td>
</tr>
<tr>
<td>Deng, L.</td>
<td>26, 172</td>
</tr>
<tr>
<td>Author Name</td>
<td>Pages</td>
</tr>
<tr>
<td>-------------</td>
<td>-------</td>
</tr>
<tr>
<td>Deng, Y.</td>
<td>12, 24, 25, 34, 40, 44, 77, 81, 96, 111, 219</td>
</tr>
<tr>
<td>Derkowski, A.</td>
<td>21, 23, 141, 215</td>
</tr>
<tr>
<td>Des Marais, D. J.</td>
<td>18, 194</td>
</tr>
<tr>
<td>Detellier, C.</td>
<td>13, 189</td>
</tr>
<tr>
<td>Dixon, J. B.</td>
<td>25, 81</td>
</tr>
<tr>
<td>Dohrmann, R.</td>
<td>20, 130</td>
</tr>
<tr>
<td>Dong, H.</td>
<td>4, 211</td>
</tr>
<tr>
<td>Douglas, A.</td>
<td>25, 82</td>
</tr>
<tr>
<td>Downs, R. T.</td>
<td>10, 18, 194, 222, 227</td>
</tr>
<tr>
<td>Dronov, A. V.</td>
<td>24, 114</td>
</tr>
<tr>
<td>Duman, M.</td>
<td>9, 83</td>
</tr>
<tr>
<td>Dyar, M. D.</td>
<td>92</td>
</tr>
<tr>
<td>Dypvik, H.</td>
<td>11, 84</td>
</tr>
<tr>
<td>Ehlmann, B. L.</td>
<td>86</td>
</tr>
<tr>
<td>Eigenbrode, J. L.</td>
<td>18, 164</td>
</tr>
<tr>
<td>Elliott, W. C.</td>
<td>11, 87</td>
</tr>
<tr>
<td>Elwood Madden, A. S.</td>
<td>19, 46</td>
</tr>
<tr>
<td>Emmerich, K.</td>
<td>20, 130</td>
</tr>
<tr>
<td>Erastova, V.</td>
<td>5, 105</td>
</tr>
<tr>
<td>Everett, W. N.</td>
<td>16, 212</td>
</tr>
<tr>
<td>Ewan, K.</td>
<td>10, 231</td>
</tr>
<tr>
<td>Fackrell, L. E.</td>
<td>12, 88</td>
</tr>
<tr>
<td>Faria, D. L. A.</td>
<td>25, 48</td>
</tr>
<tr>
<td>Farmer, J. D.</td>
<td>18, 194, 227</td>
</tr>
<tr>
<td>Farrell, M.</td>
<td>20, 242</td>
</tr>
<tr>
<td>Fendorf, S.</td>
<td>11, 184</td>
</tr>
<tr>
<td>Ferrell, R.</td>
<td>11, 89</td>
</tr>
<tr>
<td>Fialips, C. I.</td>
<td>20, 90</td>
</tr>
<tr>
<td>Flatt, R. J.</td>
<td>13, 234</td>
</tr>
<tr>
<td>Fleury, M.</td>
<td>9, 134</td>
</tr>
<tr>
<td>Fontes, M. P. F.</td>
<td>11, 184</td>
</tr>
<tr>
<td>Fraaij, J. G. E. M.</td>
<td>21, 209</td>
</tr>
<tr>
<td>Franz, H. B.</td>
<td>18, 164</td>
</tr>
<tr>
<td>Friedlander, L. R.</td>
<td>92</td>
</tr>
<tr>
<td>Fritsch, K.</td>
<td>7, 203</td>
</tr>
<tr>
<td>Geesey, G.</td>
<td>13, 136</td>
</tr>
<tr>
<td>Gentry, T.</td>
<td>20, 181, 208</td>
</tr>
<tr>
<td>Georgelin, T.</td>
<td>18, 71</td>
</tr>
<tr>
<td>Gionis, V.</td>
<td>10, 23, 79, 141</td>
</tr>
<tr>
<td>Glotch, T. D.</td>
<td>92</td>
</tr>
<tr>
<td>Gómez-Vidales, V.</td>
<td>19, 57</td>
</tr>
<tr>
<td>Goss, M.</td>
<td>25, 101</td>
</tr>
<tr>
<td>Graft, T. G.</td>
<td>10, 222</td>
</tr>
<tr>
<td>Gragg, E. J.</td>
<td>10, 52</td>
</tr>
<tr>
<td>Graham, H. V.</td>
<td>18, 164</td>
</tr>
<tr>
<td>Greenwell, H. C.</td>
<td>5, 105</td>
</tr>
<tr>
<td>Groen, D.</td>
<td>23, 213</td>
</tr>
<tr>
<td>Grotzinger, J. P.</td>
<td>18, 227</td>
</tr>
<tr>
<td>Grove, J. H.</td>
<td>11, 160</td>
</tr>
<tr>
<td>Grunlan, J. C.</td>
<td>19, 23, 54, 198</td>
</tr>
<tr>
<td>Gu, C.</td>
<td>4, 211</td>
</tr>
<tr>
<td>Guimarães, M. A.</td>
<td>12, 201</td>
</tr>
<tr>
<td>Gutman, R.</td>
<td>23, 199</td>
</tr>
<tr>
<td>Haberlah, D.</td>
<td>20, 90</td>
</tr>
<tr>
<td>Hamilton, A. R.</td>
<td>19, 102</td>
</tr>
<tr>
<td>Hang, X.</td>
<td>11, 94</td>
</tr>
<tr>
<td>Harris, P.</td>
<td>25, 104</td>
</tr>
<tr>
<td>Harris, R.</td>
<td>18, 241</td>
</tr>
<tr>
<td>Hart, G.</td>
<td>11, 89</td>
</tr>
<tr>
<td>Hawkins, S.</td>
<td>7, 235</td>
</tr>
<tr>
<td>He, H.</td>
<td>21, 22, 25, 26, 159, 254, 256</td>
</tr>
<tr>
<td>Heinz, H.</td>
<td>5, 105</td>
</tr>
<tr>
<td>Hellevang, H.</td>
<td>11, 84</td>
</tr>
<tr>
<td>Henderson, B. G.</td>
<td>24, 107</td>
</tr>
<tr>
<td>Hercman, H.</td>
<td>10, 108</td>
</tr>
<tr>
<td>Holmboe, M.</td>
<td>5, 50</td>
</tr>
<tr>
<td>Hong, I.-T.</td>
<td>13, 110</td>
</tr>
<tr>
<td>Hons, F.</td>
<td>20, 181</td>
</tr>
<tr>
<td>Hoppie, B.</td>
<td>18, 241</td>
</tr>
<tr>
<td>Horiuchi, Y.</td>
<td>16, 170</td>
</tr>
<tr>
<td>Howard, K. T.</td>
<td>23, 166</td>
</tr>
<tr>
<td>Hsu, C.-C.</td>
<td>12, 111</td>
</tr>
<tr>
<td>Hsu, L.-C.</td>
<td>19, 112</td>
</tr>
<tr>
<td>Hu, P.</td>
<td>16, 237</td>
</tr>
<tr>
<td>Huang, Q.</td>
<td>12, 96</td>
</tr>
<tr>
<td>Huff, W. D.</td>
<td>24, 25, 114, 115</td>
</tr>
<tr>
<td>Hutcheon, G. A.</td>
<td>19, 102</td>
</tr>
</tbody>
</table>
I

Inoué, S. ......................................... 19, 116
IODP Expedition 329 shipboard scientists
........................................ 16, 18, 132, 241
İşçi, S...................................... 7, 16, 118, 119
İşçi, Y........................................ 7, 16, 118, 119

J

Jaber, M........................................... 18, 71
Jaisi, D. P................................... 20, 120
Jaynes, W.................................... 20, 121
Jean, J. S.......................................... 59
Jean, J.-S.................................. 20
Jeong, G. Y............................... 11, 13, 123, 124
Ji, J........................................... 25, 125
Jiang, W........................................ 59
Jiang, W.-T................................... 20
Jo, M. R........................................ 16, 129
Johnston, C. T. 11, 20, 23, 76, 126, 127, 242
Joseph, C..................................... 7, 203
Jove-Colon, C.................................. 65
Jung, H......................................... 16, 128
Jung, J.......................................... 16, 129

K

Kalinichev, A.................................. 21, 215
Kalinichev, A. G .... 5, 10, 21, 108, 152, 154
Kang, M......................................... 16, 129
Kang, Y.-M.................................. 16, 129
Karathanasis, A. D...................... 11, 160
Kasama, T..................................... 24, 133
Kaufhold, S.................................. 20, 130
Khenoussy, N............................ 9, 176
Kim, A........................................... 16, 128
Kim, H.-M.................................... 18, 183
Kim, J........................................ 16, 18, 132, 241
Kim, J. G.................................... 68
Kim, J.-G.................................... 13
Kim, J.-w.................................... 13
Kim, J.-W.................................... 136
Kim, S. O..................................... 67
Kim, S.-O.................................... 13
Kim, T.-H.................................... 13, 110, 131
Kim, T.-I.................................... 13, 131
Koch, C. B................................... 24, 133
Kogure, T................................. 19, 116
Kohler, E...................................... 9, 134
Komadel, P.................................. 4, 23, 36
Komishke, B................................ 24, 135
Konovalova, Y........................... 23, 199
Koo, T.-H..................................... 13, 136
Kookana, R.................................. 20, 242
Koteja, A..................................... 9, 137
Kruichak, J................................... 7, 162
Krupskaya, V. K.......................... 12, 139
Kuligiewicz, A............................. 23, 141
Kuo, C. Y..................................... 59
Kuo, C.-Y.................................. 20

L

Labeyrie, B............................. 20, 90
Lambert, J. F.............................. 71
Lambert, J.-F.............................. 18
Lasserre, B.................................. 20, 90
Lauer, H. V................................. 11, 38
Laurent, J.-P.............................. 20, 90
Lavi, R...................................... 23, 199
Lebeau, B.................................. 9, 176
Lee, D. H.................................... 16, 129
Lee, G. J.................................... 13, 131
Leite, J. R. S. A........................... 12, 201
Leng, Y................................. 5, 196
Leshin, L. A.................................. 18, 164
Lezama-Pacheco, J. S.................. 11, 184
Li, L........................................... 8, 145
Li, P......................................... 7, 9, 146, 235
Li, Y........................................... 19, 54, 143
Li, Y.-C....................................... 23
Li, Z........................................... 20, 59
Liko, W. J................................. 10, 32
Lim, D....................................... 11, 87
Lima, F. C. D. A............................. 12, 201
Lin, C....................................... 9, 146
Liu, J........................................... 7, 245
Liu, Q....................................... 9, 12, 63, 147
Liu, S.-T................................. 9, 149
Liu, X.................................... 8, 10, 21, 145, 151, 246
Liu, Y.-T.................................. 19, 112
Lopez, R................................. 20, 208
Loganathan, N......................... 5, 21, 152, 154
Londono, S. C............................. 19, 156
Long, P. E. ........................................... 11, 87
López, F. ............................................. 13, 55
Lu, X. ........................................ 5, 8, 10, 21, 145, 151, 246, 249
Luo, Z. ........................................ 7, 245
Lv, G. C. .......................................... 59
Lv, G.-C. ............................................ 20

M

M’Hamdi, J. ........................................ 9, 134
Ma, L. .................................................. 25, 26, 159, 254
Ma, W. ........................................ 4, 9, 158, 217
Ma, Y. ................................................ 11, 12, 94, 96
Madejová, J. .................................... 23, 36
Mahaffy, P. R. .................................. 18, 164
Maj-Szeliga, K. .................................. 11, 206
Marais, D. J. .................................... 18, 227
Martin, B. R. .................................... 7, 245
Martínez, C. N. .................................. 23, 244
Mas, P. P. ........................................... 13, 189
Matocha, C. J. .................................. 11, 160
Matteo, E. N. .................................... 7, 162
Matusik, J. ........................................ 9, 137
McAdams, A. C. .................................. 18, 164
McAdam, M. M. .................................. 23, 166
McCoy, T. M. ..................................... 23, 166
Megharaj, M. ..................................... 16, 250
Meijer, E. J. ....................................... 8, 225
Mejía-Pérez Campos, E. ....................... 13, 55
Mexias, A. ......................................... 13, 189
Michalski, J. R. .................................. 92
Miehë-Brendlé, J. .................................. 12, 201
Miller, A. W. ..................................... 7, 162
Mills, M. .......................................... 7, 162
Ming, D. W. .................................. 10, 11, 15, 18, 38, 72, 164, 168, 187, 194, 222, 227
Miyoshi, Y. ........................................ 16, 170
Montoya, A. ....................................... 13, 19, 55, 57
Morgan, L. ........................................ 26, 172
Moroookian, J. M. .................................. 18, 194, 227
Morris, R. V. .................................. 10, 11, 18, 38, 164, 194, 222, 227
Morrison, K. D. .................................. 19, 174
Morrison, S. M. .................................. 18, 194, 227
MSL Science Team ................................ 11, 38
Muhamed, S. A. .................................. 9, 176
Muliana, A. ........................................ 9, 146

Munguía P, R. ...................................... 12, 219
Muñoz, L. .......................................... 13, 55
Murdock, L. W. .................................. 11, 160

N

Naidu, R. ............................................. 16, 250
Nam, I. ................................................. 68
Nam, I.-H. ........................................ 13
Nash, T. L. ....................................... 24, 178
Neeway, J. ..................................... 12, 179, 180
Ng, J. ................................................. 20, 181
Nieto-Camacho, A. .......................... 19, 57
Niles, P. ............................................. 18, 194
Niles, P. B. ........................................ 11, 38
Nishimura, R. .................................. 9, 146
Nolen, C. R. ...................................... 23, 54
Norrant, F. ....................................... 9, 134

O

Ogawa, M. ........................................... 28, 182
Oh, J.-M. ........................................... 13, 18, 110, 131, 183
Ouvrard, G. ...................................... 23, 61

P

Pacheco, A. A. .................................. 11, 184
Palacios, E. ....................................... 13, 19, 55, 57
Park, D.-H. ...................................... 19, 186
Pasay, K. ........................................... 24, 135
Pavlova, A. ........................................ 8, 225
Pawlak, J. ......................................... 7, 162
Peng, T. ............................................. 4, 211
Pentrák, M. ........................................ 23, 36
Peretyazhko, T. ................................ 11, 187
Petersen, P. A. D. .............................. 28, 74
Petit, S. ........................................... 13, 23, 25, 189, 191, 192
Petrilli, H. M. .................................. 12, 28, 74, 201
Piao, H. ............................................. 13, 239
Pickering, R. ..................................... 11, 87
Ploetz, M. ........................................... 20, 193
Poch, O. ........................................... 18, 71

R

Ramírez-Apán, M. T. ....................... 19, 57
Ramos, E. ........................................... 13, 55
51st Annual Meeting of CMS

Abstracts

Everything is big: From nanoparticles to planets

Swindle, A. L. ........................................ 19, 46
Szczerba, M. .................................. 21, 23, 141, 215
Szopa, C. ........................................ 18, 71
Zyszmański, W. ................................ 11, 206

T

Takagi, T. .......................................... 16, 170
Takahara, A. .................................. 4, 9, 158, 217, 235
Tambach, T. J. ................................ 21, 209
Tang, J. ........................................... 16, 250
Tao, D. ............................................ 4, 217
Tao, Q. ............................................ 25, 159
Tenorio Arvide, M. G. ..................... 12, 219
Tinnacher, R. ................................... 5, 50
Toshihiro, K. .................................. 16, 18, 132, 241
Tournassat, C. .................................. 5, 50, 51
Treiman, A. H. .......................... 10, 15, 18, 194, 220, 222, 227
Trinh, T. T. ...................................... 8, 225
Tzou, Y.-M. ............................... 10, 12, 19, 58, 112, 226

U

Ufer, K. ........................................... 20, 130
Umbhauer, F. .................................. 20, 90

V

Valera P, M. A. ............................... 12, 219
Van Rans, E. .................................. 9, 83
Vandiviere, M. V. ....................... 11, 160
Vaniman, D. T. ...................... 10, 18, 194, 222, 227
Velbel, M. A. .................................. 23, 229
Veras, L. M. C. .............................. 12, 201

W

Wadt, P. G. S. .................................. 25, 77
Wakou, B. F. N. ............................. 5, 154
Walker, B. F. N. ............................ 10, 231
Wall, N. A. ..................................... 7, 232
Wang, H. ........................................ 24, 233
Wang, L. ........................................ 24, 135, 233
Wang, R. ....................................... 8, 10, 21, 145, 151, 246
Wang, Y. ........................................... 7, 162
Wangler, T. P. ................................ 13, 234
Wasim, M. ...................................... 25, 81
Webb, N. D. .................................... 10, 52

S

Sakai, V. Y. .................................... 12, 201
Santen, R. A. .................................. 8, 225
Sarrazin, P. .................................. 18, 194, 227
Schacher, L. .................................. 9, 176
Schmeide, K. .................................. 7, 203
Schoonheydt, R. A. .................. 23, 127
Schooeder, P. A. .................... 12, 25, 88, 205
Shahab, A. R. ................................ 13, 234
Sharp, T. G. ................................... 92
Silva Uribe, Y. P. .................... 12, 219
Singh, B. ....................................... 20, 242
Skiba, M. ....................................... 11, 206
Smith, C. ........................................ 24, 44
Somenahally, A. .................... 20, 208
Song, H. ....................................... 13, 68
Souza Junior, V. S. ............... 25, 77
Sparks, D. ...................................... 20, 242
Spiering, P. .................................. 21, 209
Sprik, M. ....................................... 10, 151
Środoń, J. ................................. 21, 22, 215
Stalport, F. ................................... 18, 71
Stern, J. C. ..................................... 18, 164
Steudel, A. .................................. 20, 130
Sue, H.-J. .................................. 9, 16, 146, 212, 235
Sun, D. ........................................... 16, 212
Sun, H. .......................................... 4, 211
Sun, L. .......................................... 7, 245
Sung, J.-C. ..................................... 19, 112
Sunshine, J. M. ....................... 23, 166
Suter, J. L. ..................................... 8, 213
Sutter, B. .................................... 11, 18, 38, 164, 187
Swadling, J. B. ....................... 8, 213

261
### Author Index

#### Everything is big: From nanoparticles to planets

<table>
<thead>
<tr>
<th>Author</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Webster, C. R.</td>
<td>18, 164</td>
</tr>
<tr>
<td>Wei, J.</td>
<td>26, 254</td>
</tr>
<tr>
<td>Weigum, S.</td>
<td>25, 82</td>
</tr>
<tr>
<td>Wentineck, R.</td>
<td>21, 209</td>
</tr>
<tr>
<td>Werner, S.</td>
<td>11, 84</td>
</tr>
<tr>
<td>Westrop, J. P.</td>
<td>19, 46</td>
</tr>
<tr>
<td>Wheeler, J.</td>
<td>10, 231</td>
</tr>
<tr>
<td>White, K. L.</td>
<td>7, 9, 146, 235</td>
</tr>
<tr>
<td>Williams, K. H.</td>
<td>11, 87</td>
</tr>
<tr>
<td>Williams, L. B.</td>
<td>19, 156, 174</td>
</tr>
<tr>
<td>Wright, D. W.</td>
<td>8, 213</td>
</tr>
<tr>
<td>Wu, H.</td>
<td>4, 217</td>
</tr>
<tr>
<td>Wu, Q.</td>
<td>20, 59</td>
</tr>
<tr>
<td>Wu, W.</td>
<td>16, 250</td>
</tr>
<tr>
<td>Xiang, Y.</td>
<td>5, 196</td>
</tr>
<tr>
<td>Xiang, L.</td>
<td>7, 245</td>
</tr>
<tr>
<td>Xie, Z.</td>
<td>16, 250</td>
</tr>
<tr>
<td>Yah, W.-O.</td>
<td>3, 4, 15, 217</td>
</tr>
<tr>
<td>Yan, W.</td>
<td>20, 208</td>
</tr>
<tr>
<td>Yancey, T. E.</td>
<td>24, 44</td>
</tr>
<tr>
<td>Yang, H.</td>
<td>16, 237</td>
</tr>
<tr>
<td>Yang, J. H.</td>
<td>16, 129</td>
</tr>
<tr>
<td>Yang, J.-H.</td>
<td>13, 16, 238, 239, 240</td>
</tr>
<tr>
<td>Yang, K.</td>
<td>16, 18, 21, 132, 241, 246</td>
</tr>
<tr>
<td>Yao, H.</td>
<td>235</td>
</tr>
<tr>
<td>Ye, Y.</td>
<td>9, 16, 149, 247</td>
</tr>
<tr>
<td>Yeasmin, S.</td>
<td>20, 242</td>
</tr>
<tr>
<td>Yen, A. S.</td>
<td>18, 194, 227</td>
</tr>
<tr>
<td>Yoon, S.-j.</td>
<td>13, 23, 68, 244</td>
</tr>
<tr>
<td>Yu, J.</td>
<td>7, 245</td>
</tr>
<tr>
<td>Yuan, L.</td>
<td>24, 233</td>
</tr>
<tr>
<td>Zakusin, S. V.</td>
<td>12, 139</td>
</tr>
<tr>
<td>Zartman, R.</td>
<td>20, 121</td>
</tr>
<tr>
<td>Zaunbrecher, L. K.</td>
<td>11, 87</td>
</tr>
<tr>
<td>Zhang, A.-B.</td>
<td>9, 16, 149, 247</td>
</tr>
<tr>
<td>Zhang, L.</td>
<td>21, 246</td>
</tr>
<tr>
<td>Zhang, W.</td>
<td>13, 240</td>
</tr>
<tr>
<td>Zhang, X.</td>
<td>16, 212</td>
</tr>
<tr>
<td>Zhang, Y.</td>
<td>9, 147</td>
</tr>
<tr>
<td>Zhao, H.</td>
<td>11, 94</td>
</tr>
<tr>
<td>Zhou, H.</td>
<td>21, 246</td>
</tr>
<tr>
<td>Zhou, J.</td>
<td>5, 11, 20, 24, 94, 181, 233, 249</td>
</tr>
<tr>
<td>Zhou, Q.</td>
<td>21, 22, 256</td>
</tr>
<tr>
<td>Zhou, R.</td>
<td>16, 250</td>
</tr>
<tr>
<td>Zhou, Z.</td>
<td>24, 233</td>
</tr>
<tr>
<td>Zhu, J.</td>
<td>21, 22, 25, 26, 159, 254, 256</td>
</tr>
<tr>
<td>Zhu, R.</td>
<td>21, 22, 25, 26, 159, 254, 256</td>
</tr>
<tr>
<td>Zhu, X.</td>
<td>24, 252</td>
</tr>
<tr>
<td>Zhukhlistov, A. P.</td>
<td>12, 139</td>
</tr>
<tr>
<td>Zubkov, A. A.</td>
<td>12, 139</td>
</tr>
</tbody>
</table>
Sponsors of the 2014 annual meeting

The Clay Minerals Society
Texas A&M University
Texas A&M AgriLife
Department of Soil and Crop Sciences
College of Agriculture and Life Sciences

The 51st CMS Annual Meeting Organizing Committee and The Clay Minerals Society gratefully acknowledge the generous support of our corporate sponsors

Thiele Kaolin Company
Imerys