53RD ANNUAL MEETING OF THE CLAY MINERALS SOCIETY

RESURGENT CLAYS

June 5–8, 2016
Georgia Tech Hotel and Conference Center
Atlanta, Georgia

CONFERENCES.ILLINOIS.EDU/CMS2016/
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RESURGENT CLAYS

53RD ANNUAL MEETING OF THE CLAY MINERALS SOCIETY
Atlanta | June 5-8, 2016
Held at the Georgia Tech Hotel and Conference Center, Atlanta, Georgia

ORGANIZING COMMITTEE
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Scott Randall, Conference Program Coordinator
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Gretchen Wieshuber, Graphic Design

THE CLAY MINERALS SOCIETY ADMINISTRATION
Mary S. Gray
The Clay Minerals Society
3635 Concorde Parkway, Suite 500
Chantilly, VA 20151-1125 USA
Phone: 703-652-9960 | Fax: 703-652-9951 | Email: cms@clays.org

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Deb Jaisi
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Thru 2017
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Victoria Krupskaya
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Thru 2018
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Philip S. Neuhoff
Elizabeth Rampe
C. Dean Rokosh
Ruhaida Rusmin
Mitsuyuki Soma
Michael A. Velbel

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Richard K. Brown
Randall T. Cygan
Will P. Gates
Joseph Reed Glasmann
Stephen Guggenheim
R. James Kirkpatrick
Paul A. Schroeder
Joseph W. Stucki
Andrew R. Thomas
Michael A. Velbel
Lynda B. Williams

Past Presidents
Chair, Interdivisional Committee on Clay Minerals of the National Academy of Sciences—National Research Council

1952–1956 Richards A. Rowland
1967–1959 James W. Earley
1960–1962 Haydn H. Murray
1963 Marion L. Jackson
Presidents

1963–1964 Richards A. Rowland
1964–1965 James W. Earley
1965–1966 Haydn H. Murray
1966–1967 Marion L. Jackson
1967–1968 Charles E. Weaver
1968–1969 Paul G. Nahin
1969–1970 George W. Brindley, Katherine Mather
1971–1972 Sturges W. Bailey
1974–1975 John C. Hathaway
1975–1976 Stanley B. McCaleb
1977–1978 John B. Hayes
1978–1979 Max M. Mortland
1979–1980 Finis Turner
1983–1984 Wayne Hower
1984–1985 Wayne M. Bundy
1985–1986 Marion G. Reed
1986–1987 Sam H. Patterson
1987–1988 Necip Guven
1989–1990 Brij L. Sawhney
1990–1991 Thomas J. Pinnavaia
1993–1994 Dennis D. Eberl
1996–1997 Stephen Guggenheim
1998–1999 David L. Bish
1999–2000 Patricia M. Costanzo
2000–2001 Darrell G. Schultze
2001–2002 Blair F. Jones
2002–2003 Jessica Elzea Kogel
2003–2004 Kathryn L. Nagy
2004–2005 Duane M. Moore
2005–2006 Cliff T. Johnston
2006–2007 Richard K. Brown
2008–2009 Andrew R. Thomas
2009–2010 Derek C. Bain
2010–2011 Paul A. Schroeder
2011–2012 David A. Laird
2012–2013 Peter Komadel
2013–2014 Michael A. Velbel
2014–2015 W. Crawford Elliott
2015–2016 Prakash B. Malla

AWARDS

The 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, endowed by Linda and David Bailey, replaces The Clay Mineral Society’s Distinguished Member Award and is not restricted to members of CMS.

Previous Recipients

1970 Paul F. Kerr 1975 José J. Fripiat 1985 Charles E. Weaver
The George W. Brindley Lecture Award

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

Previous Recipients

1990 Joe L. White
1990 John Hower
1991 Joe B. Dixon
1992 Philip F. Low
1993 Thomas J. Pinnavaia
1995 William D. Johns
1996 Victor A. Drits
1997 Udo Schwertmann
1998 Brij L. Sawhney
1999 1990 Joe L. White
1990 John Hower
1991 Joe B. Dixon
1992 Philip F. Low
1993 Thomas J. Pinnavaia
1995 William D. Johns
1996 Victor A. Drits
1997 Udo Schwertmann
1998 Brij L. Sawhney
1999 1990 Joe L. White
1990 John Hower
1991 Joe B. Dixon
1992 Philip F. Low
1993 Thomas J. Pinnavaia
1995 William D. Johns
1996 Victor A. Drits
1997 Udo Schwertmann
1998 Brij L. Sawhney
1999 1990 Joe L. White
1990 John Hower
1991 Joe B. Dixon
1992 Philip F. Low
1993 Thomas J. Pinnavaia
1995 William D. Johns
1996 Victor A. Drits
1997 Udo Schwertmann
1998 Brij L. Sawhney
1999 1990 Joe L. White
1990 John Hower
1991 Joe B. Dixon
1992 Philip F. Low
1993 Thomas J. Pinnavaia
1995 William D. Johns
1996 Victor A. Drits
1997 Udo Schwertmann
1998 Brij L. Sawhney
1999

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

The 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 is to be within the ages of 39 and 60.

Previous Recipients

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
2003 Peter Komadel
2004 Fred J. Longstaffe
2005 Samuel J. Traina
2006 J. Theo Kloprogge
2007 Paul A. Schroeder
2008 Hailiang Dong
2009 Lynda B. Williams
2010 Toshihiro Kogure
2011 Douglas K. McCarty
2012 Jeffrey E. Post
2013 George E. Christidis
2014 Will P. Gates
2015 Balwant Singh
2016 Janice Bishop

The George W. Brindley Lecture Award

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

Previous Recipients

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 G. Kalinichev
2015 R. James Kirkpatrick
Pioneer in Clay Science Lecturer

Originally proposed by Joe White, the Pioneer in Clay Science Program is intended to recognize and honor clay scientists who have made pioneering contributions to our understanding of clay structures and properties. The program also would provide younger scientists the opportunity to know these early workers on a personal basis and to learn some of the inside stories on some of the concepts and developments that we have taken for granted. The program is now a regular component of the annual meeting. The local organizing committee, together with the program committee selects the Early Pioneer designate and arranges to have the designate participate in the technical program with a lecture.

Previous Lecturers

<table>
<thead>
<tr>
<th>Year</th>
<th>Lecturer</th>
<th>Year</th>
<th>Lecturer</th>
<th>Year</th>
<th>Lecturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1987</td>
<td>Marion L. Jackson</td>
<td>1996</td>
<td>Max M. Mortland</td>
<td>2005</td>
<td>Jillian Banfield</td>
</tr>
<tr>
<td>1988</td>
<td>R. M. Barrer</td>
<td>1997</td>
<td>Koji Wada</td>
<td>2006</td>
<td>Jean-Maurice Cases</td>
</tr>
<tr>
<td>1990</td>
<td>John W. Jordan</td>
<td>1999</td>
<td>V. Colin Farmer</td>
<td>2008</td>
<td>Emilio Galan</td>
</tr>
<tr>
<td>1992</td>
<td>Udo Schwertmann</td>
<td>2001</td>
<td>Don Scafe</td>
<td>2011</td>
<td>Glenn A. Waychunas</td>
</tr>
</tbody>
</table>

CITATION OF SPECIAL RECOGNITION

<table>
<thead>
<tr>
<th>Year</th>
<th>Lecturer</th>
<th>Year</th>
<th>Lecturer</th>
<th>Year</th>
<th>Lecturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1984</td>
<td>Richards A. Rowland</td>
<td>1996</td>
<td>Don Scafe</td>
<td>2015</td>
<td>Stephen J. Hillier</td>
</tr>
<tr>
<td>1991</td>
<td>Frederick A. Mumpton</td>
<td>2013</td>
<td>Haydn H. Murray</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

EDITORS OF CLAYS AND CLAY MINERALS

<table>
<thead>
<tr>
<th>Year</th>
<th>Editors</th>
<th>Year</th>
<th>Editors</th>
<th>Year</th>
<th>Editors</th>
</tr>
</thead>
<tbody>
<tr>
<td>1953</td>
<td>Ada Swineford and Norman Plummer</td>
<td>1979–1990</td>
<td>Frederick A. Mumpton</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The 53rd Annual Meeting of the Clay Minerals Society, held June 5–8, 2016, at the Georgia Tech Hotel and Conference Center in Atlanta, Georgia, USA

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 bi-monthly 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.


The Society contact information is: The Clay Minerals Society, 3635 Concorde Pkwy, Suite 500, Chantilly, VA 20151-1110, Phone: 703-652-9960, Fax: 703-652-9951 and E-mail: cms@clays.org.
<table>
<thead>
<tr>
<th></th>
<th>Friday, June 3</th>
<th>Saturday, June 4</th>
<th>Sunday, June 5</th>
<th>Monday, June 6</th>
</tr>
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<tbody>
<tr>
<td>7:30</td>
<td></td>
<td></td>
<td></td>
<td>Registration</td>
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<tr>
<td>8:00</td>
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<td></td>
<td>Registration</td>
<td>Salon 1–3 Foyer</td>
</tr>
<tr>
<td>8:15</td>
<td></td>
<td></td>
<td></td>
<td>8:05–9:20 AM</td>
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<tr>
<td>8:30</td>
<td></td>
<td></td>
<td>Workshop–Industrial and Engineering Applications of Clays</td>
<td>Welcome Ceremony &amp; Jackson Award Lecture (Presentation of Jackson Award)</td>
</tr>
<tr>
<td>9:00</td>
<td>8:30AM–5PM</td>
<td>9:00AM–5PM</td>
<td>10AM–11:40PM</td>
<td></td>
</tr>
<tr>
<td>9:20</td>
<td>Council Meeting</td>
<td>Conference 4</td>
<td>Health (3)</td>
<td></td>
</tr>
<tr>
<td>9:40</td>
<td>Conference 8</td>
<td>Conference 4</td>
<td>Engineer (3)</td>
<td></td>
</tr>
<tr>
<td>10:00</td>
<td></td>
<td>Continuous Coffee Breaks</td>
<td>Salon 3</td>
<td></td>
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<tr>
<td>10:20</td>
<td></td>
<td>Ballroom Break Area</td>
<td>9:40–10AM Break</td>
<td></td>
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<tr>
<td>10:40</td>
<td></td>
<td></td>
<td>12–1:40PM Lunch</td>
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<tr>
<td>11:00</td>
<td></td>
<td></td>
<td>Conference Dining Room</td>
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<tr>
<td>11:20</td>
<td></td>
<td></td>
<td>Private Dining 1</td>
<td></td>
</tr>
<tr>
<td>11:40</td>
<td>11:20–12:20PM</td>
<td>11:20–12:20PM</td>
<td>12:00–1:40PM</td>
<td></td>
</tr>
<tr>
<td>12:00</td>
<td>Field Trip</td>
<td>11:40–12:20PM</td>
<td>1:40–3PM</td>
<td></td>
</tr>
<tr>
<td>12:20</td>
<td>Georgia Kaolins</td>
<td>Mars (7)</td>
<td>Structure (4)</td>
<td></td>
</tr>
<tr>
<td>12:40</td>
<td>(Leave from GGTHCC Lobby at 7:30AM sharp, box lunch provided)</td>
<td>Salons 1–2</td>
<td>Salons 1–2</td>
<td></td>
</tr>
<tr>
<td>1:00</td>
<td></td>
<td>1:20–2:40PM</td>
<td>Murray (4)</td>
<td></td>
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<tr>
<td>1:20</td>
<td>Workshop</td>
<td>1:40–3PM</td>
<td>Murray (5)</td>
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<tr>
<td>1:40</td>
<td>Industrial</td>
<td>3:20–5PM</td>
<td>Salons 1–2</td>
<td></td>
</tr>
<tr>
<td>2:00</td>
<td>and Engineering Applications of Clays</td>
<td>3:20–5PM</td>
<td>7:00–9:00PM</td>
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</tr>
<tr>
<td>2:20</td>
<td>Conference 4</td>
<td>3:20–5PM</td>
<td>Executive Committee Meeting</td>
<td></td>
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<tr>
<td>2:40</td>
<td>Conference 8</td>
<td>3:20–5PM</td>
<td>Private Dinner 1</td>
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<tr>
<td>3:00</td>
<td>9:30AM–10:00PM</td>
<td>3:20–5PM</td>
<td>6–9PM</td>
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<td>3:20</td>
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<td>3:20–5PM</td>
<td>Executive</td>
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<td>3:40</td>
<td></td>
<td>3:20–5PM</td>
<td>Committee</td>
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<td>4:00</td>
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<td>3:20–5PM</td>
<td>Meeting</td>
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<td>4:20</td>
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<td>3:20–5PM</td>
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<td>4:40</td>
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<td>3:20–5PM</td>
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<td>5:00</td>
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<td>6:00</td>
<td>6–9PM</td>
<td>3:20–5PM</td>
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<td>6:30</td>
<td>Executive</td>
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<td>7:00</td>
<td>Committee</td>
<td>3:20–5PM</td>
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<td>Meeting</td>
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<tr>
<td>8:00</td>
<td>Private Dinner 1</td>
<td>3:20–5PM</td>
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<tr>
<td>10:00</td>
<td></td>
<td>3:20–5PM</td>
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**Monday, June 6**

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<thead>
<tr>
<th></th>
<th>7PM Editorial Meeting</th>
<th>Private Dinner 1</th>
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<tbody>
<tr>
<td>7PM</td>
<td>Editorial Meeting</td>
<td>Private Dinner 1</td>
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<tr>
<td>8:00</td>
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<tr>
<td>10:00</td>
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</tr>
<tr>
<td>Time</td>
<td>Event Description</td>
<td>Location</td>
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<tr>
<td>7:30</td>
<td>Registration</td>
<td>Salon 1–3 Foyer</td>
</tr>
<tr>
<td>8:00</td>
<td>Plenary Session &amp; Bailey Award Lecture (Presentation of Bailey Award)</td>
<td>Salons 1–3</td>
</tr>
<tr>
<td>8:15</td>
<td>Plenary Session &amp; Pioneer Award Lecture (Presentation of Pioneer Award)</td>
<td>Salons 1–3</td>
</tr>
<tr>
<td>8:30</td>
<td>Plenary Session &amp; Pioneer Award Lecture (Presentation of Pioneer Award)</td>
<td>Salons 1–3</td>
</tr>
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<td>8:40–9:20 AM</td>
<td>Plenary Session &amp; Bailey Award Lecture (Presentation of Bailey Award)</td>
<td>Salons 1–3</td>
</tr>
<tr>
<td>9:00</td>
<td>Plenary Session &amp; Pioneer Award Lecture (Presentation of Pioneer Award)</td>
<td>Salons 1–3</td>
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<tr>
<td>9:20</td>
<td>Continuous Coffee Breaks</td>
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<tr>
<td>9:40</td>
<td>9:40–10 AM Break</td>
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<tr>
<td>10:00</td>
<td>10AM–12PM Nano (6) Salons 1–2</td>
<td></td>
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<tr>
<td>10:15</td>
<td>10AM–12PM Critical Zone (6) Salon 3</td>
<td></td>
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<tr>
<td>10:30</td>
<td>10AM–12PM Gen(5) Salon 1–2</td>
<td></td>
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<tr>
<td>12:00</td>
<td>Past Presidents Lunch</td>
<td></td>
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<tr>
<td>12:20</td>
<td>12PM Closing Remarks</td>
<td>Salons 1–3</td>
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<tr>
<td>12:40</td>
<td>Lunch</td>
<td>Conference Dining Room</td>
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<td>1:00</td>
<td>Lunch</td>
<td>Private Dining 1</td>
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<tr>
<td>12:40</td>
<td>Lunch</td>
<td>Conference Dining Room</td>
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<td>Continuous Coffee Breaks</td>
<td>Ballroom Break Area</td>
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<tr>
<td>1:40–3PM</td>
<td>1:40–3PM Nano (1) Contaminant (3) Salons 1–2</td>
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<tr>
<td>1:50</td>
<td>1:40–3PM Gen (4) Salon 3</td>
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<td>2:00</td>
<td>3:20–4:20 PM Break</td>
<td>Ballroom Break Area</td>
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<td>3:20–4:20 PM Contaminant (4) Salons 1–2</td>
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<td>3:20–5PM Gen (5) Salon 3</td>
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<tr>
<td>4:40</td>
<td>5–6PM Business Meeting</td>
<td>Conference 4</td>
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<td>Business Meeting</td>
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<tr>
<td>6:30PM</td>
<td>Banquet &amp; Awards</td>
<td>Salons 1–3</td>
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<tr>
<td>7:00</td>
<td>Field Trip Stone Mountain (Leave from GTHCC Lobby at 12:30PM sharp)</td>
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<tr>
<td>7:30</td>
<td>Field Trip CCZO (Group leaving directly from Stone Mountain—overnight trip)</td>
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<tr>
<td>8:00</td>
<td>10AM–11:40AM Intercalation (6) Salon 3</td>
<td></td>
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<tr>
<td>8:15</td>
<td>10AM–11:40AM Shales (3) Isotopes (2) Conference 4</td>
<td></td>
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<tr>
<td>8:30</td>
<td>10AM–11:40AM Structure (1) Salons 1–2</td>
<td></td>
</tr>
<tr>
<td>9:00</td>
<td>10AM–12PM Poster Exhibits</td>
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KEY FOR SESSION ABBREVIATIONS

**Murray:** Origin of Kaolins, Beneficiation, and Uses of Kaolins and Other Industrial Clays
(A session in Honor of Prof. Haydn Murray)

**Engineer:** Engineering Applications of Clay Minerals

**Contaminant:** Contaminant Remediation by Clays

**Nano:** Nano-Clay Mineralogy Techniques, Simulations, and Modelling

**Enviro:** Modified Clays for Environmental Applications

**Critical Zone:** Critical Zone Clay Minerals

**Shales:** Impact of Clays on Pore Development and Hydraulic Fracturing of Tight Shales

**Health:** Clay Minerals and Health

**Intercalation:** Intercalation and Nanocomposites

**Mars:** Clay Minerals on Mars and Other Planetary Bodies

**Structure:** Structure and Properties of Clays

**Isotopes:** Isotopes (Geochronology and Stable Isotopes) and Clays

**Gen:** General Session

**GTHCC:** Georgia Tech Hotel and Conference Center
## PROGRAM

### FRIDAY, JUNE 3

6:00–9:00 pm  **Executive Committee Meeting | Private Dining 1**

### SATURDAY, JUNE 4

8:30 am–5:00 pm  **CMS Council Meeting | Conference 8**

7:30 am–6:00 pm  Field Trip | **Georgia Kaolins | Meet in Georgia Tech Hotel and Conference Center Lobby**

### SUNDAY, JUNE 5

8:00 am–5:00 pm  **Registration | Conference 4 Foyer**

9:00 am–4:30 pm  Workshop | **Industrial and Engineering Applications of Clays | Conference 4**

6:30–8:00 pm  **Welcome Reception | Salons 4–6**

### MONDAY, JUNE 6

7:30 am–5:00 pm  **Registration | Salon 1–3 Foyer**

### MORNING, MONDAY, JUNE 6

**SALONS 1–3**  **Welcome Ceremony & Jackson Award Lecture (Presentation of Jackson Award)**

8:05–8:10  Introductory Remarks | **W. Crawford Elliott | Meeting Co-Chair**

8:10–8:20  Presidential Welcome | **Prakesh Malla | Meeting Co-Chair**

8:20–8:35  Welcome | **Paul Goldbart | Dean, College of Sciences, Georgia Institute of Technology**

8:35–8:40  Introduction of the 2016 Marion L. & Chrystie M. Jackson Mid-Career Clay Scientist Award Recipient | **Michael A. Velbel, Michigan State University**

8:40–9:20  Clays on Mars: How We Identified Them and What They Tell Us About the Early Environment | **Janice Bishop, SETI**
**TECHNICAL SESSIONS**

**SALONS 1–2**  
**Clay Minerals on Mars and Other Planetary Bodies**  
Organizers: Janice Bishop, James Wray and Doug Ming

10:00–10:20  

10:20–10:40  
Michael A. Velbel*, Catherine M. Corrigan, Yulia S. Goreva, and Benjamin L. Brugman: THE “IDDINGSITE” OF MARS

10:40–11:00  
James J. Wray* and Janice L. Bishop: CARBONATES MIXED WITH CLAY MINERALS ON MARS: IDENTIFICATION AND IMPLICATIONS

11:00–11:20  
Leslie Baker*: FERRUGINOUS CLAYS IN COLUMBIA RIVER BASALTS

11:20–11:40  
Thomas F. Bristow*, Arkadiusz Derkowski, David F. Blake, and Patrick De Deckker: THE MINERALOGY OF WESTERN PLAINS DISTRICT LAKES, AUSTRALIA – LESSONS FOR MARS

11:40–12:00  

12:00–12:20  
Cindy L. Young*, James J. Wray, Kevin P. Hand, Michael J. Poston, Robert W. Carlson, Roger N. Clark, John R. Spencer, and Donald E. Jennings: MID-INFRARED SPECTROSCOPY TO IDENTIFY ICY MOON SURFACE COMPOSITIONS: EVIDENCE FOR PHYLLOSILICATES?

**SALON 3**  
**Clay Minerals and Health (3)**  
Organizers: Lynda B. Williams

**Engineering Applications of Clay Minerals (3)**  
Organizers: Javiera Cervini-Silva

10:00–10:20  
Javiera Cervini-Silva*, Antonio Nieto Camacho, Eduardo Palacios, Paz del Angel, Martin Pentrak, Linda Pentrakova, Stephan Kaufhold, Kristian Ufer, María Teresa Ramírez-Apan, Virginia Gómez-Vidas, Daniela Rodríguez Montaño, Ascención Montoya, Joseph W. Stucki, and Benny K.G. Then: ANTI-INFLAMMATORY, ANTIBACTERIAL, AND CYTOTOXIC ACTIVITY BY NATURAL MATRICES OF NANO-IRON (HYDR)OXIDE/HALLOYSITE

10:20–10:40  
Lynda B. Williams*, Sandra C. Londoño, and Keith D. Morrison: HOW TO IDENTIFY ANTIBACTERIAL CLAYS

10:40–11:00  

11:00–11:20  
Patrik Sellin*: USING THE SCIENTIFIC UNDERSTANDING OF BENTONITE TO DEVELOP TECHNICAL DESIGN REQUIREMENTS FOR A NUCLEAR WASTE BARRIER

11:20–11:40  
NOON, MONDAY, JUNE 6

12:00–1:40 pm  Lunch | Conference Dining Room
12:20–1:40 pm  Sustaining Members’ Lunch (by invitation) | Private Dining 1

AFTERNOON, MONDAY, JUNE 6

SALONS 1–2  Structure and Properties of Clays

Organizers: Michael Plötze, Daniel Svensson, and Arek Derkowski

1:40–2:00  Xiaoli Wang*, Reinhard Kleeberg, and Kristian Ufer: RIETVELD REFINEMENT OF SELECTED STRUCTURAL PARAMETERS OF DIOCTAHEDRAL SMECTITES
2:00–2:20  Liva Dzene*, Eric Ferrage, Fabien Hubert, Alfred Delville, and Emmanuel Tertre: EXPERIMENTAL EVIDENCE OF CONTRASTED REACTIVITY OF EXTERNAL VERSUS INTERLAYER ADSORPTION SITES ON SWELLING CLAY MINERALS: THE CASE OF Sr2+-FOR-Ca2+ EXCHANGE IN VERMICULITE
2:20–2:40  Daniel Svensson* and Staffan Hansen: SWELLING OF MONTMORILLONITE WITH DIVALENT INTERLAYER CATIONS IN LIQUID WATER – EFFECT BY CATION, LAYER CHARGE, AND TEMPERATURE
2:40–3:00  Michael Plötze*: INFLUENCE OF NEUTRON IRRADIATION ON PHYSICOCHEMICAL PROPERTIES OF CLAY MINERALS
3:00–3:20  Coffee Break
3:40–4:00  Stephen Aja*: CHLORITE THERMOCHEMISTRY: INSIGHTS FROM COMBINING CALORIMETRIC AND SOLUTION EQUILIBRATION DATA
4:00–4:20  Suraj Shiv Charan Pushparaj*, Claude Forano, Line B. Petersen, Vanessa Prevot, Andrew S. Lipton, Gregory Rees, John Hanna, and Ulla Gro Nielsen: SOLID STATE NMR STUDY OF CRYSTAL CHEMISTRY AND PATHWAYS OF FORMATION OF ZINC-ALUMINUM LAYERED DOUBLE HYDROXIDES
4:20–4:40  Martin Pentrak*, Linda Pentrakova, and Joseph W. Stucki: THE MÖSSBAUER SPECTROSCOPIC SIGNATURE OF TETRAHEDRAL IRON IN SMECTITES
4:40–5:00  Artur Kuligiewicz*, Arkadiusz Derkowski, Vassilis Gionis, and Georgios D. Chryssikos: LOWER LIMIT OF SMECTITE LAYER CHARGE AS SEEN BY THE O-D METHOD

SALON 3  Origin of Kaolins, Beneficiation, and Uses of Kaolins and Other Industrial Clays (A session in Honor of Prof. Haydn Murray)

Organizers: Andrew Thomas and Jessica E. Kogel

1:40–2:00  Tetsuichi Takagi*, Sadahisa Sudo, Mayumi Jige, Yoshiaki Kon, and Kazuya Morimoto: THE SETOTONO KAOLIN FIELD, THE LARGEST SEDIMENTARY KAOLIN CLAY DEPOSIT IN THE JAPAN ARC
2:00–2:20  Eduardo Domínguez*, Michelle Dondi, and Claudio Iglesias: GEOLOGY, GENESIS, MINERALOGY, INDUSTRIAL APPLICATIONS, AND RESOURCES OF PATAGONIAN KAOLINS

2:20–2:40  Jun Yuan*: CHARACTERISTICS AND ORIGIN OF A WHITE SMECTITIC KAOLIN FROM GEORGIA, USA

2:40–3:00  H. Albert Gilg*: PENCIL CLAYS: HAYDN H. MURRAY’S FIRST PATENT AND THE PENCIL CLAY DEPOSITS IN GERMANY

3:00–3:20  Coffee Break

3:20–3:40  Andrew R. Thomas*, Tom Dunn, Wade Williams, Alan Morrison, Hal Riordan, Rosario Scheerhorn, Julie Parra, and Bill Lawrence: GEOCHEMICAL EVALUATION PREVENTS PRODUCTIVITY LOSS IN THE GORGON FIELD, OFFSHORE WESTERN AUSTRALIA

3:40–4:00  Cliff T. Johnston*, Xueming Dong, Ravikiran Yerabolu, Bryan C. Clayton, and Hilkka L. Kenttämäa: MOLECULAR INTERACTIONS OF CRUDE OIL WITH KAOLINITE

4:00–4:20  Huitang Zhou*: BRIEF DISCUSSION OF THE PALY-MONT DEPOSIT IN MINGGUANG, ANHUI PROVINCE, P.R. CHINA

4:20–4:40  William J. Miles*: BENTONITE COMMODITY MARKETS AND FUTURE TRENDS

EVENING, MONDAY, JUNE 6

POSTER SESSION 1

4:00–5:00 pm  Poster Presentations Setup | Conference Break Area

5:00–6:00 pm  Authors Present at Poster Presentations | Conference Break Area

•  Origin of Kaolins, Beneficiation, and Uses of Kaolins and Other Industrial Clays
   (A session in Honor of Prof. Haydn Murray)

•  Clay Minerals on Mars and Other Planetary Bodies

6:00–6:30  Student Reception | Conference 4

7:00–  Editorial Board Meeting and Dinner | Private Dining 1

POSTERS

Origin of Kaolins, Beneficiation, and Uses of Kaolins and Other Industrial Clays (A session in Honor of Prof. Haydn Murray)

Clay Minerals on Mars and Other Planetary Bodies

1  Janice L. Bishop*, Peter Schiffman, Lukas Gruendler, Enver Murad, M. Darby Dyar, Melissa D. Lane, and Randal Southard: FORMATION OF OPAL, CLAYS, AND SULFATES FROM VOLCANIC ASH AT KILAUEA CALDERA AS AN ANALOG FOR SURFACE ALTERATION ON MARS

2  Christian Mavris*, Janice Bishop, Javier Cuadros, Jose Miguel Nieto, and Joe Michalski: DECODING MULTIPLE ACIDIC ALTERATION PATHWAYS THROUGH CLAY MINERALOGY: RIOTINTO AREA (SW SPAIN) AS EARTH ANALOG
TUESDAY, JUNE 7
7:30 am–5:00 pm  Registration | Salon 1–3 Foyer

MORNING, TUESDAY, JUNE 7

SALONS 1–3  Plenary Session & Bailey Award Lecture
(Presentation of Bailey Award)

8:40–8:50  Morning Announcements  |  W. Crawford Elliott, Prakash Malla

8:50–9:00  Introduction of the 2016 Marilyn and Sturges W. Bailey Distinguished Member Award Recipient  |  Joseph W. Stucki, University of Illinois

9:00–9:20  Lisa Heller  |  How a crystallographer revolutionized the study of surface chemistry of clays, presented by Uri Mingelgrin, Agricultural Research Organization, the Volcani Center, Israel

TECHNICAL SESSIONS

SALONS 1–2  Nano-Clay Mineralogy Techniques, Simulations, and Modelling
Organizer: Jeffery A. Greathouse

10:00–10:20  Katsuhiro Tsukimura*: ANALYSIS OF NANO-PARTICLES IN CLAYS WITH A SMALL-ANGLE X-RAY SCATTERING METHOD

10:20–10:40  Yongsheng Leng* and Qi Rao: MOLECULAR SIMULATIONS OF CARBON DIOXIDE AND WATER IN MONTMORILLONITE CLAY INTERLAYERS UNDER CO2 GEOLOGICAL SEQUESTRATION CONDITIONS

10:40–11:00  J. A. Greathouse*, R. T. Cygan, J. T. Fredrich, and G. R. Jerauld: COMPARISON OF ELECTRICAL CONDUCTIVITY IN MONTMORILLONITE INTERLAYERS AND CORRESPONDING BULK FLUIDS THROUGH MOLECULAR DYNAMICS SIMULATION


11:40–12:00  Thomas Underwood*, Valentina Erastova, and H. Chris Greenwell: MOLECULAR DYNAMICS SIMULATIONS OF LOW-SALINITY ENHANCED OIL RECOVERY

SALON 3  Critical Zone Clay Minerals
Organizers: Paul A. Schroeder, Jason C. Austin

10:00–10:20  P.C. Ryan*and Javier Huertas: ORIGIN OF HALLOYSITE AND KAOLINITE BY ALTERATION OF EARLY-STAGE PEDOGENIC SMECTITE AND KAOLINITE-SMECTITE: IMPLICATIONS FOR UNDERSTANDING AND PREDICTING TROPICAL SOIL MINERALOGY

10:20–10:40  Rona J. Donahoe* and Patrick D. Hawkins: CONTROLS BY CRITICAL ZONE CLAY MINERALS OF STREAM WATER SOLUTES IN A WATERSHED IMPACTED BY ACID MINE DRAINAGE
10:40–11:00  Paul A. Schroeder*, Jason C. Austin, and Daniel deB. Richter: DEEP REGOLITH BULK MINERALOGY OF THE CALHOUN CRITICAL ZONE OBSERVATORY USING X-RAY POWDER DIFFRACTION

11:00–11:20  Jason C. Austin*, Paul A. Schroeder, and Daniel deB. Richter: SEMI-QUANTITATIVE DEEP REGOLITH CLAY MINERALOGY OF THE CALHOUN CRITICAL ZONE OBSERVATORY USING NEWMOD 2

11:20–11:40  Rebecca Lybrand* and Craig Rasmussen: CLAY MINERAL ASSEMBLAGES IN DESERT AND CONIFER SOILS OF THE CATALINA CRITICAL ZONE OBSERVATORY


NOON, TUESDAY, JUNE 7

12:00–1:40 pm  Lunch | Conference Dining Room

12:00–1:40 pm  Past Presidents’ Lunch (by invitation) | Private Dining 1

AFTERNOON, TUESDAY, JUNE 7

SALONS 1–2  Nano-Clay Mineralogy Techniques, Simulations, and Modelling and Contaminant Remediation by Clays (1)

Contaminant Remediation by Clays (3)
Organizers: Ian C. Bourg, Linda Pentrakova, and Martin Pentrak

1:40–2:00  Ian C. Bourg*, Laura N. Lammers, Masahiko Okumura, Kedarnath Kolluri, Garrison Sposito, and Masahiko Machida: MOLECULAR DYNAMICS SIMULATIONS OF CESIUM ADSORPTION ON ILLITE

2:00–2:20  Eleanor Olegario-Sanchez* and Paul Clarence Francisco: THE POTENTIAL USE OF PHILIPPINE NATURAL ZEOLITE FOR THE TREATMENT OF ACID MINE DRAINAGE

2:20–2:40  Donald L. Sparks*: DRILLING INTO NEW DEPTHS OF CLAY SCIENCE

2:40–3:00  Uri Mingelgrin*, Ahmed Nasser, and Mohamed Samara: CLAYS AS AGENTS IN THE MECHANOCHEMICAL DEGRADATION OF RECALCITRANT POLLUTANTS

3:00–3:20  Coffee Break


3:40–4:00  Binoy Sarkar*, Ruhaida Rusmin, Bhabananda Biswas, and Erming Liu: CROSS-DISCIPLE FERTILIZATION OF CLAY SCIENCE AND NANOTECHNOLOGY FOR ENVIRONMENTAL REMEDIATION
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<td>4:00–4:20</td>
<td>Eduardo R. Magdaluyo, Jr.*, Kimberly Cabangon, and Eleanorea Olegario-Sanchez: SORPTION-REGENERATION CHARACTERISTICS OF SODIUM-MODIFIED MORDENITE ZEOLITE IN IRON (II)</td>
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**SALON 3**

**General Session**

Organizers: J. Marion Wampler, Warren D. Huff

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<td>Reinhard Kleeberg*: OUTCOMES OF THE 8TH REYNOLDS CUP IN QUANTITATIVE MINERAL PHASE ANALYSIS</td>
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<td>2:00–2:20</td>
<td>Janice L. Bishop*: CHARACTERIZATION OF CLAYS AND HYDRATED MATERIALS AT MAWRTH VALLIS, MARS FROM ORBIT USING VISIBLE/NEAR-INFRARED SPECTROSCOPY</td>
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<td>2:40–3:00</td>
<td>J. Środoń* and S. Liivamägi: EDIACARAN CLAYS OF THE EAST EUROPEAN CRATON – A UNIQUE RECORD OF THE PALEOENVIRONMENT</td>
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<td>Coffee Break</td>
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<td>3:20–3:40</td>
<td>Warren D. Huff*: TEACHING CLAY SCIENCE IN A PROJECT-ORIENTED FORMAT</td>
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<td>3:40–4:00</td>
<td>Selahattin Kadir*, Hülya Erkoyun, Muhsin Eren, Nergis Önalgil1, and Tacit Külah: NEOGENE LACUSTRINE SEDIMENTS AND ASSOCIATED AUTHIGENIC CLAYS WITHIN ESKİŞEHİR PROVINCE, WEST CENTRAL ANATOLIA, TURKEY</td>
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<td>4:20–4:40</td>
<td>J.M. Wampler*: CHARLES E. WEAVER, CLAY SCIENTIST AND FOUNDING DIRECTOR OF GEORGIA TECH’S SCHOOL OF EARTH AND ATMOSPHERIC SCIENCES</td>
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<td>4:40–5:00</td>
<td>Nergis Önalgil*, Selahattin Kadir, Muhsin Eren, Tacit Külah, and Hülya Erkoyun: PALYGORSKITE FORMATION WITHIN CALCRETES AND ITS IMPLICATION FOR PALEOClimATE: A CASE STUDY FROM ANATOLIA, TURKEY</td>
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**EVENING, TUESDAY, JUNE 7**

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<td>Banquet and Awards</td>
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MORNING, WEDNESDAY, JUNE 8

SALONS 1–3  Plenary Session & Pioneer Award Lecture (Presentation of Pioneer Award)
8:20–8:30  Introduction of the 2016 Pioneer in Clay Science Award Recipient | Yuanzhi Tang, Georgia Institute of Technology
8:30–9:10  Drilling into new depths of clay science | Donald G. Sparks, University of Delaware

TECHNICAL SESSIONS

SALONS 1–2  General Session (5)
Organizer: Reiner Dohrmann
10:00–10:20  Reiner Dohrmann*, Thorsten Schäfer, Reiner Dohrmann, Chris Greenwell, and Mark Jensen: CMS WORKSHOP AT EUROCLAY 2015 – SUMMARY - FROM MICROSCOPIC PORE STRUCTURES TO TRANSPORT PROPERTIES IN SHALES: WHICH GAPS ARE FILLED?
10:20–10:40  Michael C. Cheshire, Andrew G. Stac1, J. William Carey, Lawrence Anovitz, Timothy Prisk, and Jan Ilavsky: WELLBORE CEMENT POROSITY EVOLUTION IN RESPONSE TO MINERAL ALTERATION DURING CO2 FLOODING
10:40–11:00  Chun-Chun Hsu* and Youjun Deng: SELECTING AND MODIFYING CLAYS TO ENHANCE THEIR ADSORPTION CAPACITIES FOR ZEARALENONE
11:00-11:20  Georgios D. Chryssikos*, Vassilis Gionis, and Constantinos Tsiantos: STRUCTURE AND PROPERTIES OF SMECTITINES BY NEAR-INFRARED SPECTROSCOPY

SALON 3  Intercalation and Nanocomposites (6)
Organizers: Youjun Deng
10:00–10:20  Peng Liu*, Xiaoliang Liang, Hongping He, Tianhu Chen, Jianxi Zhu, and Runliang Zhu1: OXIDATION OF FORMALDEHYDE OVER SYNTHESIZED CATALYSTS OF COPPER, MANGANESE, AND CERIUM OXIDES ON PALYGORSKITE
10:40–11:00  Anna Koteja* and Jakub Matusik: PHOTOACTIVITY OF AZOBENZENE INTERCALATED IN ORGANO-SMECTITINES
11:20-11:40  Sabrina S. Alam* and Youjun Deng: EFFECTS OF SURFACE MODIFICATION OF SMECTITES BY ORGANIC CATIONS ON AFLATOXIN B1 ADSORPTION FROM CORN FERMENTATION SOLUTION

CONFERENCE 4  Structure and Properties of Clays (1)
Impact of Clays on Pore Development & Hydraulic Fracturing of Tight Shales (3)
Organizers: Georg Grathoff

Isotopes (Geochronology and Stable Isotopes) and Clays (2)
Organizers: Georg Grathoff

10:00–10:20  Georg H. Grathoff*, Markus Peltz, Frieder Enzmann, and Stephan Kaufhold: PERMEABILITY CALCULATIONS OF ORGANIC RICH POSIDONIA SHALE


10:40–11:00  Arkadiusz Derkowski*: A MECHANISM OF RADIOGENIC ARGON “DIFFUSION” IN ILLITE

11:00–11:20  J. M. Wampler* and W. Crawford Elliott: TESTING EDGE EFFECTS IN POTASSIUM-ARGON DATING OF ILLITE

POSTER SESSION 2

7:00–10:00 am  Poster Presentations Setup | Conference A & Salon 1–3 Foyer

10:00 am–12:00 pm  Authors Present at Poster Presentations | Conference A & Salon 1–3 Foyer

• Engineering Applications of Clay Minerals
• Contaminant Remediation by Clays
• Nano-Clay Mineralogy Techniques, Simulations, and Modelling
• Impact of Clays on Pore Development and Hydraulic Fracturing of Tight Shales
• Clay Minerals and Health
• Intercalation and Nanocomposites
• Structure and Properties of Clays
• Isotopes (Geochronology and Stable Isotopes) and Clays
• General Session

POSTERS

Engineering Applications of Clay Minerals

1  Eduardo R. Magdaluyo, Jr.* and Anna Victoria G. Lim: EFFECT OF COFFEE EXTRACT AS A REDUCING AGENT OF SILVER IN ION-EXCHANGED ZEOLITE

Contaminant Remediation by Clays

2  Francisco J. Osuna, Agustín Cota, Esperanza Pavón, M. Carolina Pazos, and María D. Alba: DESIGNED MICAS: EFFICIENT Cs+ ADSORBENTS UNDER SUBCRITICAL CONDITIONS
3 Runliang Zhu*, Tianyuan Xu, and Hongping He: BiVO4/FeOOH/Mt FOR VISIBLE-LIGHT-DRIVEN DEGRADATION OF ACID DYE

4 Yuji Arai* and Amanda H. Meena: EFFECTS OF COMMON GROUNDWATER IONS ON CHROMATE REMOVAL WITH MAGNETITE: THE IMPORTANCE OF CHROMATE ADSORPTION

5 Eleanor Olegario-Sanchez*, Lailyn Guerrero, Jenica Mendoza, and Kim Thomas Ong, Ill2: THE MODIFICATION AND TESTING OF COPPER MODIFIED-ZEOLITE AS A POTENTIAL ALTERNATIVE TO NOBLE METAL CATALYSTS IN CATALYTIC CONVERTERS

6 Jianxi Zhu*, Lingya Ma, Xiaoli Su, Runliang Zhu, Hongping He, and Jingming Wei: SIMULTANEOUS ADSORPTION OF PHENOL, PHOSPHATE, AND CADMIUM ON INORGANIC-ORGANIC MONTMORILLONITE

7 M.F. Albornoz*, C. Pizarro, E. Pavón, and M. Escudey: EFFICIENCY OF VOLCANIC ASH-DERIVED SOILS TO ADSORB ARSENATE FROM AQUEOUS SOLUTIONS

8 Eduardo R. Magdaluyo, Jr.*, Alvin Carl E. Carreon, Jalen Rooney O. Javier, Ruth Aquino, and Persia Ada de Yro: ADSORPTION KINETICS OF METHYLENE BLUE IN SODIUM-MONTMORILLONITE

Nano-Clay Mineralogy Techniques, Simulations, and Modelling

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NOON, WEDNESDAY, JUNE 8

12:00– Closing Remarks | Salons 1–3

12:30– Field Trip | Stone Mountain | Meet in Georgia Tech Hotel and Conference Center Lobby
54th ANNUAL

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MAY 29 – JUNE 1, 2017
Workshops & Field Trips (May 29 – 30)
Conference Program (May 31 – June 1)

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ABSTRACTS

CHLORITE THERMOCHEMISTRY: INSIGHTS FROM COMBINING CALORIMETRIC AND SOLUTION EQUILIBRATION DATA

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Combining recent calorimetric and solution equilibration data (Aja et al., 2015; Aja and Dyar, 2002) for a magnesian chamosite [Fe-Chl(W)] and a ferroan clinochlore [Mg-Chl], the apparent Gibbs free energies of formation ($\Delta_g^o G°_T, i$), at saturated-vapor pressures, were retrieved thus:

$$\Delta_g^o G°_T,i = \Delta_f G°_{298,1}^o - S°_{298,1}^o (T - T_r) + \int_{T_r}^T C°_p dT - T \int_{T_r}^T \frac{C°_p}{T} dT + V°_{1,298} (P - 1) \quad \text{(Eqn. 1)}$$

Equilibrium constants for the kaolinite ⇌ Fe-Chl(W) and for the kaolinite ⇌ Mg-Chl reactions (Fig. 1) are then log $K = -1.051 + \frac{25008}{T}$ ($r^2 = 1.00$) and log $K = -57.432 + \frac{22634}{T}$ ($r^2 = 1.00$), respectively; $\Delta_f G°_{298,1}^o$ (Eqn. 1) was determined from these solution data. Solid solutions of Al-rich Fe-Mg chlorites [AlIV > 1/O10(OH)8] have been modeled in terms of the endmembers amesite, chamosite, and clinochlore (Aja, 2015); the Tschermak substitution being indexed by $X_{amesite}$. Calculated $S_{ex}^o$ have lower magnitudes than $S_{conf}$ owing to atomic site occupancies, and at 25°C, $G_{ex}^o$ vary from about −150 to 400 kJ/mol implying a significant deviation from ideality. The effect of octahedral vacancies, and hence di-trioctahedral substitutions, was evaluated by modeling the solid solutions in the amesite-chamosite-clinochlore-sudoite system; excess functions ($S_{ex}^o, G_{ex}^o$) calculated for these quaternary and ternary systems are marginally different, inherently validating the ternary model.

Table 1: Apparent free energies of formation (J/mol)

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References:
ABSTRACTS

EFFECTS OF SURFACE MODIFICATION OF SMECTITES BY ORGANIC CATIONS ON AFLATOxin B1 ADSORPTION FROM CORN FERMENTATION SOLUTION

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Aflatoxin-contaminated corn can be used to produce biofuel, but the mycotoxin needs to be removed from the distiller's grain to reduce its toxicity to animals and humans. Aflatoxin B1 (AfB1) adsorption by smectite from corn fermentation solution (FS) is difficult because of the strong competition by proteins and amino acids present in such complex solution for the adsorption sites on the clay minerals. The objective of this study was to modify smectites with small organic cations like choline chloride (CC), carnitine (Car), lysine (Lys), biotin (Bio), and tryptophan (Trp) to minimize the protein fixation in the interlayer of smectite, thus possibly and indirectly to facilitate AfB1 adsorption.

Smectites before and after the modification, and after interacting with AfB1 in aqueous solution and FS were analyzed by X-ray diffractometry (XRD) and Fourier transform infrared (FTIR) spectrometry. Smectites were examined by XRD after heating at 300°C in a furnace. For the FTIR, smectites were air dried on ZnS discs and mounted in a dewar accessory, and spectra were recorded in the transmission mode at room humidity.

Figure 1 shows that for a Mississippi smectite, 3MS, (a) the d value of the complex 3MS-AfB1-water remained the same or changed unremarkably when the smectite was treated with the five organic cations; (b) the d value of the 3MS-FS decreased when smectite was modified with CC, Car, Lys, Bio, and Trp before exposure to FS, suggesting that these compounds at least partially limited the access of large proteins or amino acids from that solution into the interlayer of smectite; (c) the d value was also reduced when modified 3MS was exposed to both AfB1 and FS, suggesting that those organic cations were still capable of limiting the access of the proteins or amino acids into the smectite. FTIR spectra of organo-smectites (data not shown) revealed AfB1 bands, suggesting modification preserved at least part of the capacity of the smectite to adsorb AfB1 from either aqueous solution or FS. Yet protein bands at 1744, 1653, 1532, 1451, and 1235 cm⁻¹ still existed in the modified smectite complexes, suggesting that a complete elimination of the protein adsorption has not been achieved.

In conclusion, this work demonstrated a positive effect of organic cation modification on reducing protein fixation by smectites, which might indirectly reduce their interference on AfB1 adsorption as there will be less competition of protein for the clay's adsorption sites. The overall study suggested that choline and carnitine showed the best capacity to reduce protein’s fixation into the smectite.
EFFICIENCY OF VOLCANIC ASH- DERIVED SOILS TO ADSORB ARSENATE FROM AQUEOUS SOLUTIONS

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The presence of arsenate in environmental aqueous matrices is affecting the health conditions of the world population (Smith et al., 1998). In this work, the arsenate adsorption capacity of volcanic ash-derived soils was studied. The maximum arsenate adsorption capacity of the soils Santa Bárbara (SB, Andisol) and Collipulli (CL, Ultisol) was determined and compared with that of ferrihydrite, a synthetic amorphous iron oxide (Fe₅HO₈*4H₂O). Both soils are characterized by their high clay fraction content (25% and 70% for SB and CL, respectively). The adsorption evaluation was carried out through kinetic studies and adsorption isotherms. Faster adsorption and a higher adsorption capacity were determined for both soils when compared with ferrihydrite. The complexity of the natural systems involving a significant presence of a clay fraction coated with iron oxides results in better behavior as arsenate adsorbents than synthetic ferrihydrite, an iron oxide recognized as one of the best arsenate adsorbents.

Acknowledgments: Work supported by CEDENNA FB-0807 (Chile). Dr(c) Albornoz also thanks Dirección de Postgrado de la Vicerrectoría Académica de la Universidad de Santiago. Dr. Pavón also thanks her grant project, approved by the Andalucía Talent Hub Program launched by the Andalusian Knowledge Agency, co-funded by the European Union’s Seventh Framework Program, Marie Skłodowska-Curie actions (COFUND – Grant Agreement nº 291780) and the Ministry of Economy, Innovation, Science and Employment of the Junta de Andalucía.
EFFECTS OF COMMON GROUNDWATER IONS ON CHROMATE REMOVAL WITH MAGNETITE: THE IMPORTANCE OF CHROMATE ADSORPTION

Amanda H. Meena¹ and Yuji Arai*²

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Reductive precipitation of hexavalent chromium, Cr(VI), with magnetite is a well-known Cr(VI) remediation method to improve water quality. The rapid (< a few hours) reduction of soluble Cr(VI) to insoluble Cr(III) species by Fe(II) in magnetite has been the primary focus of Cr(VI) removal processes in the past. However, the contribution of simultaneous Cr(VI) adsorption processes in aged magnetite has been largely ignored, leaving uncertainties in evaluating the application of in-situ Cr remediation technology for aqueous systems. In this study, effects of common groundwater ions (nitrate and sulfate) on Cr(VI) sorption in magnetite were investigated using batch geochemical experiments in conjunction with X-ray absorption spectroscopy. In both nitrate and sulfate electrolytes, batch sorption experiments showed that Cr(VI) sorption decreases with increasing pH from 4 to 8. In this pH range, Cr(VI) sorption decreased with increasing concentration of sulfate from 0.01 to 0.1M whereas varying nitrate concentration did not alter the Cr(VI) sorption behavior. This indicates a background-electrolyte-specific Cr(VI) sorption process in magnetite. Under the same ionic strength, Cr(VI) removal in sulfate solution was greater than in nitrate solution. This is attributed to the oxidation of Fe(II) in magnetite by nitrate being more thermodynamically favorable than that by sulfate, leaving less reduction capacity of magnetite to reduce Cr(VI) in the nitrate media. This indicates the majority of Cr(VI) removal in the nitrate media is contributed by the Cr(VI) adsorption process. X-ray absorption spectroscopy analysis supports the macroscopic evidence that more than 75% of total Cr on the magnetite surfaces was adsorbed Cr(VI) species after 48 hours.
SEMI-QUANTITATIVE DEEP REGOLITH CLAY MINERALOGY OF THE CALHOUN CRITICAL ZONE OBSERVATORY USING NEWMOD 2

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Semi-quantitative analyses of the clay mineralogy of a 70 m deep core taken at the Calhoun Critical Zone Observatory (CCZO) (Bacon et al., 2012) show an upward transition from chlorite, smectite, I-S mixed-layer, and weathered mica to kaolin group, K-I mixed-layer, and weathered mica between 18 and 27 meters. Near the surface (<10 m), there is a further transition to kaolin group, I-V mixed layer, K-S mixed-layer, K-I mixed layer, HIV, and weathered mica.

The clay fraction of each sample was separated using standard settling techniques, and X-ray diffraction (XRD) patterns were obtained under Ca, Mg, and K saturation, in both the air-dried and ethylene glycol saturated states. Additionally, the K saturated samples were heated to 110, 330, and 550 °C. Mineralogy was quantified by modeling XRD patterns of the clay fraction (<2 µm) using NEWMOD2. Individual sample model results, verified by modeling each saturation and solvation condition and comparing the results, generally agreed within 10%.

Understanding the clay mineral transformation sequence through 70 meters allows for more complete modeling of weathering in the critical zone throughout the weathering front. Additionally, the sequence of minerals as they occur throughout the weathering zone provides insight into the mineralogical transitions that occur as primary minerals are weathered into clays. Combining this clay mineralogical information with the bulk mineralogy, bulk chemistry, geophysical data, and cosmogenic nuclide concentrations gives a better understanding of the complex open system that is the critical zone (Bacon et al., 2012; St. Clair et al., 2015).


FERRUGINOUS CLAYS IN COLUMBIA RIVER BASALTS

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Clay minerals found in and near the surface of Mars contain unique information about the geochemical environment in the martian near-surface in the ancient past. In order to interpret this information, it is necessary to fully understand the environments in which different clay minerals form. Studies of terrestrial analog materials and environments are a useful way to address such questions, and some terrestrial materials are also important standards for remote sensing as well as chemical and mineralogical analyses. The formation of Fe-Mg smectites in particular is not fully understood on Earth but is important for interpretation of clays observed on Mars.

Nontronites and other ferruginous clay minerals are known to occur in the Columbia River Basalts, and several clay mineral standards were collected from this source area. Analyses have been published of samples including the well-known standards Garfield nontronite and SWa-1 ferruginous smectite, the less commonly used nontronites from Manito and Cheney, and several poorly documented samples from the Spokane area. These samples range in composition from a nearly pure Fe endmember to ferruginous smectites with Al:Fe ratios ranging up to 1:2.

Ferruginous clays of the Columbia River Basalts occur in two types of setting. One type fills cracks, vesicles, or void spaces in the rock. Nontronites of this type have Fe-rich composition with Al:Fe ratio of 1:10 or lower. These nontronites formed by weathering of the basalt at low water-rock ratios, dissolution of ferromagnesian minerals such as olivine, and precipitation of waxy, green nontronite. This type of occurrence is found in saprolites underlying paleosols developed on the basalt, as well as filling cracks and void spaces in the uppermost flows. The nontronite standard from Garfield, Washington (API 33a) is a well-documented example of this type.

The second type of nontronite occurrence is found at contacts where interbedded sediments or paleosols have been capped by younger basalt flows. These clays appear to have formed through hydrothermal reaction between the interbedded clays and the basalts immediately after basalt emplacement, whereby the uppermost sediments were enriched in Fe, Mg, and Mn. Nontronite samples from such contacts may have more aluminous compositions than void- or crack-filling nontronites. The SWa-1 ferruginous smectite is an example of this type of occurrence. However, further study of a range of clay-sediment contacts is necessary to determine the reactions involved, the range of possible mineral assemblages formed, and the role of sediment moisture content. This type of occurrence has important implications for interpreting the stratigraphic relationships observed on Mars between aluminous clays and ferromagnesian clay minerals.
CHARACTERIZATION OF CLAYS AND HYDRATED MATERIALS AT MAWRTH VALLIS, MARS FROM ORBIT USING VISIBLE/NEAR-INFRARED SPECTROSCOPY

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The Mawrth Vallis region on Mars exhibits a common stratigraphy with several different layered, hydrated units across a broad area that spans thousands of kilometers. The mineralogy of these units has been characterized [1,2] using numerous ~10 km wide images collected by the Compact Reconnaissance Imaging Spectrometer for Mars on the Mars Reconnaissance Orbiter.

Recent work has focused on discriminating among the different types of clay minerals and aqueous materials in the strata [3]. This has enabled identification of five distinct units that document changes over time in the geochemical environment. The older clay units are more consistent with a neutral to slightly basic environment, while the doublet/sulfate-bearing unit is attributed to acidic conditions. The change from Fe$^{3+}$-clay to Fe$^{2+}$-clay is consistent with chemical energy in the system that could have also been supportive of life, if present on early Mars. Montmorillonite in the Al-phyllosilicate unit likely formed in a high water/rock ratio environment, while the nanophase aluminosilicate-bearing unit required a well-drained system without ponding water.

The observations point to an ancient wet and warm geologic period on Mars when the thick nontronite unit formed, then a period of wet–dry cycling to create acid alteration, followed by leaching or pedogenesis to result in Al-phyllosilicates, and finally a drier, colder climate that left the altered ash in the form of nanophase aluminosilicates, rather than crystalline clays.

FORMATION OF OPAL, CLAYS, AND SULFATES FROM VOLCANIC ASH AT KILAUEA CALDERA AS AN ANALOG FOR SURFACE ALTERATION ON MARS

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Hydrothermal and/or acidic alteration of basaltic ash on Mars may be an important surface weathering process and may have produced the sulfates and hydrated silica observed in many aqueous outcrops. This study considers solfataric alteration as a potential formation mechanism for opal, sulfate, and clays on Mars. Alteration via fumaroles in the Kilauea caldera, Hawaii, has created a light-toned solfataric bank on the south wall of the caldera where Keanakakoi ash was deposited. Bands of orange and light-toned material are present where iron oxides, jarosite, and gypsum are observed in a silica/clay matrix. Friable patches of white and yellow material have also formed from solfataric alteration of the ash. We have analyzed the chemistry and mineralogy of several chunks and particulate samples from this site using visible and near-IR (VNIR), mid-IR, and Mössbauer spectroscopies as well as XRD, SEM, and BSE imaging.

Mineralogical analyses show the presence of opal, saponite, gypsum, jarosite, and ferric oxides/hydroxides in the ash as well as remnants of the original basaltic components and volcanic glass. The alternating bands of light-toned gypsum-bearing material and orange-colored bands of Fe-bearing material mark changes in the alteration environment. SEM reveals Fe sulfate, Mg smectite, and palagonitic rinds surrounding sideromelane and pyroxene crystals.

Mössbauer spectra indicate the presence of ferric oxide-bearing species in addition to jarosite. The VNIR spectra show changes in the Fe bands for the light and orange bands in the outcrop. The VNIR spectra also include features consistent with hydrated silica, gypsum, jarosite, and saponite. XRD shows that opal-A is prevalent over opal-CT. Mid-IR reflectance and emissivity spectra are consistent with sulfate and silica. Bulk chemical analyses and BSE imaging indicate basaltic components in addition to the opal, sulfates, and saponite. Using multiple laboratory techniques to characterize the alteration products of hydrothermal and solfataric alteration at Kilauea, we hope to enable improved interpretation of orbital and in situ data from Mars.

![Figure 1. Solfatarically altered Keanakakoi ash deposit at Kilauea, Hawaii showing banded orange and white ash units and friable white and yellow material.](image-url)
Clays are products of alteration of primary minerals. On Mars, they indicate sustained aqueous activity in previous geological times. The use of satellite and in-situ measurements of the Martian surface in combination has allowed detection of mineral assemblages indicating processes for which Earth analogues exist. Among them, aluminous clay-sulphate assemblages have been observed, which suggest alteration by acidic fluids [1].

The Riotinto mining district (Andalucia, SW Spain) provides the setting for an ideal Earth analogue for such extreme Martian processes [2]. The parent rocks belong to an upper Palaeozoic (late Famennian–Tournaisian) volcanic-sedimentary complex including siliciclastic sediments and mafic and felsic volcanics. All of them underwent hydrothermal alteration, which enriched them with quartz and illite. Oxidation of an extensive pyrite-rich orebody, caused by fluctuation of the water table, contributed mild to extreme acidic fluxes that leached the surrounding rocks for over 20 million years [3]. The resulting mineral assemblages are strongly dependent on their acidic alteration intensity.

The paragenetic assemblages clearly reflect three different leaching patterns and alteration sequences, which can be summarized as follows:

- Mild: from chlorite to vermiculite, mixed-layered phases, and kaolinite;
- Strong i): from kaolinite and mixed-layered phases to jarosite-group phases;
- Strong ii): from kaolinite to alunite, jarosite-group phases, and iron oxides.

Our findings suggest that, even within this general scheme, the specific alteration pathways can vary. The presentation will focus on the latest mineralogical and chemical discoveries that lead to validation of the observed alteration sequences.

Radioactive cesium isotopes ($^{134}$Cs, $^{137}$Cs) released during the Fukushima nuclear disaster of March 11, 2011 remain the main source of external radiation dose, five years after the nuclear disaster, in a region covering 3% to 8% of the land area of Japan. Cesium has a well-known affinity for clay minerals and is likely to be primarily adsorbed on 2:1 clay minerals (illite, vermiculite) in surface soils near the disaster site. Experimental data indicate that illite, in particular, carries a small density of surface sites with a very strong affinity for cesium. These sites are widely thought to be located on the “frayed edges” of nanoparticles, but they are difficult to characterize at molecular scales. Here we discuss the methodological challenges associated with atomistic simulations of illite edge surfaces and present both large-scale molecular dynamics and thermodynamic integration calculations of cesium adsorption by illite nanoparticles contacting liquid water. New insights into the identities of different illite surface sites and their respective affinities for cesium are provided by our results.
SEALING SHALES VERSUS BRITTLE SHALES: A THRESHOLD IN THE PROPERTIES AND USES OF FINE-GRAINED SEDIMENTARY ROCKS

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Fine-grained sedimentary rocks (shale, mudstone) play important roles in global CO$_2$ abatement efforts through their importance in carbon capture and storage (CCS), radioactive waste storage, and shale gas extraction. These different technologies rely on seemingly conflicting premises regarding the sealing properties of shale and mudstone, suggesting that fine-grained rocks that lend themselves to hydrocarbon extraction may not be optimal seals for CCS or radioactive waste storage, and vice versa. In this paper, a compilation of experimental data on the properties of well-characterized shale and mudstone formations is used to demonstrate that clay mineral mass fraction, $X_{\text{clay}}$, is a master variable that controls key material properties of these formations and that a remarkably sharp threshold at $X_{\text{clay}} \sim 1/3$ separates fine-grained rocks with very different properties. This threshold coincides with the predictions of a simple conceptual model of the microstructure of sedimentary rocks and is reflected in the applications of shale and mudstone formations for CCS, radioactive waste storage, and shale gas extraction.
ABSTRACTS

THE MINERALOGY OF WESTERN PLAINS DISTRICT LAKES, AUSTRALIA – LESSONS FOR MARS

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The Mars Science Laboratory rover, Curiosity, recently documented a ~3.5 Ga section of fluvio-lacustrine sedimentary rocks on the floor of Gale Crater, informally known as the Yellowknife Bay formation. Terrestrial analogues for such sediments and more generally documentation of early diagenetic processes influencing lake sediments in basaltic catchments are scarce, despite their potential importance as indicators of aqueous conditions on ancient Mars. With this in mind, we sampled and analyzed sediment cores from nine lakes and their catchments from the Western Plains District of Victoria, SE Australia. The Western Plains are a ~ 50 km × 100 km area of poorly integrated internal drainage located ~150 km west of Melbourne.

The Plains are largely underlain by olivine tholeiite basalts, similar in composition to average martian basalts. Lakes occupy craters and depressions in the Plains and chemistries vary considerably. The contemporary pH of lakes sampled varies from 7.7 to 9.8 and salinities range from 5 to 200 per mil. With the exception of plagioclase feldspars and, more rarely, magnetite, no basaltic minerals were detected in lake sediments. Comparisons of sediments from the various lakes and various depths in sediment cores indicate increasing degrees of saponite (Mg-rich trioctahedral smectite) authigenesis correlating with increased salinity and pH. In addition, chemical trends combined with deconvolution of their XRD 06l region reveal possible formation of an Fe-rich illite-type clay mineral. Authigenic clay minerals formed in conjunction with dolomite and magnesite and are detected in samples within centimeters of the sediment-water interface, indicating rapid precipitation under suitable geochemical conditions. In highly alkaline crater lakes, low density gels are found centimeters below sandy black crusts. The gels contain ~30 wt.% X-ray amorphous material in addition to authigenic clay minerals and carbonates.

The Sheepbed mudstone member of the Yellowknife Bay formation in Gale Crater also contains ~20 wt.% saponite and ~30 wt.% X-ray amorphous material. However, no carbonates have been detected in the mudstones and detrital Fe-forsterite and pyroxenes derived from basalts of the crater rim are present. The mineralogy and bulk geochemistry of the Sheepbed mudstone indicate minimal chemical weathering of materials in the catchment, and saponite, which is Fe-rich, is thought to have formed via in situ aqueous alteration of olivine. Thus comparisons between the lake sediments from the Western Plains and ancient Gale Crater reveal significant differences in weathering regimes, which could be linked to climate, atmospheric composition, and absence of biotic processes on ancient Mars.
ANTI-INFLAMMATORY, ANTIBACTERIAL, AND CYTOTOXIC ACTIVITY BY NATURAL MATRICES OF NANO-IRON (HYDR)OXIDE/HALLOYSITE

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In this presentation we report the effects of natural Fe-halloysite matrices on infiltration and migration of neutrophils (polymorphonuclear (PMN) leukocytes), which, after the skin, constitute the primary protection of organisms against pathogens. Speciation of mineral Fe was quantified before and after treatment with citrate-bicarbonate-dithionite (CBD). Infiltration and migration of inflammatory and immune effector cells, and cell viability, were quantified using the 12-O-tetradecanoylphorbol-13-acetate (TPA) and myeloperoxidase (MPO) enzymatic activity methods and the Griess assay. Halloysite was collected ~2 km from Opotiki, Bay of Plenty, New Zealand. HRSEM images confirmed typical morphological features of spheroidal Hal (S-Hal). Mössbauer spectroscopy of S-Hal confirmed the presence of octahedrally coordinated Fe in the form of substituted Fe(III) in magnetically ordered goethite or ferrihydrite. HRTEM images showed the presence of small domains of Fe (~3 nm), predominantly in the form of ferrihydrite. EPR analyses of S-Hal (0–5,000 ppm) before and after reaction with desferroxamine-B confirmed the fast release of Fe from the nanodomains of ferrihydrite. Early inhibition of edema by S-Hal doubled that by CBD-treated Hal (t-S-Hal), explained because labile Fe (2-L-ferrihydrite) enhanced the 4-h anti-inflammatory response. On the other hand, prolonged inhibition of edema by S-Hal and t-S-Hal were comparable, consistent with the release of Fe from the Hal structure. The presence of S-Hal or t-S-Hal related to the inhibition of MPO content. After 4 h, the inhibition of MPO content by S-Hal or t-S-Hal was comparable to that by commercial indomethacin (~80%). S-Hal and t-S-Hal produced high inhibition of MPO contents shortly after exposure, but the effect decreased sharply afterwards. On the other hand, tubular halloysite caused inhibition of MPO that increased with time, explained because the clay structure restricted the kinetics and mechanism of MPO inhibition. Evidence showed that the release of mineral Fe related to infiltration and migration of inflammatory and immune effector cells, expanding the knowledge that metal ions affect inflammatory responses. Finally, dose-response experiments confirmed that the inhibition of edema and cell viability were surface-mediated. Natural clay reservoirs are complex in composition, therefore identifying the molecular mechanism(s) regulating cell migration and infiltration becomes necessary prior to recommending their use for healing purposes.

Clay minerals, sepiolite and palygorskite, collected from Torrejón El Rubio and Vallecas, Spain, respectively, altered the expression of four pro-inflammatory cytokines, namely, interleukins IL-1 and IL-6, tumor necrosis factor (TNF-α), and interferon gamma (IFN-γ), as determined using a 12-O-tetradecanoylphorbol-13-acetate model for inflammation [1]. Quantitative RT-PCR analyses after 4 and 24 h inflammatory stimuli showed that sepiolite or palygorskite brought about a reduction in mRNA expression. Sepiolite provoked the highest mRNA expression inhibition for all cytokines, except for TNF-α, and primarily after 4 h. Conversely, the anti-inflammatory effect for cytokine TNF-α was found to be true in the presence of palygorskite. Most notably, the significant reduction in mRNA expression of IL-1 registered just shortly after exposure indicated that the anti-inflammatory effect may be important for modulation of the late inflammatory response. These clay minerals brought about modifications in the mRNA expression of IL-1 and its receptor in endothelial cells and downstreaming inflammatory cascades resulting in the recruitment of neutrophils. In addition, polymorphonuclear peroxidase activity was severely reduced just after short exposure to either sepiolite or palygorskite. Evidence provided herein agrees well with the idea that these clay minerals impaired neutrophils infiltration to inflamed skin, notwithstanding ear edema and deficient cell localization to skin coupled with such impairment may affect the later stages of inflammation.

THE ROLE OF SEPIOLITE AND PALYGORSKITE IN THE MIGRATION OF LEUKOCYTE CELLS TO AN INFLAMMATION SITE.

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Sepiolite and palygorskite have shown beneficial health effects but understanding human cell–clay interactions has yet to become unveiled. In this presentation we report on the effects of sepiolite (Vallecas, Spain) and palygorskite (Torrejón El Rubio, Spain) on the infiltration of human blood leukocytes to an inflammation site [1]. Human blood leukocyte cells were quantified under pro- and anti-inflammatory conditions by visualizing cells in an Axioscope (Carl Zeiss; Oberkochen, Germany). Images were recorded with an Axiocam Mrm monochromatic camera and ZEN Pro software (Carl Zeiss). The distribution of human blood leukocyte cells at the inflammation site varied before and after adding the clay. The relative proportion of polymorphonuclear leukocytes (PMN) to monocytes (MN) (PMN/MN) exposed to the inflammatory activity by 12-O-tetradecanoylphorbol-13-acetate (TPA) changed in the presence of sepiolite (TPA + sepiolite) or palygorskite (TPA + palygorskite) either after 4 or 24 h, namely, 0.60, 2.5, and 2.33; and 4.33, 1.53, and 2.8, respectively. PMN/MN values were comparable in the presence of TPA or TPA and palygorskite, but they decreased sharply in the presence of TPA and sepiolite. It is proposed that decreases in PMN/MN values caused by adding sepiolite may alter PMN and MN immunological functions, by lessening the destruction extent of invasive bacteria via phagocytosis and the conversion of MN to macrophages. It is further proposed that limiting conversion of MN to macrophages impedes resolving inflammation because of incomplete digestion of aged cells. Evidently, shifting from pro- to anti-inflammatory conditions by addition of clay altered the mechanism of infiltration of different leukocyte cells to an inflammation site. Finally, the presence of few macrophages at the inflammation site was attributed to resolution of inflammation, whereby macrophages participated in anti-inflammatory mechanisms leading to the return to homeostasis in tissues.

Bentonites, naturally occurring clays, are produced industrially because of their adsorbent capacity but little is known about their effects on human health. This manuscript reports on the effect of bentonites on cell growth behavior [1]. Bentonites collected from India (Bent-India), Hungary (Bent-Hungary), Argentina (Bent-Argentina), and Indonesia (Bent-Indonesia) were studied. All four bentonites were screened in-vitro against two human cancer cell lines [U251 (central nervous system, glioblastoma) and SKLU-1 (lung adenocarcinoma)] supplied by the National Cancer Institute (USA). Bentonites induced growth inhibition of U251 cells and growth increment of SKLU-1 cells, showing that interactions between bentonite and cell surfaces were highly specific. Our results showing inhibition of the proliferation response for U251 cells were consistent with the idea that smectites controlled the levels of metabolic growth components [e.g., epidermal growth factor receptor (EGFR)], thereby inhibiting the development of high-grade gliomas, particularly primary glioblastomas. Arguably, our results showing the proliferation response for SKLU-1 was mediated by smectite surface–cell interactions. The exacerbated growth may be due to overexpression of activin A, although more tests need to be conducted to test this hypothesis. Inhibition of proliferation response by both bentonites (expandable) and non-expandable (fibrous) clays was interpreted to mean that structural features common to both clay groups (e.g., siloxane basal planes) might bind biomolecules pivotal to cell proliferation (e.g., EGFR). Unlike fibrous clays, bentonite clays favored increments in the proliferation response for SKLU-1. Structural characteristics of bentonites, such as swelling, are thought to favor cell proliferation owing to an accumulation of solutes and to their hydration and transformation. Bentonite clay reservoirs are complex in composition, therefore, identifying the molecular mechanism(s) regulating cell migration and infiltration becomes necessary prior to recommending their use for healing purposes.

ANTIPHLOGISTIC EFFECT OF ZEOLITE AS DETERMINED BY A MURINE INFLAMMATION MODEL


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Natural zeolites are microporous crystalline aluminosilicates with channels and cavities of molecular dimensions of interest for biomedical applications. The antiphlogistic effect was investigated on the basis of a murine inflammation model using 12-O-tetradecanoylphorbol-13-acetate (TPA) as inflammatory agent and the quantification of the activity of myeloperoxidase (MPO), an enzyme that serves as an indicator for neutrophil migration. The zeolite used in this study was collected from San Andrés, Cuba, and it provided evidence to show the quantitative adsorption of histamine, a biogenic compound strongly involved in inflammation processes. Furthermore, a related work showed that this zeolite sample is free of hazardous materials and apt for health use. The zeolite of this study contained 65% clinoptilolite, 30% mordenite, and 5% smectite. The application of this zeolite reduced the edema formation induced by TPA within 24 hours by $57 \pm 18\%$, while the migration of neutrophils was not altered. The anti-inflammatory activity of zeolite was explained in part as due to its quantitative adsorption of histamine, whilst natural cell repair mechanisms appeared not to be influenced. The outcome of this work expanded on reports concluding that antiphlogistic properties of zeolite, proven in vivo with mice for inflammatory diseases, are also important for both oral application (gastrointestinal tract) and topical treatment (skin).

ABSTRACTS

TEMPLATED SYNTHESIS OF NITROGEN AND SULFUR CO-DOPED GRAPHENE-LIKE CARBON MATERIALS USING SPENT MONTMORILLONITE

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With 2-dimensional nano-sized structure and high cation exchange capacity, montmorillonite (Mt) as a low-cost and highly efficient adsorbent for cationic dyes has a promising application in dye wastewater treatment. However, proper disposal of the spent Mt is still a big challenge hindering the application of Mt. Owing to the high interaction affinity between organic dyes and Mt, desorption of cationic dyes from the spent Mt can be really difficult. Traditional methods such as incineration and direct landfill disposal may cause serious environmental problems and be a huge waste of resources. On the other hand, the templated synthesis of carbon materials from inorganic-organic precursors is drawing increasing interest. In this strategy, the adsorbed organic compounds as carbon sources can be transformed into carbon materials with various microstructures (by pyrolysis under an inert atmosphere). Mt has been used as an ideal template to synthesize graphene-like carbon materials because of the expandable interlayer structure and chemically inert siloxane surface. Given that the absorbed cationic dyes usually contain heteroatoms (e.g., N and S), one may propose that the spent Mt as precursor may be employed for synthesizing heteroatom-doped graphene-like materials.

In this work, N and S co-doped graphene-like carbon materials were successfully synthesized through a facile method using the spent Mt after the adsorption of methyl blue (MB). The spent Mt was pyrolyzed under the protection of N2 to carbonize the adsorbed MB within the interlayer space of Mt. The resulting pyrolyzed carbon–Mt composite showed a basal spacing value of ~0.44 nm, close to the thickness of a single graphene layer. After demineralization, the carbon material was released from the interlayer space of Mt. Atomic force microscopy and transmission electron microscopy results directly revealed the stacking of thin carbon sheets.

Raman spectra revealed the presence of both the D-band and G-band on the obtained carbon materials, and their intensity ratio slightly decreased with increasing pyrolysis temperature. X-ray photoelectron spectroscopy disclosed the simultaneous presence of C, S, and N atoms on the carbon materials. N atoms were doped into the graphene network with three kinds of binding configurations (pyridinic, pyrrolic, and graphitic N), while S atoms were in a major form of thiophene-S. Finally, the obtained materials exhibited efficient electrocatalytic activity as a metal-free electrocatalyst for the oxygen reduction reaction. Our work provided a facile method that can simultaneously recycle the spent Mt and synthesize heteroatom-doped graphene-like materials.
WELLBORE CEMENT POROSITY EVOLUTION IN RESPONSE TO MINERAL ALTERATION DURING CO₂ FLOODING

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Porous media are the principal hosts for subsurface fluids and, therefore, are the main source for reactions associated with CO₂-sequestration. How these media affect the reactions and kinetics is poorly understood, especially when considering potential pore-size dependences of geochemical reactions. Mineral reactions during CO₂ sequestration may change the porosity distribution, a process often not considered when predicting permeability evolution.

To address possible pore-scale-dependent modifications under CO₂-saturated conditions, we have examined a wellbore cement sample from an enhanced oil recovery operation in which CO₂ was injected into a subsurface formation, specifically the SACROC unit in West Texas. Here, porosity and pore-size alterations in a wellbore cement exposed to CO₂ for decades have been measured using high spatial resolution small-angle X-ray scattering.

An observed reaction front consisted of a narrow zone (~1 mm) of low porosity (0.179 - 0.203) at the leading edge, a high porosity zone (0.387 – 0.471) behind it (~2 mm), and following areas of porosity (0.27(5)) like that of the parent cement (0.29(4)). Empirical expressions predict five orders of magnitude permeability variation across this front. Moreover, smaller nanopores remain un-occluded in the low porosity zone, whereas dilation in the high porosity zone occurs across all pore sizes and allows subsequent reaction in smaller nanopores. Carbonation reactions altered the parent cement to have a smoother solid-pore interface and a more-open pore network. These results suggest that the pore-size dependence of geochemical reactions partly controls how porosity and permeability evolve in the subsurface.
RARE-EARTH ELEMENT GEOCHEMISTRY OF GEORGIA’S SEDIMENTARY KAOLINS

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This study is of the nature of the original sediments, their depositional environment(s), and diagenetic reactions that have occurred within them to produce kaolin deposits located in Georgia, USA. The rare-earth element (REE) chemistry was examined to provide further information on the provenance of and diagenetic influences on the kaolins.

The light REEs are associated with phosphate (i.e., florencite) and have experienced variable degrees of fractionation and mobilization within the sediment during diagenesis. Older kaolins (of the Buffalo Creek Fm.) display a greater degree of light REE mobility whereas younger kaolins (of the Jeffersonville Mbr.) show very little REE fractionation. In all samples, the heavy REEs are associated with detrital zircons and do not display evidence of diagenetic mobility. Variations in light REE mobility appear to be due to variations in physical properties of the kaolins and the presence of acidic groundwater produced by organic acids.

During burial and early diagenesis of organic matter, a majority of the indigenous organic matter would have been aerobically decomposed into a variety of organic constituents, but none more important that the low molecular weight organic acids. The presence of organic acids during diagenesis potentially had significant influence on the transport of rare-earth elements and ferric iron. Unfortunately, there is no direct evidence for the interaction of organic acids with the various metals based on data from this study. However, the mobility of rare-earths, ferric iron, and aluminum in aerobic conditions generally requires a complexing agent to increase the solubility of these comparatively insoluble elements. The transport of metals coordinated with organic acids is also extremely sensitive to the redox conditions of the pores in the kaolins. Organic acids complexed with metals can be oxidized under reducing conditions by anaerobic bacteria, thereby releasing the various metals in the environment for further reactions with the surface of the kaolinite or for crystallization of authigenic minerals, e.g., iron sulfides, florencite, and new kaolinite.
STRUCTURE AND PROPERTIES OF SMECTITES BY NEAR-INFRARED SPECTROSCOPY

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Near-infrared spectroscopy is an attractive vibrational technique for studying clays and clay minerals, primarily because it offers good separation between the H$_2$O and structural OH modes in the ($\nu+\delta$) combination range, and also because no sample preparation is needed (e.g. Madejová and Komadel, 2001). A number of sampling accessories such as optical fibers, integrating spheres, and external illumination heads enable the fast collection of good quality Fourier-transform spectra in the diffuse reflectance mode, without the need to bring the sample in the spectrometer.

The purpose of this presentation is two-fold. First, we highlight near-infrared sampling techniques that are relevant to the industrial monitoring of processes involving clays and provide examples of PLS chemometric algorithms that can be applied in situ and in real time for clay identification and property prediction purposes. Second, we take advantage of large spectral sets available on dioctahedral smectite (montmorillonite and beidellite) specimens to identify phenomenological trends regarding the position and width of the ubiquitous H$_2$O and structural Al$_2$OH combination modes in the spectra at approximately 5250 cm$^{-1}$ and 4525 cm$^{-1}$, respectively. Interestingly, these trends can now be discussed in terms of layer charge and the nature of interlayer cations. This discussion is made possible by the recent mid-infrared study of H$_2$O in dioctahedral smectites (Kuligiewicz et al., 2015a) that led to a new, infrared spectroscopic tool for measuring layer charge by monitoring the exact position of a sharp D$_2$O (H$_2$O) stretching mode at ~2690 (3630) cm$^{-1}$ (Kuligiewicz et al., 2015b).


A MINERALOGICAL ANALYSIS OF THE NORTHERN AWASH RIVER VALLEY IN ETHIOPIA: SAMPLES FROM HSPDP HADAR FORMATION

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The Northern Awash Valley is in the southwestern portion of the Afar Depression in Ethiopia. During the 2014 field season, 600 meters of drill core were collected as part of the international Hominin Sites and Paleolakes Drilling Project (hspdp.asu.edu). The cored rocks are mudstones. The purpose of this project is to construct a high resolution mineralogical record for integration with biological and other records of environmental and climate change in the Afar region during the Pliocene. This will further our understanding of the relationship between environmental change and hominin evolution, in this important archaeological and paleontological locality and beyond.

Drilling targeted the Hadar Formation, known to be Pliocene (~3.8–2.9 Ma). Samples were collected at ~16 centimeter intervals throughout each of two cores, NAW 14-1A and NAO14-1B (from ~ 3 kilometers apart). Bulk minerology was obtained by X-ray diffraction analyses of randomly oriented powders. Samples were analyzed for 15 minutes from 10 to 65 degrees 2θ. The NAO and NAW cores have similar mineral assemblages. An abundance of quartz and quartz polymorphs was found. Na-plagioclase feldspars are present in NAW, along with minimal K-feldspar. Pyroxenes are abundant as well, Mg-calcite is common, and some samples contain pyrite. The main distinctions between the two sites are that NAW doesn’t have much zeolite, whereas NAO has a moderate amount, predominately phillipsite. Furthermore, both gypsum and pyrite are present in NAW but NAO has abundant gypsum but almost no pyrite. Whereas the pyrite must have formed under reducing conditions, it is likely that the gypsum represents subsequent oxidation. Therefore, these two core sites may have undergone different post-depositional histories, with greater oxidation occurring at NAO. Future work will provide a higher resolution mineralogical and geochemical record for the core and help us to understand climate change and evolution in East Africa during the Pliocene.
CHARACTERIZATION OF CHITOSAN-MONTMORILLONITE NANOCOMPOSITE AND ITS ADSORPTION OF HEAVY METALS

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Chitosan is a linear polysaccharide derived from the 2nd most abundant natural biopolymer—chitin, which occurs in shells of shrimp, other crustacean animals, and fungal cell walls. Owing to chitosan's abundant availability and broad applications in medicine, polymer and nanocomposite materials, agriculture, industry, and environmental remediation, the synthesis and applications of chitosan-montmorillonite nanocomposites have received great interest in several disciplines in the last decade. Yet, the properties of chitosan-montmorillonite have not been well characterized and many controversies and confusions exist in its applications. One possible synergistic effect of chitosan and montmorillonite is the combination of the cation exchange capacity of the clay mineral and the chelating power of functional OH and NH\textsubscript{2} groups in chitosan, this combination may enhance the adsorption of heavy metals by the composite for environmental applications. The objectives of this study were to investigate the adsorption and bonding mechanism of chitosan on montmorillonite and the adsorption of heavy metals by the composite. Two chitosans, one of low molar mass and one of medium molar mass, were dissolved in 1 M HCl and then the pH of the chitosan solutions was adjusted to desired values; these solutions were used in the adsorption experiments and the synthesis of chitosan-montmorillonite composites. The isotherms for adsorption of the chitosans on the montmorillonite and the pH dependency of chitosan adsorption were measured. Variable temperature X-ray diffractometry and Fourier transform infrared spectroscopy were used to characterize the chitosan-montmorillonite composites. Increasing pH in the range of 3 to 5.5 enhanced the adsorption of both chitosans on the montmorillonite. When the equilibrium concentration of chitosans approached 300 mg/L at pH 5.5, the amount of adsorbed chitosan reached the highest level of about 0.2 mg/mg. The increasing chitosan adsorption with increasing pH was attributed to decreasing protonation of the amino groups on chitosan, which reduced the positive charge on the polymer. A washing experiment indicated that chitosan adsorption on montmorillonite was virtually irreversible. The variable temperature X-ray diffractometry of the chitosan-montmorillonite composites revealed an about 1.3 nm \textit{d}(001) value after 300 °C heating, confirming the interlayer adsorption of the polymer in montmorillonite. The infrared spectra of adsorbed chitosan were very similar to that of acidified chitosan film, and were not affected by cation exchange treatment with Na, K, Al, Cu, Mn, or Hg. These infrared spectroscopic responses suggested the major bonding between the chitosan and montmorillonite was due to the cation exchange reaction. This bonding mechanism implied the clay mineral may lose its capacity for heavy metal removal by cation exchange. The adsorption isotherms of Cu on montmorillonite and the composite suggested that the composite had lower affinity but higher capacity for Cu than montmorillonite. It could not be concluded which type of bonding, chelating by the chitosan or cation exchange by montmorillonite, dominated the adsorption of Cu by the composite.
AUTHIGENIC CLAY MINERALS IN LACUSTRINE SEDIMENTS: GEOCHEMICAL INDICATORS OF PALEOHYDROLOGY AND PALEOLIMNOLOGY

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Some lake basins have the aquatic geochemical conditions required for the precipitation and accumulation of substantial amounts of authigenic clay minerals. Such aquatic environments include alkaline lakes, such as those in the Pacific Northwest and the East African Rift, and wetland complexes such as the Pantanal in Brazil. Examples of where paleolimnology has been inferred from ancient sediments are Quaternary basins in East Africa, the Miocene Barstow Formation, the Eocene Green River Formation, and others. Authigenic clay minerals tend to accumulate where surface or pore waters are alkaline, aqueous silica activity is high, at least some dissolved Mg is available, and detrital input is relatively low. In such settings, detrital dioctahedral clays (Al- or Fe-rich) are commonly altered to form Mg-rich smectite; in the absence of detrital input, either sepiolite or kerolite is favored. Authigenic clays from around the world suggest that illitization and octahedral alterations are decoupled, and therefore indicative of different processes. Understanding clay mineral reactions in such settings therefore requires not only conventional basal layer X-ray diffraction analyses, but also analyses of hkl reflections and geochemistry of purified phases. In general, authigenic clay minerals are more common in underfilled lake basins, usually associated with evaporitic basins with siliceous input from weathering of volcaniclastics or from hydrothermal discharge.

Figure 1. A. Classification of lake basins (Carroll and Bohacs, 1999, Geology), with approximate ranges of authigenic clay octahedral occupancies (OCI=(Mg/(Al+Fe))) based on basin salinity (assuming high alkalinity and abundant sources of aqueous silica). B. Ternary plot of octahedral cation compositions, M=montmorillonite (SWy-1), K=kaolinite; N=nantronite (Nau-1); P=palygorskite (PFI-1); Se=sepiolite (SepSp-1); St=stevensite (Martin de Vidales et al., 1991); Sa=saponite. Figure from Deocampo (2015).
A MECHANISM OF RADIOGENIC ARGON “DIFFUSION” IN ILLITE

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Radiogenic argon removal from micas through heating is the basis of K-Ar and $^{40}$Ar/$^{39}$Ar geochronology methods. The mechanism, rate, kinetics, and temperature of Ar diffusion has been a subject of discussion for five decades, linked to Ar retention and “closure temperature” for thermochronological studies [1,2]. Very fine illite with sub-μm particle size offers a way to test the Ar removal, avoiding the two- and three-dimensional diffusion issues and effects of local crystal deformations and stacking faults [2].

For a pilot study two pure illites were tested. They were very similar in crystallinity, 3D periodicity (1M), stacking order (R3), and chemical composition, differing only by their octahedral vacancy position (cis-vacant and trans-vacant), which results in different temperatures of maximum dehydroxylation (Fig. 1A; [3]). Ex-situ preheating of the illites under thermogravimetric (TG) experimental conditions resulted in $^{40}$Ar* reduction at a degree corresponding to the fraction of removed OH groups (Fig. 1B). The result is believed to prove that thermally-induced $^{40}$Ar* removal from the mica interlayer is caused by a pressure of H$_2$O formed within a 2:1 layer during dehydroxylation [1,3].


Figure 1. First derivative TG (DTG) curves of the cis-vacant (cv) and trans-vacant (tv) illites studied and their normalized mass loss data overlapped with the normalized $^{40}$Ar* contents (B).
CLAY MINERALS BIONANOCOMPOSITES: PREPARATION, CHARACTERIZATION, AND TESTS FOR DRUG RELEASE APPLICATIONS

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There is interest in the use of biopolymers for the preparation of nanocomposites, owing to their biodegradability and derivation from renewable resources. SWy-2, a well-characterized montmorillonite reference clay mineral, was used with the biopolymers guar gum and scleroglucan for the preparation of bionanocomposites. In addition, other sets of nanocomposites were prepared with clay minerals from deposits in Portugal. The two sets of nanocomposites were determined to be highly comparable in terms of interlayer structure and morphology, as determined by X-ray diffraction and transmission electron microscopy.

Ibuprofen, a model drug chosen for this study, was loaded onto both sets of guar gum bionanocomposites: the reference clay-based and the Portuguese clay-based. Sustained release was successfully achieved in simulated intestinal fluid with both sets of guar gum nanocomposites.
CMS WORKSHOP AT EUROCLAY 2015 – SUMMARY - FROM MICROSCOPIC PORE STRUCTURES TO TRANSPORT PROPERTIES IN SHALES: WHICH GAPS ARE FILLED?

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This presentation provides an overview of a CMS workshop held in conjunction with the EUROCLAY 2015 conference in Edinburgh, Scotland, UK, July 5\(^{th}\), 2015 on advances in the microscopic characterization of clay-rich sediments. The aim of the workshop was to provide a comprehensive overview of the current state of the art in spectroscopic and microscopic techniques as they are used to improve understanding of clay pore structure, in part as it relates to mass transport at larger time and space scales. The workshop, among other contributions, delivered eighteen peer reviewed papers, which will be published open access as Volume 21 of the CMS workshop lectures.

The workshop was initiated by the NEA Clay Club, the Clay Minerals Society, and the Euroclay conference series. It focused on current and emerging developments in the field to explore successes and remaining challenges in the application of such knowledge to the evaluation of up-scaled geomechanical and fluid transport properties and behaviour within these characteristically low permeability sediments. This is the second workshop on this topic; the first, entitled “Clays under Nano- to Microscopic resolution,” took place in Karlsruhe, Germany, September 6-8, 2011 (NEA-CLAYCLUB, 2013). The EUROCLAY 2015 workshop also provided an excellent opportunity for exchange of knowledge with multidisciplinary research communities concerned with the safe long-term management of radioactive waste within argillaceous sediments and with shale gas and oil exploration.

GEOLOGY, GENESIS, MINERALOGY, INDUSTRIAL APPLICATIONS, AND RESOURCES OF PATAGONIAN KAOLINS

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The presence of kaolin in Patagonia has been known since 1886 and its utilization started around 1939. By 1983 the country had a consolidated paper industry and in that year Dr. H. H. Murray was invited to Argentina to advise on the paper-kaolin mineral potential for fulfilling the country’s needs. This work is a review of the research conducted by Dr. Murray and the work done following his teachings. The research started with the kaolin deposits located along the lower Chubut River Valley (Chubut, Argentina) and continued in the most important natural white kaolinite deposit in Santa Cruz, Argentina. Residual kaolin deposits occur over an extended Jurassic rhyolite province: Bahía Laura Group in Santa Cruz and Marifil Formation in Chubut. Sedimentary ball clays derived from the erosion of kaolinized volcanic parent rocks occur in the Baquero Cretaceous Formation in Santa Cruz or the Danian-Paleocene Salamanca Formation in Chubut. In order to establish the kaolin’s origin, a considerable number of isotope determinations were performed after the pioneering work of Murray and Jansen (1984). The isotopic evidence indicates that the residual kaolin was formed by weathering in a humid-warm climate in the Jurassic–Cretaceous time interval. In residual deposits, the clay-sized fraction is composed of kaolinite, 7Å halloysite, illite, and quartz with minor amounts of mixed-layered illite-smectite clays or smectites. Kaolinite predominates in the upper and whiter part of the altered layer, and amounts of illite and smectite increase with depth. Kaolinite shows an open texture, with stacks that grew after feldspar. While the ball clays related to the erosion of Bajo Grande are kaolinitic–smectitic, those coming from the Bahia Laura Group are kaolinitic.

During paper-kaolin beneficiation, it was evident that the quartz phenocrysts are easily removed by screening, but fine quartz from the groundmass remains in all size fractions. Using the clay fraction and a careful selection of the raw mineral, a filler of high brightness and moderately low abrasion could be produced. For the coating grade, the low recovery and a marginal abrasion preclude an economic factory installation.

For ceramic applications, the Patagonian clays naturally have qualities that allow almost the entire range of applications. The ball clay properties are analogous to those of clays used in European porcelain stoneware production (Westerwald, Germany) or to the highly plastic Ukrainian ball clays. The current annual kaolin demand in the country is about 300,000 tons used for flat ceramics, sanitary ware, and glazes. Remaining resources were estimated at 12 MT.

The Patagonian region was the southernmost part of a continent where Gondwana paleosurfaces of Late Mesozoic age developed on Jurassic rhyolite volcanic units. This paleosurface is today exposed over tens of thousands of square kilometers in the cratonic units of northern and southern Patagonia and has a strong potential for discovery of new kaolin deposits.
ABSTRACTS

CONTROLS BY CRITICAL ZONE CLAY MINERALS OF STREAM WATER SOLUTES IN A WATERSHED IMPACTED BY ACID MINE DRAINAGE

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Lake Harris, a 220-acre reservoir in Tuscaloosa County, Alabama, was constructed in 1929 through damming of Yellow Creek to create a secondary source of drinking water for the city of Tuscaloosa. After construction of Lake Tuscaloosa in 1970, Lake Harris became the tertiary drinking water supply and is primarily used as a source of water for local industry.

Between 1969 and 1976, strip mining was employed to recover coal resources in the Lake Harris watershed. The strip mine, located just a few hundred meters from Lake Harris, was abandoned in 1976 without reclamation. Subsequently, the exposed spoil was subject to weathering and erosion prior to a 1982 project funded by the Rural Abandoned Mines Program which reclaimed about 80 acres at the Lake Harris site. By that time, the lake was threatened by sedimentation which had created a two acre delta at the mouth of Lake Harris Stream, a first-order stream originating in the mined area. Thirty four years after reclamation, Lake Harris Stream still shows negative impacts of acid mine drainage (AMD). This study examines clay minerals formed by critical zone processes and their role in controlling stream water solute concentrations and mobility.

Soil and stream sediment samples were collected and characterized by XRD and XRF analyses. The dominant clay in the soil is kaolinite or smectite, with smaller amounts of illite. Relative to the parent Pottsville Sandstone bedrock, the soil shows depletion of soluble elements (Ca, Na, Mn, Mg, Fe, K, Zn, Ni, and Sr). Stream sediment samples contain ferric hydroxide and show elevated concentrations of V and Cr. Stream water pH typically falls below 4 during base flow discharge, with values as low as 3.3 having been measured in 2005. The acidic conditions result in mobilization of metals and sterilization of aquatic life. Stream water samples exhibit elevated conductivity and levels of sulfate, Mn, Al, and Fe that exceed secondary drinking water standards. Relative to lake water, the stream water also has elevated levels of Zn, Ni, Co, Cr, and Cu, but concentrations do not exceed drinking water MCL values. Water samples collected from the lake and stream mouth are supersaturated with respect to smectites, kaolinite, illite, and iron oxyhydroxide phases. A model for stream water solute sources and sediment sinks indicates that clay mineral dissolution, precipitation, and ion exchange reactions are the fundamental controls for stream water solute concentrations in the AMD-impacted watershed.
ABSTRACTS

EXPERIMENTAL EVIDENCE OF CONTRASTED REACTIVITY OF EXTERNAL VERSUS INTERLAYER ADSORPTION SITES ON SWELLING CLAY MINERALS: THE CASE OF \( \text{Sr}^{2+} \)-FOR-\( \text{Ca}^{2+} \) EXCHANGE IN VERMICULITE

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In superficial environments, calcium is one of the main cations compensating the layer charge of clay minerals in soils. In the case of polluted soils, related to accidents in nuclear power plants, calcium (\( \text{Ca}^{2+} \)) can be exchanged by strontium cations (\( \text{Sr}^{2+} \)) present in surrounding waters. Clay minerals display a wide range of particle size in soil environments (from ~50 nm to ~5 μm). In the case of swelling clay minerals (smectite and vermiculite), the difference in size and geometry of clay particles induces a contrasted ratio between external adsorption sites (edge+basal) and total (edges+basal+interlayer) adsorption sites. The chemical modelling of \( \text{Ca}^{2+} \) and \( \text{Sr}^{2+} \) behavior in natural environments deserves a full assessment and understanding of potentially contrasted chemical reactivity of these different types of adsorption sites.

In our experiments, we used three vermiculite particle size fractions (10–20, 1–2 and 0.1–0.2 μm), which had different proportions between external and interlayer sites (Reinholdt et al., 2013). \( \text{Sr}^{2+} \)-FOR-\( \text{Ca}^{2+} \) isotherms were obtained on these different size fractions to derive information on adsorption processes related to the total adsorption sites. Information on the specific reactivity of interlayer adsorption sites was obtained by modelling of 00ℓ reflections from experimental X-ray diffraction patterns.

Experimental results show that global \( \text{Sr}^{2+} \) selectivity in respect to \( \text{Ca}^{2+} \) decreases with decreasing particle size. Based on information derived from both chemical and crystal structure data, selectivity for \( \text{Sr}^{2+} \) and \( \text{Ca}^{2+} \) at interlayer sites was found to be similar and independent of particle size. This result is consistent with additional results from grand-canonical Monte Carlo simulations showing very similar \( \text{Sr}^{2+} \) and \( \text{Ca}^{2+} \) distribution in the interlayer space and thus suggesting similar interaction between the siloxane surface and both cations. In contrast, the external adsorption sites remain mainly \( \text{Ca}^{2+} \)-saturated for all size fractions through the experiment. Experimental chemistry data obtained for the three size fractions were well fitted assuming a two-site model using two selectivity constants: \( \log K_\text{int} = 0 \) and \(-2.5 < \log K_\text{ext} < -1.0 \), for interlayer and external adsorption sites, respectively.

ABSTRACTS

POTASSIUM-ARGON AGE CONSTRAINTS ON BENTONITE-HOSTING MIOCENE VOLCANIC-SEDIMENTARY UNITS OF THE ANKARA-ÇANKIRI BASIN, CENTRAL ANATOLIA, TURKEY

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Many of the bentonite deposits of the Ankara-Çankırı Basin, Central Anatolia, Turkey occur within the Miocene Hancılı Formation, which comprises alternating sandstone, siltstone, marl, clayey limestone, and tuffite. The Hancılı formation discordantly overlies late Cretaceous ophiolitic rocks and Triassic Karakaya complex rocks composed of meta-sediments and meta-volcanics. The Hancılı formation shows lateral and vertical transitions with Miocene volcanic and pyroclastic rocks (tuff, agglomerate, and lava flows) having basaltic, andesitic, rhyolitic, and dacitic character. The chronostratigraphic range of the Hancılı Formation has been variously reported to span from as early as the early Miocene to as late as the Pliocene, so K-Ar dating of associated volcanic rocks can be useful to constrain the age of the parent materials from which the bentonites were formed. Four samples of volcanic rock from the southern part of the study area in the Ankara-Çankırı Basin were indistinguishable in K-Ar age. Age values for the four whole-rock samples ranged from 17.9 ± 0.4 Ma to 18.4 ± 0.4 Ma. The age value for feldspar separated from the four rocks was in no case significantly different from that for the whole-rock sample. The bentonite near Madenli, in the northern part of the study area, is overlain by tuff dated at 16.5 ± 0.6 Ma by concordant K-Ar age values obtained from separated hydrobiotite and feldspar. The K-Ar age of feldspar separated from a tuff underlying the Karayatak bentonite is 20.6 ± 1.6 Ma. These early results from an ongoing study indicate that the volcanic rocks associated most closely with bentonites of the Hancılı Formation were formed over a narrow range of time within the early Miocene (Burdigalian Age).

In parts of the Ankara-Çankırı Basin, the Hancılı Formation unconformably overlies ophiolitic basement rocks. Underlying the 20.6 ± 1.6 Ma tuff below the Karayatak bentonite is another tuff, a locally restricted lens, dated at 94 ± 4 Ma by the K-Ar age of feldspar separated from it. This result indicates the presence of Late Cretaceous volcanics above the ophiolitic basement. Claystone below the 94 ± 4 Ma tuff probably consists of products of weathering of ophiolitic basement rock. These results suggest that the bentonites were derived mainly by diagenesis of volcanic materials deposited during the Miocene Epoch and partially from the late Cretaceous ophiolitic basement. This conclusion is also consistent with the results of an ongoing mineralogical and geochemical investigation of the genesis of the bentonites.
The description and quantification of the mineralogy and petrographical characteristics of reservoir rock samples constitute key information for the evaluation of reservoir properties and hydrocarbons in place. In particular, accurate quantification of mineral contents is essential for interpreting and calibrating well logs, which are used for predicting effective porosity and hydrocarbons saturation throughout the logged intervals.

Quantitative mineralogical analyses are generally performed on bulk sample powders using X-ray diffraction (XRD) in combination with other analyses, such as bulk elemental analyses, solid density, and cationic exchange capacity measurements. Ideally, these analyses should be done on core samples selected in light of the geological and structural context, and covering all sedimentological lithofacies. However, in most wells, only short sections of the reservoir formations are cored nowadays to save cost. As a consequence, mineralogical analyses and petrographic observations are increasingly conducted on drill cuttings rather than or in addition to core samples. Sub-continuous XRD mineralogical analyses of crushed drill cuttings, often performed on the rig side to monitor lithofacies changes, are usually not usable for well log calibration owing to insufficient accuracy. In addition, the representativeness of drill cuttings may be significantly impaired by contamination with drilling mud, mixing of cuttings from different levels, and/or partial loss of fine clay phases during drilling and/or sample washing.

Our reference approach to quantitative mineralogy integrates XRD analysis on bulk powders with a specific selection of chemical and physical measurements totaling more than 15 parameters. Over the years, this approach proved to be of great added value. However, it is time-consuming and labor-intensive and not adapted to the analysis of drill cuttings. In order to circumvent this difficulty, we have tested and implemented an alternative workflow based on the non-destructive 2D elemental and mineral mapping of thin sections or resin-impregnated polished sections of cores and drill cuttings.

The chemical/mineralogical mapping uses a well-site scanning electron microscopy (SEM) system equipped with energy dispersive X-ray spectroscopy (EDS). A proprietary Spectral Analysis Engine (SAE) allows the automatic 2D-quantification of mineralogy through the deconvolution of the X-ray spectrum of each analyzed pixel combining up to three reference mineral spectra. In conventional reservoir rocks, this technique also allows evaluating macro- and micro-porosity from back-scattered electron (BSE) images and density maps. One significant limitation of the method is the poor determination of organic matter content, but RockEval data are easily integrated in the workflow.

Provided appropriate calibration on a representative set of samples using the reference method, the well-site SEM-EDS approach produces fairly accurate quantitative mineralogy in a time- and cost-efficient manner, including for clay-rich formations. In sandstone reservoir rocks, it is particularly useful for identifying and quantifying lithics and evaluating the nature and distribution of cement materials. This approach also appears particularly well adapted to the analysis of cuttings because it allows to correct for drilling mud contamination and/or to specifically map the largest, best-preserved particles, which are most representative of the drilled formations.
Carbon dioxide (CO$_2$) storage in the subsurface requires an understanding of reservoir heterogeneity to predict the distribution and trapping of the CO$_2$ plume. Just under one-million metric tons of anthropogenic CO$_2$ has been injected into the Middle Cambrian Mt. Simon Sandstone as part of the Illinois Basin Decatur Project. In this study, a thin mudstone overlying the Mt. Simon injection zone is characterized using focused ion beam scanning electron microscopy (FIB-SEM) and mercury (Hg) intrusion in order to model and predict potential for vertical breakthrough of CO$_2$.

The Mt. Simon Sandstone reservoir represents a diverse set of depositional environments including coastal, fluvial, and eolian. A thin mudstone, interpreted as a lagoon deposit, is interbedded with and overlies highly porous sandstones within the Mt. Simon injection zone. Dynamic measurements of pressure above and below the mudstone during and after CO$_2$ injection suggest the mudstone acts as a pressure baffle. Time lapse CO$_2$ saturation profiles from pulsed neutron logs also suggest that breakthrough in the mudstone has yet to occur. Whole core analysis of the mudstone gives a porosity of 1.5%. FIB-SEM and Hg intrusion data indicate that 90% of pore throats within the pore volume are less than 30 nm wide. The mudstone is dominantly composed of illite-smectite clay minerals and thus a CO$_2$ migration pathway is unlikely in a water saturated clay–pore throat interface. Pore network data indicate that the intra-reservoir mudstone has high CO$_2$–brine capillary entry pressure (>400 psi, 2.75 Mpa), which could provide a long-term impediment to vertical CO$_2$ migration.
ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF SODIUM MONTMORILLONITE WITH DECREASING WATER CONTENT

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Electrochemical impedance spectroscopy is a useful technique for studying solids electrolytes. In that context, the electrical conductivity of clays such as montmorillonite has also been studied\textsuperscript{1,2,3}. In this technique the real and imaginary parts of impedance (Z) are recorded over an interval of frequencies. When the imaginary part (Z") is plotted against the real one (Z') a Cole-Cole graph is obtained, which is fitted against an equivalent electrical circuit where the resistance of the sample is estimated. The experimental steps summarized above are carried out with an impedance meter controlled with a computer through specific software (Figure 1).

In this report measurements carried out on Na-montmorillonite (Lago Pellegrini, Argentina) at relative humidity (RH) lower than 100% are presented. Graphite was used as electrical contact between clay and circuitry. The homoionic sample, free of electrolyte, was prepared after removal of impurities such as quartz and feldspar. Powdered samples at RH 100\% were pressed at about 2,000 kg/cm\textsuperscript{2}, in order to get pellets of compacted clay. The measuring cell was mounted into a Lucite holder at 298 K, where RH was fixed by means of saturated inorganic solutions at the bottom of the holder. Impedance was recorded on samples at the desorption branch of the isotherms of adsorption, with the following water content:

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>Water content (%)</th>
<th>Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0</td>
<td>10.4</td>
</tr>
<tr>
<td>20</td>
<td>11.6</td>
<td>13.0</td>
</tr>
<tr>
<td>32.5</td>
<td>15.4</td>
<td>18.6</td>
</tr>
<tr>
<td>57.5</td>
<td>20.7</td>
<td>20.7</td>
</tr>
<tr>
<td>75.5</td>
<td>30.7</td>
<td>30.7</td>
</tr>
</tbody>
</table>

Water content was calculated against samples dried at 105 °C for 24 hours. The range of water content found is that usually reported for montmorillonites at RH under 100\%\textsuperscript{4,5,6}. In this range, water is located at the surface of the clay layers (with a thickness up to two or three water layers at interlayer spaces) and is strongly influenced by the surface of the montmorillonite layer, which includes the exchangeable cations with restricted mobility.

While removal of water proceeds, the maximum of Z" moves towards low values of frequency (w), indicating changes in the sample as can be seen in Figure 2. The frequency w is related to the capacitance (C) and resistance (R) of the equivalent circuit through the relation w = 1/RC, and it can be considered an intrinsic property of the sample because the geometric parameters of C and R cancel each other.

The values of electrical conductivities (\(\sigma\)) found in the range of (RH) studied, are in the following table:

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>Water content (%)</th>
<th>Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0</td>
<td>2.82 \times 10^{-8}</td>
</tr>
<tr>
<td>20</td>
<td>11.6</td>
<td>1.30 \times 10^{-5}</td>
</tr>
<tr>
<td>32.5</td>
<td>15.4</td>
<td>8.32 \times 10^{-5}</td>
</tr>
<tr>
<td>57.5</td>
<td>18.6</td>
<td>2.75 \times 10^{-4}</td>
</tr>
<tr>
<td>75.5</td>
<td>20.7</td>
<td>1.45 \times 10^{-3}</td>
</tr>
<tr>
<td>85</td>
<td></td>
<td>2.04 \times 10^{-3}</td>
</tr>
<tr>
<td>98</td>
<td></td>
<td>2.45 \times 10^{-3}</td>
</tr>
</tbody>
</table>

Research on clays as solid electrolyte is carried out in the range of RH and water content of the present report, that is to say on the under-saturation domain\textsuperscript{5,6}. In this range the conductivity is explained through a process involving water molecules in the solvation shells of exchangeable cations.

According to the model proposed\textsuperscript{1,2}, some molecules of water are polarized by the electric field of the cations. This effect is reinforced when an external electric field is applied, which allows the transfer of charge via protons with the help of the rotational movement of water molecules.

Since the model considered here is for water content lower than 30\%, it is not pertinent to conductivity at higher values. On the other hand, the ordering effect of exchangeable cations on the stacking of montmorillonite layers and hence on the electrical conductivity is also present at water content lower than 30\%, as was observed at higher values\textsuperscript{7}. 


INFLUENCE OF OIL SANDS ORE COMPOSITION ON SOLVENT EXTRACTION PERFORMANCE

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The aim of the present work is to identify the effects of oil sands ore composition (i.e., water, bitumen, and solids content as well as mineralogy) on non-aqueous bitumen extraction. This investigation was carried out on three different ore grades (low, medium, and high) from Alberta oil sands deposits and compared with the four petrological end members of the deposit (namely marine clay, marine sand, estuarine clay, and estuarine sand). Each ore or end member sample was mixed with cyclohexane at different solvent:ore ratios and water and bitumen contents. Following the cyclohexane extraction, the bitumen-cyclohexane solutions were collected at different settling times from 1 min to 48 h. The fine suspended solids in the collected solution were separated by centrifugation. The original ore and end member samples, as well as the suspended fine solids and bitumen product, were characterized by X-ray diffractometry (XRD), quantitative XRD, thermogravimetric analysis, Fourier transform infrared spectroscopy, elemental analysis, and determination of cation exchange capacity and particle size distribution.

Solids from as-received ores (low, medium, and high grades) were found to contain quartz, K-feldspar, and carbonate as the main non-clay minerals. Kaolinite, illite, and mixed-layered clay minerals were the dominant clay minerals and were concentrated in the fine and ultrafine fractions.

The oil sands mined from different areas consist of different mixtures of the geological end members and, therefore, have different mineralogical and chemical compositions. Comparison between ores of different grade and the four end members showed that high and medium grade ores contain estuarine sands and clays with approximate ratios of 88:12 and 76:24, respectively. The low grade ores contained a mixture of marine sands and clays with an approximate ratio of 64:36. The quality of the bitumen product is affected by oil sands ore composition as well as the cyclohexane:ore ratio and settling time. Illite and kaolinite were identified as the main minerals in the bitumen product for long settling times.
PENCIL CLAYS: HAYDN H. MURRAY’S FIRST PATENT AND THE PENCIL CLAY DEPOSITS IN GERMANY

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In February 1959, Haydn H. Murray filed his first patent in collaboration with Harold M. Johnson on pencil clay at the United States Patent Office; the patent was finally granted in May 30, 1961 (No. 2,986,472). Two other patents followed, related to reducing dilatancy of kaolin slurries using lithium hydroxide (No. 2,995,458 filed May 22, 1959) and to improving the color of calcined kaolin by adding a blue agent (No. 6,379,452 filed March 23, 2000). His first patented invention was based on previous unsuccessful attempts to produce a satisfactory natural clay for quality pencil leads in the United States of America, the absence of a suitable and commercially available processed clay material, and the need for independence from imported clays. Pencil clays are designed to be admixed with graphite for the production of “leads” to control their hardness. He proposed a mixture of degritted natural alkaline earth metal (“southern”) bentonite with a processed kaolin of ultrafine particle size, preferably from Georgia. The clay mixture is blended with graphite into a slip, extruded, dried, fired, and finally dipped into wax. In his experiments, he found that mixtures having 40% to 60% bentonite yielded the best products.

At the time of Haydn Murray’s experiments, the Klingenberg deposit in the Spessart region of Northern Bavaria, Germany, was the sole producer of natural clay suitable for pencil lead production. After 270 years of continuous mining, mostly from underground operation, the deposit finally closed in December 2011. However, Germany is still a leading producer of natural pencil clays with most of the production coming today from the Kärlich deposit in the Neuwied Basin near Koblenz. Some specialty clays from the Westerwald and Northern Rhenish Massif are also used in pencil clay manufacture, however, only after processing and blending with bentonite. The geological settings and the mineralogical and geochemical compositions of German natural pencil clays will be compared in this presentation. The clays are all extremely fine-grained, were deposited in quiet lacustrine settings during late Paleogene times, and consist primarily of disordered kaolinite and R0 illite-smectite. The relative proportions of 2- and 3-layer silicates in the German natural pencil clays are in fact very similar to those proposed by Haydn H. Murray in his patent. The high kaolinite content is important for the firing properties, while the expandable 3-layer clay minerals impart strength and plasticity to the ceramic body.
SOURCE-SEPARATED URINE PROCESSING USING CLAYS: NITROGEN RECOVERY AND PATHOGEN REMOVAL

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Urine accounts for 80% of the N and 50% of the P in municipal wastewater, but accounts for only 1% of the total wastewater volume. Therefore, it is beneficial to separate urine from wastewater to generate low-value fertilizer products, similar to our methods for recycling plastics. Previous attempts in this direction include ammonium recovery using natural zeolites such as clinopilitite. However, no studies have been conducted to examine pathogens that thrive in source-separated urine. Urine is not sterile; the urine of healthy adults contains *Pseudomonas*, *Clostridia*, and *Staphylococcus*, each of which can contain pathogenic species and can survive through the initial steps of urine processing (aging to allow urea to break down into ammonia and drive pH to >9). Clays such as bentonite have antibacterial properties and are well known bactericidal agents for treating infections in animals. Therefore, we are examining the capabilities of clays beyond clinopilitite to both recover nutrients and reduce the risks of pathogens in fertilizer products derived from source-separated urine. Clinopilitite, bentonite, and chabazite are cheap and abundant in countries like USA, India, China, and Africa. Sanitation remains a prime concern for developing countries as lack of sanitation severely impacts the well-being of people. The use of low cost technologies can aid in closed loop sanitation systems and improving lives of people around the globe. Moreover, producing low value fertilizer products may reduce our dependence on high-end synthetic fertilizers.

This research involves design and construction of a pilot scale reactor to examine and optimize N recovery and the removal of pathogens from source-separated urine using the untested bentonite and chabazite and comparing to well-studied clinopilitite. The fates of three types of organisms in the genera *Clostridium*, *Pseudomonas*, and *Escherichia* are being investigated throughout recovery of nutrients from urine using clinopilitite, bentonite and chabazite. A well-established PCR-Chip method is being used to rapidly monitor pathogens. Minerals are also being characterized using analytical techniques to quantify cation exchange capacity, chemical composition, specific surface area, Si-Al ratio, and thermal stability to ensure sample purity. The influence of the sampling level, grain size, and working regime (column beds with varying heights of sorption media) on the persistence of microorganisms and the recovery of nitrogen is being studied.

Existing studies demonstrate nutrient recovery, clay sorption of ammonium ions, and success of bench scale reactors; thus, it is logical to extend these successful technologies to additional types of clays and to monitor pathogen fate. Anticipated outcomes include understanding of the fate of pathogens at each phase of the reaction in a pilot scale reactor at Michigan State University campus.
PERMEABILITY CALCULATIONS OF ORGANIC RICH POSIDONIA SHALE

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Permeability in organic rich shales is important to understanding fluid and gas flow in source rocks. We investigated, using focused ion beam – scanning electron microscopy (FIB-SEM), two samples (WIC and HAD, both from the mid Jurassic organic-rich Posidonia Shale in central Germany) of different maturity (WIC Ro of 0.53% and HAD Ro of 1.45%). The permeability calculations were performed using GeoDict and visualized through Avizo. Both samples are composed of pore clusters that can be several micrometers in size but do not connect the different axes (10 × 20 × 20 µm). In other words the pore clusters have no axis connectivity in the x, y, and z direction (=> no permeability). A reason for the lack of connectivity is that the pore clusters are too small and that FIB-SEM can only visualize pores >25 nm. This results in a FIB-SEM porosity of 1.5% for WIC and 2.6% for HAD. Organic matter, 22 vol% of WIC and 15 vol% of HAD, has axis connectivity in the x, y, and z directions in both samples. Adding the organics with a permeability of 1×10⁻²² m² to the calculations, the total permeability increased by one to two orders of magnitude depending on the direction. The permeability for WIC ranged from 1.2×10⁻²⁰ m² to 1.2×10⁻²¹ m² and for HAD from 9.9×10⁻²² m² to 1.8×10⁻²¹ m².

Overall the flow is mainly diffusion controlled through the organics with minor parts showing flow in the pore clusters. The above figure shows the pressure field in the z direction on the left as well as the velocity in the z direction on the right. The highest velocities can be seen within the pore clusters. With increasing maturity the amount of small pores increases, even with an increase in the total FIB-SEM porosity but with little influence on the permeability. The volume and connectivity of the organic matter is what controls the permeability in our samples.
THE STABILITY OF BENTONITES AND SAPONITIC CLAYS IN AQUEOUS SOLUTIONS RELEVANT TO THE UNDERGROUND SEALING OF RADIOACTIVE WASTE DEPOSITS

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Smectites, in natural bentonites and saponitic clays, vary in their physical and chemical behavior and thus show a range of stabilities when subjected to various natural waters. Despite having been well studied, the suitability of these clays as effective long-term seals for underground radioactive waste disposal remains a question of debate. We present first results on the mineralogical and geochemical behavior of selected bentonites and saponitic clays subjected to aqueous solutions that simulate i) shale pore waters and ii) alteration of a gypsum seal in a salt diapir (NaCl-CaSO₄-saturated), which are relevant to the underground disposal of nuclear waste in different types of host rock. Most of the barrier materials we use have been well characterized in previous studies that document a broad range of clay mineral stabilities (e.g. Kaufhold and Dohrmann, 2010). In this investigation, we also include saponite clays, which have been reported to remain stable at crustal depths >3 km and bore hole temperatures >100°C (Lochner et al., 2011). The aim of this work is to constrain further the controlling mechanisms that lead to alteration of smectites in response to repository fluid-rock interaction at varying temperatures (25–120 °C), and to determine which phases show the highest degree of stability under these conditions. Using laboratory batch experiments and flow-through reactors to accelerate the rates of alteration, the changes in smectite composition are monitored using a broad range of analytical techniques (CEC, XRD, TEM, FT-IR, and STA methods). Phase changes are monitored using TEM-based chemical analyses that combine elemental mapping and mica standards to increase the accuracy of compositional determinations at the sub-micrometer scale. Overall, our results confirm that smectite displays a broad range of stabilities when subjected to shale pore waters or saline-CaSO₄ solutions. The mechanisms behind these differences are discussed in terms of current reaction models.


COMPARISON OF ELECTRICAL CONDUCTIVITY IN MONTMORILLONITE INTERLAYERS AND CORRESPONDING BULK FLUIDS THROUGH MOLECULAR DYNAMICS SIMULATION

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The diffusion of water and ions in the interlayer region of smectite clay minerals represents a direct probe of the type and strength of clay-fluid interactions in Na- and Ca-montmorillonite hydrates. Molecular dynamics (MD) simulations were used to investigate trends in cation and water diffusion in montmorillonite interlayers, looking specifically at the effects of layer charge, interlayer cation and cation charge (sodium or calcium), water content, and temperature (300 K – 366 K). For Na-montmorillonite, the largest increase in ion and water diffusion coefficients occurs between the one-layer (1W) and two-layer (2W) hydrates, corresponding to the transition from inner-sphere to outer-sphere surface complexes. A comparison of interlayer diffusion with that of bulk electrolyte solutions reveals a clear trend of decreasing interlayer diffusion coefficient with increasing electrolyte concentration, and in most cases the interlayer diffusion results are nearly coincident with those of the corresponding bulk solutions. Trends in electrical conductivities computed from the ion diffusion coefficients are also compared.

By varying the layer charge (low and high charge), interlayer cation, water content, and temperature, we have developed a better understanding of some of the key factors governing interlayer transport in clays. Not surprisingly, reduced layer charge leads to a more hydrophobic interlayer environment with significantly faster diffusional motion compared to the high charge models. In the 2W and three-layer (3W) hydrates of Na-montmorillonite and for Ca-montmorillonite at all hydration states, additional water has very little effect on ion or water diffusion. In those cases, the interlayer cations are fully hydrated, and an Arrhenius analysis indicates that water and ion activation energies are similar to each other and to the hydrogen bond energy in water. Thus, we can conclude that hydrogen bond breaking is a likely mechanism in the diffusion of interlayer water and ions. While diffusion coefficients from MD simulations of clay interlayers have often been carefully compared to high quality experimental measurements using synchrotron techniques, our results suggest that further comparison of simulated and experimental conductivity measurements would yield additional insight into the dynamic behavior in clays.

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 National Nuclear Security Administration under contract DE-AC04- 94AL85000. This work was funded by BP America, and BP management is thanked for permission to present this work.
ABSTRACTS

LAYERED DOUBLE HYDROXIDES AS NANOREACTORS FOR PREBIOTIC CHEMISTRY

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

To correlate the structure of the interlayer domain with its reactivity, having well-crystallized material with only aspartate molecules in the interlayer galleries was a prerequisite. Synthesis of this material can only be done by exchange reactions. Solid-state analysis performed on samples indicated the successful intercalation of the target molecules, and no trace of other anions was detected. Interestingly, by varying the layer charge density of the LDH or the water content of the interlayer gallery, the aspartate is accommodated in different orientations. Since the driving force for the formation of peptides is dehydration, the LDH materials were heated to 250 °C and changes in the structure were monitored by in-situ infrared and in-situ Raman spectroscopy and in-situ X-ray diffractometry. Combining these techniques is particularly interesting in elucidating the structure and the chemistry of the interlayer domain. Similar experiments were performed on the aspartate salt, serving as a reference sample. It has been shown that the interlayer domain of the LDH enhances the thermal stability of the amino acid, where its degradation requires a temperature 100 °C higher than for the pristine aspartate salt. At around 250 °C, chemical reactions take place both in the aspartate salt and in the aspartate-LDH. Interestingly, the nature of the products formed was found to be completely different. Upon heating, the salt formed exclusively polysuccinimide species, while the presence of amide bonds was detected in the interlayer domain of the LDH. Though these experiments were not carried out under geochemical conditions representative of the Hadean, the data demonstrate that lamellar species such as LDH are an ideal environment to protect and promote the condensation of amino-acids to form peptides. In addition, as emphasized by Greenwell et al., these materials provide a high coding environment and have the theoretical capability of self-replication with a high degree of fidelity.
SELECTING AND MODIFYING CLAYS TO ENHANCE THEIR ADSORPTION CAPACITIES FOR ZEARALENONE

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Zearalenone is one of the five major groups of agriculturally important mycotoxins produced by Fusarium mold. These mycotoxins occur frequently on corn, wheat, barley, oats, tree nuts, rice, peanuts, sorghum, hay, fruits, and other crops. The Food and Agriculture Organization of the United Nations estimates that 25% of the world’s food crops are affected by mycotoxin-producing fungi and that a nearly one billion tonnes of foodstuffs loss due to mycotoxins occurs every year. Minimizing the health risks and economic losses from mycotoxin 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 aflatoxins and zearalenone, we aimed to select and modify clay minerals to detoxify and decontaminate this mycotoxin by adsorption.

We used three approaches to modify the interlayer surface polarity of smectites on the nanometer scale: 1) Selecting smectites with different layer charge densities. Six smectites with different layer charge densities were chosen in this study to evaluate their adsorption capacities for zearalenone. 2) Replacing the interlayer cations in smectites with different hydration energies and valences. By varying the exchange cations and the layer charge density, the space between the hydrated cations was varied to match the size of the targeted mycotoxins, 3) Characterizing smectite-mycotoxin complexes. Once the optimum conditions for smectite-zearalenone interactions were identified, zearalenone-smectite complex was synthesized and characterized with variable-temperature X-ray diffractometry (XRD) and Fourier transform infrared (FTIR) spectroscopy. The XRD and FTIR data were used to verify that interlayer adsorption occurred on smectites and to determine the bonding mechanisms between zearalenone and smectites.

Experimental results indicated that smectites with CEC ranging from 107.7 to 136.6 cmol/kg showed higher adsorption capacities, up to 0.055 mol/kg (1.78% by weight) for zearalenone. Among eight different interlayer saturating cations, monovalent-cations saturated smectites showed higher adsorption capacities than divalent-cations saturated smectites. The highest adsorption capacity was for Na-clay, 0.111 mol/kg (3.50% by weight). In FTIR characterization, the results confirmed the presence of strong interaction between zearalenone and the smectite. This indicated the stability of the adsorbed zearalenone as the samples were washed twice with water. The XRD of Li-clay suggested interlayer adsorption of zearalenone, which was confirmed by heating the sample at high temperature. On the other hand, the interlayer adsorption of zearalenone was not observed in Mg-clay by the XRD result. The mechanism of the Mg-clay adsorption needs further study. Overall, the preliminary results indicated that the zearalenone adsorption capacity can be enhanced by changing layer charge densities of smectite and changing their interlayer cations. The adsorption mechanism was interlayer adsorption. Yet, the results also suggested that it is possible to enhance the adsorption by modifying the adsorbing environment on a nanometer scale.
ABSTRACTS

TEACHING CLAY SCIENCE IN A PROJECT-ORIENTED FORMAT

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The study of clay science is offered in two formats in the Department of Geology: a traditional lecture-based, laboratory-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, 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. In addition to XRD 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 Mössbauer 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 Geological Society of America. 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.
MOLECULAR INTERACTIONS OF CRUDE OIL WITH KAOLINITE

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Haydn Murray’s legacy about the structure and properties of kaolinite continues to find new areas of application, including those related to energy production. The presence of kaolinite in hydrocarbon-bearing reservoirs is a common feature in many diverse geologic settings. Understanding the molecular mechanisms that underlie rock-fluid interactions is playing an increasingly important role to optimize efficiencies for extraction of hydrocarbons. Recently, we have developed new methods to fractionate and characterize complex crude oil mixtures using a combined strategy of chemical fractionation and advanced mass spectrometry methods combined with FTIR spectroscopy and thermal analysis with evolved gas analysis. In this study, we investigate the retention of a light crude oil from the Illinois Basin by KGa-1b kaolinite using this framework.

The dipolar nature of kaolinite gives it the potential to interact with both polar and nonpolar oil constituents. Surfaces include the polar hydroxylated surfaces, neutral basal siloxane surfaces, and plate edges with “broken-edge” sites. In this study we ‘dosed’ KGa-1b kaolinite with a light crude oil from the Illinois Basin for 7 days. We then selectively fractionated the oil retained by kaolinite using a modified form of Saturate, Aromatic, Resin and Asphaltene (SARA) Analysis. We employed thermogravimetric analysis and evolved gas analysis to quantify the amount of oil retained by KGa-1b kaolinite. Initially, ~350 mg/g of crude oil was retained by kaolinite and this was sequentially lowered with each additional fractionation step to a final surface loading of 5 mg/g of crude oil. FTIR spectroscopy was used to study the oil constituents retained by the kaolinite after each fractionation. Finally, high resolution mass spectrometry was used to characterize each of the oil constituents eluted from the kaolinite surface. Atmospheric pressure chemical ionization mass spectrometry using CS2 was used to characterize the crude oil, each of its SARA fractions, and each fraction of the oil retained by kaolinite. The crude oil retained by kaolinite was compared with the original crude oil on the basis of average carbon number, molecular weight, and aromatic core size from mass spectrometry and of aromatic and aliphatic spectroscopic signatures derived from FTIR and Raman spectroscopy.
NEOGENE LACUSTRINE SEDIMENTS AND ASSOCIATED AUTHIGENIC CLAYS WITHIN ESKİŞEHİR PROVINCE, WEST CENTRAL ANATOLIA, TURKEY

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Neogene lacustrine sediments within the Eskişehir area are dolomite, marlstone, and argillaceous limestone. Sepiolite, palygorskite, magnesite, quartz, feldspar, and amphibole occur within these sediments. The limestone and dolomite are predominantly micrite but have been partly converted to microsparite by recrystallization. Calcite and dolomite crystals appear in euhedral and subhedral forms, and minor palygorskite and sepiolite fibers have grown as bridges between relicts of carbonate crystals as a result of continuous flushing of meteoric water during and after the formation of carbonate minerals in a vadose diagenetic environment.

The carbonate samples have high MgO, CaO, and LOI values. SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$ values indicate the presence of clays. Depletion in K, Ba, Rb, Nb, and Ce; enrichment in Sr; and degradation of feldspar and hornblende caused an increase of the LREE/(MREE+HREE) ratio in both argillaceous dolomite and limestone, suggesting a volcanogenic origin. Enrichment of Ni is related to weathering of olivine and pyroxene derived from ophiolitic basement units. The $\delta^{13}$C and $\delta^{18}$O values of dolomite and calcite show a negative correlation and suggest an evaporitic, hydrologically closed system, as well as a meteoric origin of the solutions and an edaphic source for the carbon. A slight enrichment of $^{13}$C and $^{18}$O for dolomite compared with calcite may have been controlled by changes in evaporation temperature and the degree of fractionation between the liquid and the vapor during the dolomitization processes. The $\delta^{34}$S and $\delta^{18}$O values for gypsum suggest an evaporitic lacustrine environment.

$^{87}$Sr/$^{86}$Sr isotope ratios range from 0.707579 to 0.708203 and suggest a non-marine evaporitic source for precipitation. The Mg, Ca, S, Si, and Al required for dolomite, calcite, gypsum, palygorskite, and sepiolite formation were supplied by solutions from the Paleozoic metamorphic and Upper Cretaceous ophiolitic rocks and locally the late Miocene–early Pliocene volcanic, volcanoclastic, and fluvio-lacustrine sedimentary rocks.

Acknowledgment: This study was supported financially by the Scientific Research Projects Fund of Eskişehir Osmangazi University in the framework of Project 2014–487.
MINERALOGY, GEOCHEMISTRY, AND GENESIS OF BENTONITES IN MIOCENE VOLCANIC-SEDIMENTARY UNITS OF THE ANKARA-ÇANKIRI BASIN, CENTRAL ANATOLIA, TURKEY

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Widespread chemical weathering of Miocene volcanic units of the Ankara-Çankırı area, central Turkey has resulted in formation of significant bentonite deposits having economical potential. Above late Cretaceous ophiolitic rocks, the volcanic rocks alternate with yellow, green, and brown bentonites and argillaceous tuffaceous sediments, reflecting the fluctuation of reducing and oxidizing conditions in the depositional environment. Bentonites exhibit plastic to non-plastic character and conchoidal structure. Desiccation cracks, locally enclosed coal seams, plant rootlets, gypsum lenses, yellow sulphate-like fracture infillings, and iron oxide stains, indicate a shallow lacustrine environment. Increases in degradation of feldspar and in oxidation of the Fe of hornblende and biotite in volcanic units are indicative of chemical weathering that resulted in formation of abundant smectite. Micromorphologically, the development of spongy smectite on degraded feldspar and devitrified glass reveals in situ precipitation driven by dissolution of volcanic particles. The local occurrence of rounded organic matter in dissolution voids of smectite-rich volcanic materials reveals that the area was suitable for the growth of temperate vegetation and was affected by local climate changes. The (Na2O+K2O)/(CaO+MgO) ratios of the bentonites suggest intermediate-, Ca-, and Na-bentonite character, and the average major-element composition gives a structural formula corresponding to montmorillonitic smectite: (Si7.40Al0.61)(Al2.41Fe0.82Mg0.64Ti0.10Mn0.004)(K0.33Ca0.31Na0.28). The bentonite samples have high LREE/(MREE+HREE) ratios and negative Eu anomalies. Zr/Ni ratios show positive correlation with Zr/Co ratios, and Zr is positively correlated with ΣREE. Furthermore, values of Ba, Sr, and Rb are high. Slight increases of Ni, Co, and Cr2O3 parallel an increase of Fe2O3+MgO+TiO2 in bentonites of the middle and southern parts of the basin, near the ophiolitic basement rocks. These results associated with field observations suggest that the Si, Al, Fe, and Mg required to form smectite were supplied mainly from the decomposition of feldspars, amphiboles, and volcanic glass from volcanic materials and partially from ophiolitic basement units during chemical weathering processes.
OUTCOMES OF THE 8TH REYNOLDS CUP IN QUANTITATIVE MINERAL PHASE ANALYSIS

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The Reynolds Cup in quantitative mineral phase analysis was established in 2002 to define the state of the art of mineralogical analysis in the scientific community, to offer a tool for independent self-evaluation of individual laboratories, and, finally, to stimulate the development of analytical methods (McCarty, 2002). A growing number of scientists and groups have met the challenge since that time, and significant progress was made (Omotoso et al., 2006; Raven and Self, 2013). This presentation will summarize the results of the current 8th Reynolds Cup.

Three mixtures were prepared in 2015 and reflect three different types of samples that represent realistic mineral assemblages containing clay minerals:

- RC8-1 Fine fraction of a tailing processed from a greisen-type tin ore
- RC8-2 Carbonate bearing shale
- RC8-3 Altered/weathered ultrabasite rock

The components of the mixtures were obtained mainly from the collections of the Technical University Bergakademie Freiberg in Germany and some external suppliers. Pure minerals were hand-picked from broken single crystals or separated by chemical treatment and size fractionation in the case of clay minerals. These reference minerals have been screened for purity by XRD and other techniques. All materials were broken to < 0.1 mm size for main components and to < 0.06 mm or < 0.03 mm for the minor components, respectively. The air-dried materials were weighed in for a total mass of 400 g of each mixture. The homogenization was performed carefully by manual stirring, then passing the mixture through a 0.2 mm screen to destroy aggregates, and finally homogenizing for 24 hours by overhead tumbling in 1.5 L bottles together with some zirconia cylinders. Then, the mixtures were split into 12 portions by a rotary sample splitter and recombined 3 times. After a further splitting run, the 12 parts were split again into 8 portions of ~4 g each with a micro-rotary splitter. In this way 96 units of each mixture were obtained. In order to check the homogeneity of the splits, 4 sample sets were taken randomly from these 96 units. Three of them were divided into two parts used for XRD and XRF analysis, respectively.

In total 83 participants from 24 countries have registered, and the samples were sent out on January 22, 2016. Details of the results will be presented in this talk. The winners of the 2016 Reynolds Cup in mineral phase analysis are ... all participants!

PORE SIZE DISTRIBUTION BY NMR CRYOPOROMETRY OF BRINE SATURATED SHALES

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The characterization of shales is challenging because their pores are very small. In many previous works, we have shown that Nuclear Magnetic Resonance (NMR) relaxation techniques are well suited for detecting and quantifying water in nanopores. Existing techniques such as HPMI, T2 NMR distribution, X-ray or electronic tomography, and micro-imaging are difficult to use to estimate the pore size distribution and are very restrictive methods applied under conditions far from the natural.

The NMR cryoporometry experiment relies on the shift of the melting temperature of the saturating liquid, which is itself a function of pore size according to Gibbs-Thomson theory. In practice, a sample (a cylinder of diameter 4 mm and length 20 mm) saturated with water is rapidly frozen at about −30°C and then heated slowly while the amount of water melted at a given temperature is measured by NMR. Typically the range that can be explored lies between 2 nm and 1 µm, well suited for the study of shales. Importantly, outside this range the pore volume can be determined but a pore size cannot be associated with this volume.

We used this technique on different reference materials to test the method and on natural shale samples in brine-saturated conditions and compared the results with other techniques. The measured distributions can differ significantly and we discuss the various physical reasons for the differences. The NMR cryoporometry technique opens new horizons for characterizing shales in their natural hydrated state.
PHOTOACTIVITY OF AZOBENZENE INTERCALATED IN ORGANO-SMECTITES

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Azobenzene (AzBz) shows a trans to cis conformational change upon UV radiation, which is followed by a change of the molecules dimensions. The reaction is reversed with the visible light radiation or high temperature. The motion of the AzBz molecules incorporated into the interlayer space of smectites may be transferred into the motion of the whole organo-mineral structure. The AzBz-smectite intercalation compound will then behave as a remotely and precisely controlled nanoswitch.

A Na-montmorillonite (SWy) was ion-exchanged with a series of trimethylalkylammonium (C_n) and benzylidimethylalkylammonium (BC_n) cations, where n is the number of carbon atoms in the alkyl chain and is equal to 12, 14, or 16. So prepared organo-smectites were reacted with AzBz with an AzBz/smectite ratio equal to 0.2. The reaction was done in a hermetically closed teflon vessel at ~120°C for 24 h. The obtained yellowish powders were subjected to chemical and structural analyses. The products were treated with UV radiation (365 nm) and the XRD patterns were recorded before and after UV treatment to observe the changes of the materials’ basal spacings (d_001).

The d_001 values of the product SWy-C_n and SWy-BC_n increased with increasing alkyl chain length of intercalated cations. Also, an increase of molecules’ density in the interlayer was observed as the molar content of C_n or BC_n increased with increasing alkyl chain length. This was coupled with spectral bathochromic shifts of CH_2 stretching bands from 2928 cm^{-1} (SWy- C_{12} ) to 2922 cm^{-1} (SWy-C_{16} ) observed in the FTIR spectra. The shift revealed a conformational change of intercalated ammonium salts from disordered gauche conformers to ordered all-trans conformers. The SWy intercalates with long chain alkylammonium ions (C_{16}, BC_{16}) were reacted with AzBz more effectively as compared to the materials with shorter C_{12} and BC_{12} ions. This was revealed by the high d_{001} values: 36.9 Å for C_{16} and 35.6 Å for BC_{16} after reaction with AzBz. The presence of 2^{nd} and 3^{rd} order reflections proved a highly ordered structure of these materials. The molar content of AzBz increased from ~85 mmol/100 g (SWy-C_{12} and SWy- BC_{12}) to 115 mmol/100 g (SWy-C_{16}) and 104 mmol/100 g (SWy-BC_{16}). The results show that the obtained materials differ in the character of the interlayer environment, i.e. the density and conformation of organic molecules and rigidity of the system. This influences the efficiency of azobenzene isomerization within the interlayer space.

This project was funded by the National Science Centre, Poland under research project no. 2014/13/B/ST10/01326.
ABSTRACTS

LOWER LIMIT OF SMECTITE LAYER CHARGE AS SEEN BY THE O-D METHOD

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Measurement of layer charge (LC) is an important step during characterization of a smectite for numerous purposes. Recent developments in attenuated total reflection infrared spectroscopy of D₂O-saturated smectites allowed establishing a new LC measurement method, exploiting the correlation of the position of a high-frequency O-D stretching band (νO-D) with LC (Kuligiewicz et al., 2015; Figure 1). The aim of the presentation is to interpret the obtained LC vs νO-D correlations for a series of natural samples and reduced charge montmorillonites (RCMs; Skoubris et al., 2013) produced by Li-saturation and heating at different temperatures, assuming different LC reduction mechanisms: homogenous vs. heterogenous charge reduction, different degrees of interlayer collapse, or no interlayer collapse. Data analysis led to the conclusion that the only possible mechanism explaining the obtained correlations is a homogenous LC reduction with little or no interlayer collapse. The lowermost limit for LC detectable on smectitic surfaces was just below 0.2, which seems to be the true lowermost boundary for smectite LC.


ABSTRACTS

STUDY ON NANOPHASE IRON OXYHYDROXIDES IN FRESHWATER FERROMANGANESE NODULES FROM GREEN BAY, LAKE MICHIGAN

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Freshwater ferromanganese nodules are found in lakes throughout the northern temperate latitudes and are often associated with glacial debris. Nanophase Fe-oxyhydroxides in freshwater ferromanganese nodules from Green Bay, Lake Michigan and their incorporation of As(V) has been investigated by X-ray powder diffractometry, high-resolution transmission electron microscopy, Z-contrast imaging, and ab-initio calculations using the density functional theory.

Samples from northern Green Bay can be divided into two types: Fe-Mn nodules and Fe-rich nodules. Iron-bearing phases in Green Bay nodules are feroxyhyte, nanophase goethite, 2-line ferrihydrite, and nanophase FeOOH with guyanaite structure. Z-contrast images of Fe-oxyhydroxides show ordered FeOOH nano-domains with guyanaite structure intergrown with goethite. The FeOOH nanophase is a precursor to goethite. Ab-initio calculations indicate that goethite is more stable than proto-goethite. Our results suggest that an Fe ordering process may have been involved in the transformation from feroxyhyte to goethite via proto-goethite as an intermediate phase. Combining Z-contrast images and TEM-EDS revealed that arsenate (AsO$_4^{3-}$) tetrahedra are preferentially retained at the proto-goethite (001) surface via tridentate adsorption (Figure 1).

Results from TEM, Z-contrast imaging, and ab-initio calculations clarify the nature of the crystal structure and chemistry of nanophase Fe-oxyhydroxides. Z-contrast images and image simulation directly show the atomic positions of Fe-oxyhydroxides with associated trace elements. The methods can be applied for identifying structures of nanophases and environmental science, especially for trace elements and heavy metals.

Figure 1. (A) A [001]-zone axis Z-contrast image of proto-goethite, bright spots are positions of Fe atom columns. Very bright spots are As atoms on the surface right above Fe; (B) an intensity profile of yellow area from X to Y; (C) an intensity profile of simulated Z-contrast image; (D) simulated Z-contrast image; (E) Polyhedral drawings of arsenate adsorption on the proto-goethite (001) surface.
ABSTRACTS

MOLECULAR SIMULATIONS OF CARBON DIOXIDE AND WATER IN MONTMORILLONITE CLAY INTERLAYERS UNDER GEOLOGICAL CO₂ SEQUESTRATION CONDITIONS

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We employed the grand-canonical Monte Carlo simulation to investigate the supercritical carbon dioxide-water mixture in the Na-montmorillonite clay interlayer under typical geological CO₂ sequestration conditions (T = 323 K, P = 90 bar). We studied the effects of relative humidity (RH) and surface charge density on the intercalation of different species. The stable clay interlayer distances at different RH values are determined based on the normal pressure and free energy curves of the CO₂-H₂O-Na⁺ complex in the montmorillonite clay interlayer.

Simulation results show that stable monolayer hydrates (1W) with a basal spacing around 12 Å are formed at RH = 30-60%. As RH is increased to 60-70% and above, bilayer CO₂-H₂O mixtures with a basal spacing around 15-16Å (2W) are more stable. In general, CO₂ intercalation in the clay mineral is strongly influenced by RH but is also influenced by the clay surface charge density. Our simulation results show that high RH values and high surface charge density facilitate water molecules entering the clay interlayer and decreasing the CO₂ intercalation. The sorbed H₂O concentrations from our simulations compare remarkably well with the experimental in-situ infrared (IR) spectroscopy data of Loring et al. [Langmuir (2014) Vol. 30, pp. 6120-6128]. However, the overall sorbed CO₂ concentrations from our simulations for the low-charge-density clay interlayer are higher than the IR experimental results, while for the high-charge-density clay interlayer the CO₂ concentrations from simulations are lower than the IR experimental results.

We anticipate that the discrepancies between our simulation and the IR experimental results may be due to differing stoichiometries of the clay samples. Molecular dynamics simulations show that the hydration state of CO₂ molecules is changed from partial hydration in 1W to full hydration in 2W with the increase in RH, and CO₂ dimers are frequently seen in both 1W and 2W hydration states. Most CO₂ dimers take the slipped parallel configurations, while the remaining dimers take the perpendicular T-shaped geometry. Further, sodium ions in the interlayer tend to be fully hydrated by water molecules owing to their relatively large hydration energy. Moreover, we find that CO₂ molecules hardly migrate into the first hydration shell of sodium ions. The overall diffusion coefficients of CO₂ molecules are larger than those of water molecules and sodium ions. This comparably high mobility of CO₂ molecules in the clay interlayer, together with the low probability of CO₂ participation in the first hydration shell of Na⁺ ions, essentially prevents CO₂ and Na⁺ from direct interactions in clay interlayers.
The 060 reflection, more correctly the 06l band, is very commonly used to estimate the b unit-cell dimension of phyllosilicates. This band has also been used to postulate an increase in b unit-cell parameter with hydration and swelling (e.g., Low et al., 1970, Nature, 225, 445). Use of this “reflection” commonly ignores the fact that it is a two-dimensional diffraction band, and its centroid does not necessarily coincide with the theoretical position of 060. We have investigated the structure factor and layer-stacking disorder contributions to 06l band profiles from phyllosilicates using the Debye scattering equation. X-ray powder diffraction patterns of clay mineral nanoparticles (kaolinite, muscovite, pyrophyllite, and Na-montmorillonite) with fixed unit crystal structure and variable degree of layer stacking disorder were simulated, fully accounting for variations in the structure factor as a function of 2θ. Although the unit structure was fixed, the 06l reflection centroid shifted as a function of an increase in layer stacking disorder, asymptotically converging to a limit value for completely uncorrelated stacked layers (i.e., turbostratic; Figure 1a). Contributions to the 06l line profile for Na-montmorillonite corresponding to several different interlayer H₂O molecule configurations and layer stacking disorder were also investigated, and the deviations of the apparent b dimension (calculated from the 06l centroid) from the theoretical value (as employed in the numerical models) were compared with parameters estimated from experimental data. Our calculations reveal a shift in the 06l centroid of ~0.16 °2θ from the ideal single-crystal profile of the band for an ideally turbostratic kaolinite, yielding a shift in the derived b unit-cell parameter of ~0.021 Å (Figure 1a). Similar behavior due to the “indentation” of coherently stacked layers on the lateral side of the clay nanoparticle was also observed (Figure 1b). Care must be exercised when estimating unit-cell dimensions from two-dimensional diffraction bands from phyllosilicates that are not fully ordered. However, shifts in the centroid of the 06l profile for stoichiometric minerals such as kaolinite have the potential to provide information on the degree of layer stacking disorder (e.g., Plançon and Zacharie, 1990, Clay Min., 25, 249).
ABSTRACTS

OXIDATION OF FORMALDEHYDE OVER SYNTHESIZED CATALYSTS OF COPPER, MANGANESE, AND CERIUM OXIDES ON PALYGORSKITE

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Air pollution generated from volatile organic compounds (VOCs), such as secondary organic aerosols and photochemical ozone, has become a worldwide topic (Volkamer et al., 2006). Therefore, the abatement of VOCs before emission is an inevitable atmospheric problem. Recently, the application of transition metal oxides supported on natural clay minerals as catalysts for VOCs abatement has drawn great interest. PalYGorskite is a natural magnesium aluminum phyllosilicate clay mineral with a special rod-like or fibrous microstructure. It is an ideal kind of catalyst support because of its nano-sized properties, low price, high strength, and large surface area (Frost et al., 2010). In this work, the thermal catalytic oxidation of formaldehyde (HCHO) gas over ternary mixtures of copper, manganese, and cerium oxides supported on palygorskite has been investigated and compared to reactions over the corresponding single metal oxides on palygorskite.

Results of this work show that the activity of Cu-Mn-Ce ternary mixed metal oxide catalyst is the best among all prepared catalysts, converting 1500 ppm HCHO into CO2 completely at 225 °C. The catalytic performance of the Cu-Mn catalyst is significantly better than those of single copper and manganese oxide catalysts because of their strong, intimate interaction. Furthermore, addition of cerium enhances catalytic activity relative to Cu-Mn alone because of high oxygen storage capacity of cerium oxides. During the catalytic oxidation reaction, it is vital that the palygorskite makes the active components highly dispersed. This work shows that palygorskite as a new type of natural support can be effectively used for catalyst preparation.


Figure 1. The conversion curves of CO2 generation over various palygorskite-supported catalysts of variable metal oxides and contents
UNDERSTANDING HYDROPHILIC AND HYDROPHOBIC INTERACTIONS OF NATURAL ORGANIC MATTER AT HYDRATED HECTORITE SURFACES: A MOLECULAR DYNAMICS STUDY

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Clay minerals and natural organic matter (NOM) are environmentally important and ubiquitous components of soils and sediments. Their interaction plays a significant role in controlling the transport and sequestration of toxic pollutants and is a crucial factor in the global carbon balance, soil (bio)geochemistry, and plant nutrition. Experimental studies have shown that the mechanisms responsible for NOM adsorption on clay mineral surfaces are hydrophobic interactions and cation bridging [1,2]. These interactions are strongly influenced by the nature of the charge-compensating cation, the clay composition and charge, the composition and concentration of NOM, solution ionic strength, and pH. The molecular scale details of the interactions among NOM, mineral surfaces, and cations are, however, poorly understood. To quantitatively assess how the nature of the cations affects these interactions, we have performed classical molecular dynamics simulations of hectorite–NOM systems with two cations having significantly different hydration properties (Cs+ vs. Ca2+). These simulations used new, large hectorite models with disordered distributions of Li+ and Mg2+ substitution in the octahedral layers. In order to simulate near-neutral pH conditions, the NOM was modeled with only the carboxylic groups deprotonated, leaving other functional groups protonated. The simulation results clearly indicate that Cs+ ions do not develop bridging between NOM and the hectorite surface but instead promote hydrophobicity-driven formation of NOM aggregates in the pore solution. In contrast, the presence of Ca2+ ions leads both to the formation of NOM aggregates in solution and to their close association with the hectorite surface. The surface–NOM complexation in Ca-hectorite takes place both by H2O and Ca2+ ion bridges and the hydrophobic interaction between the alkyl C groups and the hectorite surface. The aggregation of NOM in the solution phase is not mediated by either Cs+ or Ca2+ ions, but is dominated by the hydrophobic interactions of the NOM molecules. The dynamical details of these simulations will be compared with available experimental data and other simulations to provide a comprehensive molecular-scale view of the NOM aggregates and their complexation with hectorite surfaces.

CLAY MINERAL ASSEMBLAGES IN DESERT AND CONIFER SOILS OF THE CATALINA CRITICAL ZONE OBSERVATORY

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Clay minerals are useful geochemical markers that document mineral weathering pathways and spatial variability across landscapes. Our research objective was to examine bioclimatic and landscape position controls on mineral transformation in granitic soils within the Catalina Critical Zone Observatory, which exhibits significant range in precipitation (25 to 85 cm yr⁻¹), temperature (24 to 10 °C), and vegetation composition (desert scrub → mixed conifer). We selected desert scrub and mixed conifer field areas to represent the two climate end members of the environmental gradient. Within each bioclimatic zone, two catena end member pairs were sampled to assess variation in topography, which included divergent, water-shedding summits and convergent, water-gathering footslopes. We collected soils and saprock from each site and determined clay mineral assemblages for all samples using semi-quantitative X-ray diffractometry.

Clay mineral assemblages primarily comprised 1:1 and 2:1 phyllosilicates that varied in composition with depth, landscape position, and ecosystem. Clay minerals in the desert scrub soils included vermiculite, smectite, hydrated halloysite, dehydrated halloysite and/or kaolinite, and interlayered halloysite/kaolinite-smectite. The dominant smectitic and halloysite mineral species in the desert scrub soils reflect complex climatic and mineral microtextural interactions within dry, silica-rich environments. Clay minerals at the mixed conifer site exhibited the greatest degree of mineral transformation in the study, consisting of vermiculite, hydroxy-interlayered vermiculite, illite, and kaolinite with minor amounts of hydrated halloysite that were most evident in conifer surface soils and saprock. Little to no smectite was identified in the conifer divergent landscapes yet smectite was prevalent in adjacent convergent soils, an observation attributed to greater concentrations of water-soluble ions accumulating downslope. Our findings indicate that bioclimatic and topographic factors interactively facilitate mineral transformation along the environmental gradient, suggesting that regional- and local-scale processes must be accounted for in the evolution of soil and the critical zone.
Many industries are using methylene blue as a cationic dye for different purposes. However, methylene blue is difficult to decompose and can be harmful to the environment and to humans, thus making its presence in waste water a major problem. Therefore, it is necessary to use the aid of a material to separate the dye from the water. In this study, we look into an alternative solution in the removal of methylene blue from industrial waste water and to utilize locally available material such as sodium-montmorillonite (Na-MMT).

The parameters used to evaluate the adsorption behavior include clay loading, rate of agitation, and treatment temperature. Statistical analysis showed that the amount of clay loading has a significant effect on the adsorption of methylene blue and that a clay loading of 0.75 g was more effective since the clay tends to agglomerate at higher loading. The adsorption follows the Langmuir isotherm, indicating that the methylene blue attaches to the Na-MMT by monolayer adsorption. Zeta potential measurements showed the Na-MMT particles to be negatively charged, making Na-MMT an effective capturing agent for cationic methylene blue dye.
EFFECT OF COFFEE EXTRACT AS A REDUCING AGENT OF SILVER IN ION-EXCHANGED ZEOLITE

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Several studies have already been done regarding the incorporation of silver into zeolite for antimicrobial applications. However, in producing stable silver nanoparticles in zeolites, toxic reducing agents such as sodium borohydride are usually used. Among the reducing agents used in the green synthesis of silver nanoparticles, coffee shows the most potential. Moreover, coffee itself exhibits antimicrobial properties.

In this study, extracts from ground coffee (GC) and ground coffee waste (GCW) were used as reducing agents in the ion-exchange of silver in zeolite. Sodium-modified mordenite was suspended in a silver acetate solution with constant stirring. Varying amounts of coffee extracts were then added to a total volume of 50 mL solution. The system was then allowed to age in a dark environment for 24 hours. Finally, the ion-exchanged mordenite was filtered, washed, dried, and tested for antimicrobial properties against Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus).

In the antimicrobial assays done, it was shown that all samples inhibited growth of both bacteria. Samples without the coffee reducing agent exhibited good inhibition against S. aureus, but showed incomplete inhibition and thinning of E. coli. Regarding the amount of coffee used, antimicrobial index results against E. coli showed similar values for both reducing agents, whereas results against S. aureus showed increased effectiveness with the use of coffee waste as a reducing agent, as well as dependence on reducing agent concentration.

Figure 1. Summary of antimicrobial results.

Figure 2. Antimicrobial assay of S. aureus with sample containing no coffee (top), and sample with 15 mL of ground coffee waste used as reducing agent (bottom).
SORPTION-REGENERATION CHARACTERISTICS OF SODIUM-MODIFIED MORDENITE ZEOLITE FOR IRON (II)

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The abundance of heavy metals such as Fe$^{2+}$ ions in agricultural and industrial wastewater poses a threat to public health and environment owing to their toxic and poisonous properties. These pollutants come from a variety of sources including, but not limited to, acid mine drainage, landfill leachate, and rainwater runoff. An adsorbent material has the capacity to remove the heavy metal wastes without altering its structure and thus can be used for regeneration. Natural and modified zeolites are well-received adsorbents owing to their good adsorbing capacities, efficiency, and low cost. The structural frameworks of these aluminosilicates have suitable ion exchange properties that are easily modifiable.

In this study, various conditioning treatments of mordenite natural zeolite using hydrochloric acid and sodium chloride were tested at different contact times and concentrations. Pretreatment with hydrochloric acid was found to be best for 1–3 mm zeolite grains, soaked for 12 hours at 3M HCl concentration. Soaking for 24 hours in 4M solution of NaCl provided optimum results for iron ion adsorption, as shown by atomic absorption spectrophotometry.

Table 1. Surface characteristics of mordenite.

<table>
<thead>
<tr>
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<th>MORDENITE</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Parent</td>
</tr>
<tr>
<td>Surface Area</td>
<td>115.84 m$^2$/g</td>
</tr>
<tr>
<td>Pore Volume</td>
<td>0.04 cm$^3$/g</td>
</tr>
<tr>
<td>Pore Size Adsorption</td>
<td>13.65 Å</td>
</tr>
<tr>
<td>Pore Size Desorption</td>
<td>139.61 Å</td>
</tr>
</tbody>
</table>

Scanning electron microscopy showed that the acid treated mordenite exhibited rough surfaces. Acid treated mordenite had better characteristics than the parent, untreated mordenite in terms of surface area, pore volume, and pore diameter. Regeneration experiments exhibited promising reusability of zeolite. Using 2M NaCl solution and 24 hours soaking, an average of 76.71% of iron ions were recovered over four cycles without the reuse of solution.

Figure 1. Regeneration of Fe$^{2+}$ by Na-modified mordenite.
KAOLINITE CO-INTERCALATED WITH BENZYLALKYLAMMONIUM SALTS AND AZOBENZENE: STRUCTURAL FEATURES AND PHOTOSWITCHING EFFECT

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Ultraviolet (UV) radiation forces the azobenzene (AzBz) molecule to change conformation from trans to cis, which simultaneously affects the molecule dimensions. A reverse reaction can be completed by using visible light radiation or high temperature. The incorporation of photoactive molecules, e.g. of AzBz, into the structure of layered solids including clay minerals leads to the development of hybrid mineral-based photoresponsive materials. The past studies concentrated mainly on using smectites as well as synthetic micas. The objective of this research is to overcome the difficulties regarding kaolinite intercalation chemistry and to synthesize a photoactive material based on 1:1 layered mineral.

Kaolinite (Hinckley index = 1.31) from the Maria III deposit, Poland (M) in a methoxy form (MM) was used as a host material. The MM sample was intercalated with benzyldimethylalkylammonium chlorides (BC\textsubscript{n}, n = 12, 14, or 16), which were dissolved in methanol (0.5 mol/L concentration). The MM sample had a basal spacing of 8.7 Å, which increased after salts intercalation. For the BC\textsubscript{12} intercalate, the basal spacing region contained two peaks with maxima at 39.5 Å and 30.0 Å. Similarly two maxima were observed for the BC\textsubscript{14} intercalate at 39.4 Å and 32.0 Å. The intercalation of BC\textsubscript{16} resulted in the appearance of a basal spacing of ~42.0 Å.

The large d\textsubscript{001} values indicate that the BC\textsubscript{n} molecules were tilted or formed an arrangement nearly perpendicular to the kaolinite layers. The BC\textsubscript{n} salts intercalation was possible exclusively owing to the hydrophobic character of the MM sample having octahedral sheets grafted with OCH\textsubscript{3} groups. The presence of BC\textsubscript{n} salts was also confirmed by FTIR spectra where bands attributed to C-H stretching and bending vibrations were observed in the 3000–2800 cm\textsuperscript{-1} and 1500–1300 cm\textsuperscript{-1} regions, respectively. Additionally, the bands connected with inner surface hydroxyls were altered as a result of intercalation. Co-intercalation of AzBz from its vapor was effected in a closed teflon vessel at 120°C for 24 h using a mass ratio of AzBz to BC\textsubscript{n} intercalate of 0.2. The co-intercalation of AzBz caused further increase of the basal spacing to ~50.0 Å. The observed peaks were broad, but their clear maxima followed the sequence: 48.7 Å (BC\textsubscript{12}), 50.0 Å (BC\textsubscript{14}), and 53.3 Å (BC\textsubscript{16}). Such a trend could be induced by the π-π interactions between rings of BC\textsubscript{n} salts and AzBz. Such a phenomenon was not observed when AzBz was co-intercalated with alkyltrimethylammonium salts, which do not contain aromatic π electrons. In the FTIR spectra, the co-intercalated AzBz led to an appearance of bands at 3060–3030 cm\textsuperscript{-1} (C-H ring stretching) and at 780 and 690 cm\textsuperscript{-1} (C-H ring bending). The CHN analyses showed the AzBz/BC\textsubscript{n} molar ratio was in the 1.6–2.5 range. Alternate exposure to UV (365 nm, 5 mW/cm\textsuperscript{2}, 2 h) and visible light (sunlight, 2 h) showed that the d value reversibly changed by about 2 Å. No other structural differences were noticed by X-ray diffractometry after three cycles of the irradiation.

This project was funded by the National Science Centre, Poland under research project no. 2014/13/B/ST10/01326.
BENTONITE COMMODITY MARKETS AND FUTURE TRENDS

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This presentation includes the major uses for USA mined and produced bentonite. These data have been published annually, first by the Bureau of Mines and currently by the U.S. Geological Survey. Bentonite has many industrial mineral uses that are generally tied to the USA economy. Sodium bentonite is the predominant mineral, with minor contributions from calcium bentonite in some markets. The major bentonite markets include uses for pet litter, in oil and gas drilling, as a foundry sand binder, and in iron ore pelletizing.

The largest current bentonite market is clumping pet litter, exceeding one million metric tons annually for over ten years. This market utilizes sodium bentonite that expands rapidly when exposed to water, exceeding its dry volume by 16 to 25 times. However a minor portion of the pet litter market utilizes non-clumping calcium bentonite and other minerals. Before their use, these mineral blends are heated to strengthen granules and increase their porosity. The second major use of (sodium) bentonite is for oil and gas drilling. During the fracking boom for shales, this market exceeded one million metric tons annually for several years.
AUTHIGENESIS AND DIAGENESIS OF THE MURRAY FORMATION MUDSTONE IN GALE CRATER, MARS


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The Mars Science Laboratory rover Curiosity has been exploring sedimentary deposits in Gale crater since August, 2012. The rover has traversed up section through ~150 m of sedimentary rocks deposited in fluvial, deltaic, and lacustrine environments (Bradbury group and overlying Mount Sharp group). The Murray formation lies at the base of the Mt. Sharp group and has been interpreted to be a finely laminated mudstone likely deposited in a subaqueous lacustrine environment. Four drill samples from several elevations in the Murray fm have been acquired by the rover’s sampling system and delivered to the CheMin XRD instrument. The lower section of the Murray fm contains 2:1 phyllosilicate(s), hematite, jarosite, XRD-amorphous materials, and primary basaltic minerals. Further up section, the Murray fm contains magnetite, cristobalite, tridymite, and abundant Si-rich XRD-amorphous materials along with plagioclase and K-feldspars. Murray formation materials appear to have been altered under an open hydrologic system based on the bulk chemistry of these materials measured by the alpha particle X-ray spectrometer. The 2:1 phyllosilicate occurs only in the lowermost section of the Murray fm and may be detrital or may have formed during authigenesis, as did the Fe-saponite and magnetite detected in a mudstone in the Yellowknife Bay fm near Curiosity’s landing site (stratigraphically at the base of the Bradbury group). The occurrence of jarosite and hematite in the lower section indicates an acidic diagenetic event. These phases may have formed via several acidic alteration mechanisms, including 1) oxidative weathering of mafic igneous rocks containing sulfides; 2) sulfuric acid weathering of Fe-bearing phases; and 3) effects of excess acidity due to rapid oxidation of Fe$^{2+}$ in originally near-neutral subsurface solutions rich in Fe$^{2+}$. The transition from abundant hematite in the lowermost Murray fm to magnetite moving up section may indicate changes in lake chemistry, i.e., variable redox conditions, possibly during authigenesis or subsequent diagenetic events. Tridymite, a high temperature mineral, (and possibly cristobalite) is detrital, perhaps deposited in a lake from a distal silicic volcanic rock source or from crustal materials present prior to the Gale crater impact event. Abundant Si-rich XRD-amorphous materials in the upper sections of the Murray fm may be detrital or an aqueous-alteration product of primary igneous phases and phyllosilicates. Curiosity’s science team is still deciphering the authigenesis and diagenetic events that formed the Murray fm. The mineralogy and geochemistry of the formation suggest a complicated history with several (many?) episodes of aqueous alteration under a variety of environmental conditions.
CLAYS AS AGENTS IN THE MECHANOCHEMICAL DEGRADATION OF RECALCITRANT POLLUTANTS

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A mechanochemical process is defined as a chemical reaction driven by application of a mechanical force. Application of such a force may cleave solid particles and thereby both increase their surface area and expose freshly formed surfaces and free radicals that come into being owing to bond breakage at the planes of cleavage. Examples of clay-induced mechanochemical reactions abound. Thus, grinding carbendazim (methyl 1H-benzimidazol-2-ylcarbamate; a fungicide) with Al-montmorillonite (Al-mont) for 5 min with a mortar and pestle resulted in the degradation of 85% of the pesticide present. The degradation mechanism is, most likely, related to the high acidity of the surface of Al-mont. Other minerals, including kaolinite, attapulgite, and Na- or Ca-montmorillonite, were far less effective in degrading carbendazim. The mechanochemical degradation of the herbicide imazaquin (2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl)-3-quinolinecarboxylic acid) presents an interesting case study. Grinding of imazaquin for 5 min with Cu-montmorillonite (Cu-mont) or Al-mont resulted in 90% and 56% degradation of the herbicide, respectively. Grinding was less efficient in inducing degradation of imazaquin by Ca-montmorillonite. Na-montmorillonite (Na-mont) was the least effective in degrading imazaquin, but when a solution of CuCl₂ was added during the grinding of imazaquin with Na-mont, the rate of degradation of the herbicide equaled that achieved upon grinding imazaquin with Cu-mont. Grinding imazaquin in the presence of CuCl₂ solution but in the absence of the mineral did not result in degradation of the herbicide, suggesting that some Cu²⁺ exchanged with Na⁺ during the grinding of Na-mont in the presence of the CuCl₂ solution and that the formed Cu-mont is the species responsible for the degradation of imazaquin. A comparison of the X-ray diffractograms of Na- and Cu-mont and of Na-mont ground in the presence of the CuCl₂ solution supports this hypothesis.

Carbamazepine (CBZ) is a persistent PPCP often detected in various environmental compartments and in crops irrigated with treated sewage effluent or grown on soils loaded with biosolids. Al-mont enhanced the degradation of CBZ even without the application of a mechanical force, but application of such a force did not increase the rate of CBZ degradation, possibly because the mechanism of degradation (acid hydrolysis) did not involve the free radicals which are produced at the fresh surfaces created by an applied mechanical force. In contrast, free radicals are involved in many mechanochemical degradation processes, including those described above. A different pattern of activity was displayed by Cu-mont in the surface degradation of pyrene (C₁₆H₁₀), a recalcitrant PAH frequently found in soils. Samples of Na- and Cu-mont loaded with pyrene were ground with a mortar and pestle for 5 min. Na-mont did not generate degradation of pyrene either with or without grinding, while grinding with Cu-mont actually retarded pyrene degradation as compared to the rate of degradation observed when pyrene was incubated in the presence of Cu-mont but with no mechanical force applied. Pyrene loaded on Cu-mont degraded spontaneously (~50% in 24 h), however when the system was ground, some pyrene degradation (~25%) took place during grinding but it stopped altogether following grinding. A collapse of the card house structure of Cu-mont upon grinding was observed by SEM, causing a reduction in the surface area available to the interaction with pyrene. This was, most likely, the reason for the observed pattern of degradation.
THE MODIFICATION AND TESTING OF COPPER MODIFIED-ZEOLITE AS A POTENTIAL ALTERNATIVE TO NOBLE METAL CATALYSTS IN CATALYTIC CONVERTERS

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Incomplete combustion in automotive vehicles leads to emission of hydrocarbons (HC), CO, and NOx. Catalytic converters with ion-exchanged zeolites as catalysts are useful in reducing such harmful pollutants (Karthkeyan and Saravanan, 2013). A copper-exchanged zeolite has been characterized and tested as a catalytic converter for a gasoline-fueled engine. The catalyst’s efficacy for reducing CO, HC, and NOx was tested at low, medium, and high engine speeds.

Experimental method: The natural zeolite sample was taken from the SAILE Mines in Pangasinan, Philippines. It was sieved to granules with sizes of 2 mm to 6 mm. It was purified with hydrochloric acid (3M) for 6 h. It was saturated with Na using 4M NaCl solution for 24 h and washed with deionized water to remove Cl\(^{-}\) ions. Copper-exchanged zeolite was then prepared by contact with a solution of CuSO\(_4\)\(\cdot\)5H\(_2\)O (1M) in deionized water. It was air dried overnight and calcined for 4 h at 300°C. The zeolite was characterized by XRD, XRF, and SEM-EDX. In the emissions tests, the initial and final concentrations of CO, HC, and NOx were determined with a FGA-4100 automotive emission analyzer. The analyzer can determine emission at speeds ranging from 1 to 10,000 rpm. A two-stroke, single cylinder engine, Kawasaki Model HD3 125, was used. The tests were performed at low, medium, and high speeds and emissions were recorded each second for 20 s.

Results and discussion: The zeolite was identified as mordenite by XRD. The XRF results indicated 1.28% Cu was loaded in the zeolite. The modified Cu-zeolite reduced CO emission by 63.7%, 60.7%, and 52%; NOx emission by 31.8%, 73%, and 77.5%; and HC emission by 66.1%, 64.8%, and 59.8% at low, medium, and high engine speeds, respectively. The figures below show comparisons of NOx, HC, and CO emission results for tests with no catalytic converter and those for the catalyst-aided set-up.

Conclusions: Cu-exchanged zeolite significantly reduced HC, CO, and NOx emission in a gasoline-fueled motor engine. The catalyst performed best at low engine speeds for reducing HC and CO. The conversion efficiency decreased as the engine speed increased. The reduction of NOx was efficient at high engine speed and its conversion efficiency decreased as engine speed decreased.

ABSTRACTS

THE POTENTIAL USE OF PHILIPPINE NATURAL ZEOLITE FOR THE TREATMENT OF ACID MINE DRAINAGE

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Various mining companies are facing serious problems with acid mine drainage (AMD) owing to its negative repercussions. In this study the efficiency of natural zeolite (clinoptilolite and mordenite) for removal of heavy metal ions from solution was investigated and compared with that of alumina. Five metal ions were considered in this investigation, namely Cu, Ni, As, Pb, and Zn; all are present in the Rapu-Rapu in the Philippines (a polymetallic gold mine).

Experimental method: The metal solutions (100 ml each) were prepared by dissolving the following reagents in deionized water: CuSO$_4$.5H$_2$O, NiSO$_4$.6H$_2$O, As$_2$O$_3$, Pb(NO$_3$)$_2$, and ZnSO$_4$.7H$_2$O. The zeolite was ground to a particle size range of 35 μm < Dp < 180 μm. Pure high grade alumina, gamma Al$_2$O$_3$, 325 mesh powder was used as comparative metal adsorbent. A 3.7 g portion of the adsorbent was added to 100 ml metal solution of Cu, Ni, As, Pb and Zn. It was agitated with a magnetic stirrer (650 rpm) at room temperature. The pH of the mixture was lowered to 2.5 with a 2% sulfuric acid solution. The suspension was then mixed for 6 hours at 100 rpm at 18–22 °C. The zeolite was characterized by XRD, SEM-EDX, and TG/DTG methods. Metal concentrations in solution, before and after sorption, were determined by ICP-AES.

Results and discussion: The zeolite was characterized as clinoptilolite and mordenite. The zeolite was shown to have plate-like morphology with rough surfaces and some open pores. The heavy metal uptake by the zeolite was 35.9% for Cu, 35.4% for Ni, 95.8% for As, 99.0% for Pb, 33.9% for Zn. The metal uptake by alumina was 17.7% for Cu, 12.7% for Ni, 92.5% for As, 97.0% for Pb, 11.3% for Zn and 12.7% for Ni. Zeolite shows high metal uptake capacity for Zn, Ni, and Cu ions. Compared with alumina, natural zeolites show higher uptake capacity for Pb and As ions even though these are anionic metal solutions. Arsenic ions may have bound to the iron ions of the natural zeolite; the process is irreversible, i.e. stable complexes of arsenic and iron occurred.

Conclusions: The zeolite studied has an excellent uptake capacity for heavy metals, thereby reducing hazardous contaminants like heavy metals and anions in acidic aqueous environments. Its high porosity and thermal stability makes it suitable for passive aqueous remediation techniques for AMD.

Aguila, et al., Acid Mine Drainage (AMD) Formation and Treatment: A Study of the Potentially-Acid-Forming (PAF) Rocks and Copper Ore from Rapu-Rapu. 2010
PALYGORSKITE FORMATION WITHIN CALCRETES AND ITS IMPLICATION FOR PALEOCLIMATE: A CASE STUDY FROM ANATOLIA, TURKEY

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Quaternary calcretes are widespread in southern and central Anatolia and occur in a variety of forms, such as nodules, tubes, laminar crusts, and fracture infills. The thickness of the calcrete profiles ranges from 1 m to 7 m. Nodules occur in roughly spherical to ellipsoidal shapes with diameters of 5–15 cm. The mineralogical characteristics of the calcretes and their siliciclastic mudstone host rocks were examined by polarized-light microscopy, X-ray diffractometry, scanning and transmission electron microscopy, and energy-dispersive X-ray spectrometry, as well as by chemical and isotopic methods. Palygorskite often occurs as beige colored layers, forming a minor component within the mudstone or calcrete, especially in nodules and tubes. Textural images show that the calcrete is composed mainly of micrite, with microsparite and sparite, associated with biogenic lamination, coatings, and filaments. The presence of sparite-type meniscus cement in dessication cracks, rhizoliths and root cast, calcite needles, and locally pisoliths characterize a vadose zone.

The SEM and TEM images show palygorskite fibers and fiber bundles on and/or between calcite crystals, indicating direct precipitation from percolating alkaline water rich in Si, Al, and Fe and low in Mg in the vadose zone following precipitation of calcite, which is the major component of the calcretes. Thus, palygorskite occurrences reflect a formation at the advanced stage of evaporation during calcrete formation. Stable isotope values ($\delta^{13}$C and $\delta^{18}$O) of calcite in calcretes suggest formation under semi-arid climatic conditions. The presence of palygorskite in calcretes indicates conditions more arid than those required for calcite precipitation. The required ions for palygorskite and calcite were provided from host rocks (mostly smectitic mudstone) and soils by dissolution of smectite and also by weathering of the neighboring rocks (e.g. ignimbrite and ophiolitic rocks).
PREDICTION OF SWELLING PRESSURE IN SMECTITES: A MOLECULAR DYNAMICS STUDY

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The behavior of buffers and fillers to be used in the deposition of nuclear waste in bedrock is crucial to the reliability of the safety justification. The physicochemical nature of the buffer material is very complicated because of the diversity of the clay mineral compositions and the complex behavior of cations in the electrolyte media inside and between the clay flakes. The key functional property of the buffer material is the swelling pressure of the clay mineral. It depends on the compositions of the clay and solution as well as on environmental conditions such as temperature and external pressure. Swelling pressure can be studied experimentally for clay samples at various conditions. The main difficulty is, however, to have a comprehensive understanding of the swelling phenomena in natural clay buffers, where there is a multitude of compositional and environmental variables. A modeling method that reliably predicts the swelling pressure in a given clay system is vital in the safety justification of the buffer concept. Molecular dynamics and quantum chemical studies are becoming increasingly popular in the field. The main advantage provided by the computational approaches is the capability to look into systems and phenomena that may be very challenging to or even beyond current experimental research technologies.

We have recently demonstrated that the swelling pressure of montmorillonite can be predicted by a molecular dynamics method [1]. Montmorillonite sheets are placed into a water simulation box where swelling takes place. A pressure probe is connected to the sheets restraining the swelling. Interlayer cation composition, charge location, layer charge, and the ion composition in the water are used as simulation variables. The predicted pressures reproduce experimental trends for montmorillonite clays in water and electrolyte solutions. The swelling pressure simulation method can be straightforwardly applied to various clay compositions in different electrolytes and environmental conditions.

DESIGNED MICAS: EFFICIENT Cs⁺ ADSORBENTS UNDER SUBCRITICAL CONDITIONS

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For the management of radioactive waste, a highly charged fluorophlogopite family, Na-Mica-n (n = 2 and 4, where n is the layer charge) has been synthesized. These synthetic micas are good cesium adsorbents compared to natural clays and bentonites. Both the percentage adsorbed and the distribution coefficient are greater for Na-Mica-4 than for Na-Mica-2 and natural clays, denoting an adsorption more specific in Na-Mica-4. There is an increase of the adsorption with increasing temperature and pressure.

Acknowledgments: Thanks to the Junta de Andalucía (Spain) and FEDER for Proyecto de Excelencia de la Junta de Andalucía, (P12-FQM-567), for F.J. Osuna’s training research grant and for Dr. Pavón’s grant from Andalucía Talent Hub Program (nº 291780). Thanks for the financial support of the ENRESA (contract nº 007900237) and the Spanish Ministerio de Economia y Competitividad (ref. MAT2015-63929-R).

Figure 1. Percentage of adsorption and Kd variation as functions of concentration and temperature in Na-Mica-4.
In recent times, a widespread recognition of the need to develop technologies and strategies for pollution control has arisen, and new synthetic clays have opened a new chance in this field. Organoclays derived from highly charged swelling micas have been tested for the removal of As$^{5+}$. An electrochemical method was applied to determine the arsenate in solution after the adsorption. The results demonstrated that those synthetic organomicas are good arsenate adsorbents compared to natural clays and bentonites.

Acknowledgments: Thanks to the Junta de Andalucía (Spain) and FEDER for Proyecto de Excelencia de la Junta de Andalucía, (P12-FQM-567), for F.J. Osuna’s training research grant and for Dr. Pavón’s grant from Andalucía Talent Hub Program (nº 291780). Thanks to the Spanish Ministerio de Economía y Competitividad for financial support (ref. MAT2015-63929-R).
IMPORTANCE OF DETRITAL CLAY MINERALS IN MEDIATING BIOGEOCHEMICAL PROCESSES AND CONTAMINANT DYNAMICS IN A COAL-MINE ACID-MINE-DRAINAGE-REMEDIATION SYSTEM

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More than two centuries of surface and underground coal mining operations in the Illinois Coal Basin have left a trail of environmental problems, including coal-mine drainage, one of the most pernicious forms of water pollution worldwide. There are numerous damaging environmental impacts of coal that occur through its mining, preparation, combustion, waste storage, and transport. The number of terrestrial ecosystems impacted by coal mine-generated acid mine drainage (AMD) has increased globally, thus directly influencing the intrinsic sulfur and metal cycles in watersheds impacted by coal mining. An imperative goal for AMD remediation research is to identify the mechanisms of contaminant transport and sequestration in natural and engineered systems impacted by coal mining pollution and to develop better technologies for contaminant control. Despite wide-scale adoption of coal-mine AMD remediation systems, surprisingly little is known about the role of nano- and micro-scale detrital particulates (nDP) inherited from the coal-mine waste in AMD contaminant dynamics.

In this study we evaluated the role of clay nDP in controlling the fate of AMD contaminants, using sediment cores collected in July 2013 from a bioreactor treating coal-generated AMD at the Tab-Simco site in Southern Illinois. These sediments formed on top of organic substrates over a six-year period during which the bioreactor had actively treated acidic, sulfate- and metal-rich mine drainages. Chemical and mineralogical characterization of sediments involved ICP-MS as well as synchrotron X-ray analysis, X-ray diffractometry, scanning electron microscopy, and Fourier transform infrared spectroscopy. Results reveal that clay nDP are relatively stable under low-pH conditions in both AMD and sediments. The acid-modified clay nDP have unique properties, including high surface-area to volume ratios and increased reactivity and catalytic properties; thus, they provided a unique framework for interrelated microbial and geochemical processes in the AMD remediation system. In the AMD sediments, depending on the prevailing conditions, the clay nDP catalyzed either (1) AMD contaminant immobilization by providing support for heterogeneous crystallization followed by precipitation of Fe(III)-rich minerals (e.g., schwertmannite and goethite) in the oxic zones or (2) AMD contaminant remobilization by promoting Fe(III)-mineral transformation and reductive dissolution in anoxic zones. We estimate that during the six years of bioreactor operation >90% of the S and >50% of the Fe initially sequestered in Fe(III)-rich minerals were remobilized into solution during diagenesis of the AMD sediments through mineral transformation and dissolution. Data obtained in this work underscore the need to re-evaluate the current understanding of contaminant dynamics in coal mine-impacted watersheds as well as the factors controlling the long-term performance of coal mine treatment systems.
THE MÖSSBAUER SPECTROSCOPIC SIGNATURE OF TETRAHEDRAL IRON IN SMECTITES

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The common coordination of iron in natural smectites is octahedral, but in some Fe-rich smectites it also is present in tetrahedral coordination. Some uncertainty exists, however, because the methods for measuring tetrahedral Fe have yet to be well developed and verified. A direct, simple method is still missing. A number of methods have been tried, including selective dissolution, XANES, and UV-visible and Mössbauer spectroscopy, but discrepancies and ambiguities are common. The goal of the present study was to focus on Mössbauer spectroscopy and to seek the best strategy for using that method to measure tetrahedral Fe in smectites. Five samples from the Source Clays Repository of The Clay Minerals Society were studied, namely ferruginous smectite SWa-1 and nontronites NAu-1, NAu-2, Garfield, and NG-1. The tetrahedral Fe(III) in these samples, which are believed to represent a wide range of tetrahedral Fe contents, was determined by other methods. Mössbauer spectra of powdered samples were obtained at room temperature and 4 K. Spectra were fitted using WinNormos-for-Igor, supplied by WissEl–Wissenschaftliche Elektronik GmbH, Germany. The starting model for fitting the room temperature Mössbauer spectra of all samples consisted of two subcomponents (doublets) with isomer shifts (IS) of ~0.35 mm/s and ~0.65 mm/s and quadrupole splittings (QS) of ~0.15 mm/s and ~0.5 mm/s, respectively, which are characteristic of octahedral Fe(III). An additional subcomponent (doublet) with IS of ~0.16 mm/s and QS of ~0.69 mm/s was also needed. This doublet is commonly attributed to tetrahedral Fe(III). These fittings were needed for all samples but were not entirely satisfactory, so a fourth subcomponent with IS ~0.35 mm/s and QS ~1.13 mm/s was added. This fitting model with four subcomponents provided the best match between measured and calculated spectra for all samples. The origin of the additional doublet is still unknown, but we hypothesize that it is also due to tetrahedral Fe(III), as its area increased with increasing tetrahedral Fe(III) content.

The Mössbauer spectra at 4 K revealed significant magnetic ordering (sextets) in the samples with greater tetrahedral Fe(III) content. The spectra for samples Garfield, NAu-1, and SWa-1, which have low tetrahedral Fe(III) content, were little changed from their corresponding room-temperature spectra, but samples NG-1 and NAu-2 with high tetrahedral Fe(III) content exhibited a high degree of magnetic ordering. The fittings of the spectra from sample NAu-2 at 4 K and NG-1 required four and two sextet subcomponents, respectively. The hyperfine field strengths corresponding to these sextets were 49.8, 47.7, 44.2, and 40.2 T for NAu-2 and 44.1 and 39.8 T for NG-1, respectively. Notice that two of these (49.8 and 47.7 T) are in the range that would be expected for octahedral Fe(III), but those below about 45 T are not. We, therefore, propose that the subcomponents with field strengths below 45 T are attributable to magnetic exchange interactions involving or influenced by tetrahedral Fe(III). In summary, two features of the Mössbauer spectra of Fe-bearing smectites may be useful for determining the tetrahedral Fe(III) content. The first of these is a fourth doublet at room temperature with IS ~0.35 mm/s and QS ~1.13 mm/s. The second feature is a magnetically ordered feature at 4 K, comprising two magnetically ordered components (sextets) with magnetic hyperfine field strengths below 45 T.
NITRATE REMOVAL AND REDUCTION BY REDOX-ACTIVE POLYMER-SMECTITE COMPOSITES

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Significant contamination of natural waters by nitrate and other anionic contaminants poses a risk to human health, but effective remediation methods that have minimal adverse impact on the environment are difficult to find. Recent studies in our laboratory revealed that reversed-charge, redox-active smectites significantly degrade nitrate. In these studies, however, the nitrate levels and speciation were measured only in the solution phase. A complete mass balance was, thus, not achieved because some of these species may have been retained in the solid phase. The objective of the present study was to fill this gap by measuring the presence of nitrate and its reduction products (such as ammonium) in the solid phase. Charge reversal was accomplished by uptake of a polymeric cation (polydiallyldimethylammonium or poly-(D), glucosamine (chitosan)), which overcompensated the cation exchange capacity, leaving a net positive charge on the clay mineral surfaces. This was followed by reduction of structural iron from Fe(III) to Fe(II) in the mineral structure. The positively charged surfaces attracted the redox-active anions (nitrate), which then were transformed to lower oxidation states by re-oxidation of Fe(II) back to Fe(III). Nitrite was the only reaction product found in the supernatant solutions, but it could not account for the amount of Fe(II) that was re-oxidized in the clay structure.

To explain this phenomenon, we hypothesized that some reaction products (ammonium and/or nitrite), as well as unreacted nitrate anions, were adsorbed on the composite surfaces. The polymer-clay solid phase was, therefore, analyzed for these species. The procedure was as follows. Chitosan in aqueous suspension at three different concentrations (0.075, 0.15, and 1.0 g/L) reacted with the fine fraction (<2 µm) of Na-saturated ferruginous smectite (SWa-1) to form clay-chitosan reversed-charge composites. All prepared composites were chemically reduced by sodium dithionite and then washed free of excess salts before use in the experiments. For reaction of the composites with sodium nitrate, a controlled atmosphere liquid exchanger apparatus and inert-atmosphere reaction tubes were used to provide an oxygen-free environment. The final supernatant solutions were analyzed for NH₄⁺-N, NO₃⁻-N, and (NO₃⁻ + NO₂⁻)-N.

The residual solid phase of the composite was then re-dispersed and washed with sodium chloride to remove adsorbed nitrogen species. This process removed both ammonium cations and nitrate anions that remained in the solid phase. The relative amounts depended on the initial loading of chitosan in the composite. The largest amount of ammonium was found in the composite loaded with chitosan at 0.15 g/L.
REVISITING THE MECHANISMS OF CLAY DAMAGE: EFFECT OF Na\(^+\), K\(^+\), AND Ca\(^{2+}\) ON STABILITY OF MONTMORILLONITES

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Molecular dynamics simulations were used to investigate the underlying mechanisms of water interaction with Wyoming-type montmorillonites. The study focused on (1) the swelling of montmorillonites, whose countercations have different ionic radius and charge, and (2) the stability of the tetrahedral and octahedral sheets that make up montmorillonite layers under insertion of water. Simulations show that the ionic radii of the cations and their hydration energies are the critical factors that determine the distribution of cations and water molecules in the interlayer space. The differences in cation distribution provide the microscopic explanation of why saturation of smectites with K\(^+\) cations retards clay damage when compared to saturation with Na\(^+\) and Ca\(^{2+}\) cations.
INFLUENCE OF NEUTRON IRRADIATION ON PHYSICOCHEMICAL PROPERTIES OF CLAY MINERALS

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In the last four decades information has been collected on effects of different kinds of ionizing radiation on the evolution of the physicochemical properties of several clay minerals, e.g. in the context of clay barriers in radioactive waste disposal (Allard et al., 2013). Various types of radiation (α, β, γ, and heavy ions) and doses were investigated. Most clay minerals show important concentrations of different radiation-induced (paramagnetic) point defects in the crystal structure. Other effects are amorphization and reduction of structural iron. The impact on physicochemical properties of clays, however, was found to be generally weak (Plötze et al., 2003; Holmboe et al., 2011). Up to now the greatest emphasis was given to investigating the effect of γ-radiation. However, there are no studies of the influence of neutron irradiation.

In the present work, the effect of neutron irradiation on physicochemical parameters of various clay minerals (Na- and Ca-smectite, illite, kaolinite, and vermiculite) was investigated. Neutron radiation has, as does gamma radiation, a high penetration power. Thus, the neutrons penetrate a sample and influence not just the surface. All clay samples were exposed to an effective neutron fluence of approximately $2 \times 10^{15}$ n/cm$^2$. Parameters determined after the cooldown are the cation exchange capacity (CEC), main layer charge, water sorption behavior, specific surface area, and "crystallinity." Results show that the specific surface area, particularly of the smectites, decreased strongly (up to 40%) owing to the neutron irradiation. No significant influence on water absorption, however, was found. Also, the CEC, the main layer charge, and the "crystallinity" of the clay minerals did not respond to neutron irradiation.

SOLID STATE NMR STUDY OF CRYSTAL CHEMISTRY AND PATHWAYS OF FORMATION OF ZINC-ALUMINUM LAYERED DOUBLE HYDROXIDES

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Layered double hydroxides (LDHs) are naturally occurring and synthetic compounds with a general chemical composition of [M(II)1-xM(III)x(OH)]x+[(A)x/n]n− where M(II), M(III), and A− denote divalent metal ions, trivalent metal ions, and anions, respectively. LDHs find application in drug delivery, catalysis, and environmental science owing to their anion exchange capability, which originates from cation substitution in the metal hydroxide sheets. Detailed knowledge about the cation distribution is essential, as it can help to understand the function of LDHs and thereby to improve their performance. Nevertheless, this information is difficult to obtain because of the structural complexity of LDHs. For example, supercell-lattice reflections are often are very weak because of the many micro-crystalline defects (stacking faults etc.) commonly seen in synthetic LDHs, which makes diffraction techniques less suited for studies of cation ordering. Solid state NMR (SSNMR) spectroscopy has emerged as a strong tool to probe the cation ordering in LDHs, as demonstrated successfully in Mg-Al1-3 and Mg-Ga4 LDHs, as SSNMR is a sensitive probe of the local environment. The current work is a detailed investigation of how the choice of synthesis parameters affects the crystal chemistry of Zn-Al LDH prepared with a Zn:Al ratio of 2:1, i.e., a theoretical composition of Zn0.67Al0.33(OH)2(CO3)2−, NO3−∙nH2O. 1H, 27Al, and 67Zn SSNMR studies of samples prepared under various synthetic conditions show, e.g., that the method of synthesis, synthesis pH, and post synthesis treatment (Figure 1) all have dramatic impacts on LDH properties such as crystallinity, purity, and local defect concentration.5 In addition we will discuss the results from a time resolved SSNMR and PXRD study of LDH formation, which provides new information about the pathways for LDH formation and the existence of Al-O-Al defects observed by SSNMR.3,5 Overall our work provides novel details about the crystal chemistry of LDHs and demonstrates that SSNMR is a strong technique for studies of complex materials.

DIRECTLY MEASURING MODEL SOIL ORGANIC-MINERAL INTERACTIONS AT THE MOLECULAR AND NANOMETER LENGTH SCALES

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Approximately 80% of Earth’s terrestrial organic carbon is stored in soil; this carbon pool contributes significantly to the carbon cycle, and knowledge of it is crucial to predicting climate and sustaining ecosystem services. In particular, detailed mechanisms describing the residence time of the carbon in soils is lacking. Soil organic matter (SOM) can associate strongly with high-surface-area clay minerals, providing a mechanism for aggregation as well as carbon stabilization. The nature of these interactions is not well understood; thus, directly quantifying and visualizing these interactions at the nanometer length scale will allow us to provide inputs into models to better predict the role soil organic matter has in the carbon cycle.

In the work presented here, we sought to systematically probe physical, chemical, and molecular-level interactions at the organo-mineral interface. By implementing dynamic force spectroscopy, we have begun to explore the energy landscape of individual functional groups (including carboxylic acid, amine, methyl, and phosphate groups) to directly measure the binding energies to the model soil minerals muscovite and goethite (Figure 1). Additionally, the measurements can be performed while varying environmental conditions such as pH, ionic strength, and buffer type. Our results suggest that altering the chemistry of the functional group results in binding forces that span from 80 pN to 300 pN, but varying the environmental conditions plays a more significant role, especially in the case of charged functional groups that directly interact with the mineral surfaces. For example, our studies show that a carboxylic acid group binds strongly to muscovite mica ($\Delta G_{bu} = 12.9$ kJ/mol) at ambient pH (pH ~6) and at an ionic strength of 10 mM; however, reducing the pH from 6 to 4 results in binding strengths greater by an order of magnitude.

To evaluate the phenomena at larger length scales, we have begun to apply in-situ transmission electron microscopy to the established model system described above. In particular, we are quantifying the dynamics of mineral particles as they are exposed to model soil organic matter to determine the forces that lead to aggregation events.
VOLCANICLASTIC SEDIMENT DIAGENESIS: INSIGHTS FROM THE HOMININ SITES AND PALEOLAKES DRILLING PROJECT AT LAKE MAGADI, KENYA

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Sediment cores have been collected at Lake Magadi in southern Kenya to construct high-resolution paleoenvironmental records of Pleistocene climate change. The goal of this project is to understand environmental and climate change in East Africa over the past several hundred thousand years and the possible impact of that change on hominin and vertebrate evolution, as well as on the development of stone tool technology. X-ray diffraction analysis of core samples obtained during the Hominin Sites and Paleolakes Drilling Project at Lake Magadi indicates that the lake waters have alternated between geochemical regimes that favored precipitation of calcium carbonate minerals during less-saline, less-alkaline phases, and favored zeolites as waters became more concentrated and alkaline.

Calcium carbonates and clay minerals are the primary authigenic mineral groups that formed during the basin’s earliest history, because the lake was either hydrologically open or supplied with sufficient dilute inflow to limit evaporative concentration. At ~100 meters below the sediment surface, the mineralogical record from Lake Magadi indicates that the geochemistry of the basin changed as conditions became increasingly more saline and alkaline, which apparently favored zeolite formation. The alkalinity was likely increased by low-temperature surface weathering and hydrothermal CO₂ outgassing. Abundant zeolites throughout the upper half of the cores suggest Lake Magadi was hydrologically closed for much of the Late Pleistocene, perhaps recharged primarily by alkaline springs at the lake margin as in the modern environment.

The most common zeolites in the cores are analcime and erionite. Phillipsite, chabazite, clinoptilolite, and mordenite are also present. Analcime seems to have formed under a variety of conditions that ranged from dilute surface waters to concentrated brines. Erionite was formed mainly by the reaction of trachytic glass with brine. Other zeolite phases formed from precursor zeolites or clay minerals that reacted with concentrated brines (e.g., erionite + Na⁺ → analcime) or as tuffaceous sediments reacted with dilute interstitial or surface waters (e.g., trachytic glass + Ca²⁺ or K⁺ → phillipsite). The cores contain only a few thin volcaniclastic deposits from a region known for abundant volcanism during the Pleistocene, implying that most of the volcaniclastic material was altered to zeolites or clay minerals. These data suggest Lake Magadi’s geochemical variation during the Pleistocene was a product of hydrothermal activity associated with rift tectonics in southern Kenya.
ORIGIN OF HALLOYSITE AND KAOLINITE BY ALTERATION OF EARLY-STAGE PEDOGENTIC SMECTITE AND KAOLINITE-SMECTITE: IMPLICATIONS FOR UNDERSTANDING AND PREDICTING TROPICAL SOIL MINERALOGY

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Tropical soils are mineralogically and chemically diverse, ranging from leached, nutrient-depleted Oxisols and Ultisols rich in halloysite or kaolinite to less-evolved Inceptisols rich in interstratified kaolinite-smectite (K-S), smectite, dioctahedral vermiculite, or related 2:1 clays. Given the strong influence of clay minerals on soil quality in the tropics, enhanced knowledge of factors influencing their occurrence is important for modelling and managing tropical environments. This study of a terrace chronosequence in the moist tropics (Nicoya Peninsula, Costa Rica) examines the effects of 120 thousand years (ka) of soil formation on rates and mechanisms associated with the alteration sequence of smectite to kaolinite by way of intermediate K-S and halloysite. Parent material is dominantly beach sediment on uplifted terraces with flat surfaces and low slopes; mean annual precipitation is 3000 ± 200 mm and mean annual temperature is 27 °C. These conditions are typical of many moist tropical environments.

Iron-rich smectite (11.6 ± 2.2% Fe2O3, anhydrous basis) is the dominant mineral in soils on Holocene terraces (1–8 ka); it forms during early-stage pedogenesis from precursor plagioclase and clinopyroxene with accessory quartz and, in some localities, volcanic glass, heulandite, or calcite (shell fragments). During the first 50 ka, pedogenic smectite is stripped of tetrahedral sheets and also fixes Al into interlayers, causing transformation to K-S that inherits flaky smectite

Figure 1. The progression of the clay mineral reaction sequence is illustrated here by representative TEM images. “ka” = thousand years. Pedogenic smectite forms during early chemical weathering from parent material (mainly plagioclase and clinopyroxene) and becomes the dominant soil mineral after 1000 years of soil formation. Smectite persists for ~8000 years, the point at which leaching of Si has occurred to the extent that tetrahedral sheets become unstable; the resulting stripping of tetrahedral sheets triggers lateral transformation of 2:1 smectite layers to 1:1 kaolinite layers, thus forming K-S. Continued leaching over time eventually drives the system to halloysite and kaolinite by the two reaction mechanisms shown above.
crystal habit. In 50 ka soils, K-S is the dominant soil mineral, particularly in C-horizons where it constitutes ~90% of soil clay; flaky Fe-kaolinite (with 5–15% residual smectite layers) and spheroidal and tubular halloysite (mean 7.8% Fe$_2$O$_3$) also occur in 50 ka soil and increase upward in the soil profile. The oldest soils in the chronosequence (120 ka) are dominated by flaky Fe-kaolinite (with < 10% residual smectite layers) and spheroidal and tubular halloysite (mean 4.9% Fe$_2$O$_3$). Fe-poor hexagonal kaolinite is also present in the oldest (120 ka) soils, constituting 5–10% of soil clay, indicating that formation of this type of kaolinite, perhaps the most abundant mineral in tropical soils globally, required ~100 ka in this moist tropical environment.

Changes in crystal chemistry of the soil clay minerals (decreasing Fe and Mg, increasing Al) over time reflect two reaction mechanisms. The first is layer-by-layer, cell-preserved transformation of smectite layers to kaolinite layers that accompanies conversion of smectite to K-S—this transformation mechanism results in the formation of flaky Fe-rich kaolinites with smectite crystal habit. The second mechanism involves dissolution of K-S followed by neoformation of spheroidal and tubular halloysite. The likely sequences of reactions, defined by the changes in chemistry, are: (A) smectite $\rightarrow$ K-S $\rightarrow$ Fe-kaolinite (solid state, cell-preserved), and (B) smectite $\rightarrow$ K-S $\rightarrow$ spheroidal halloysite $\rightarrow$ tubular halloysite (dissolution-precipitation). Neoformation of hexagonal kaolinite with low Fe (< 3% Fe$_2$O$_3$) follows dissolution of Fe-kaolinite or halloysite after 100 ka of soil development. Based on other reports in the literature, this reaction sequence is likely common in moist tropical soils, and the time constraints presented by the Nicoya chronosequence can be applied to modeling soil composition in landscapes where soil age is known or can be inferred. These findings are especially pertinent for tropical environments where tectonic, volcanic, or geomorphic activity periodically exposes (e.g. by uplift, deposition, or erosion) fresh, unweathered parent material; periodic soil renewal will result in a range of soil ages.
CROSS-DISCIPLINE FERTILIZATION OF CLAY SCIENCE AND NANOTECHNOLOGY FOR ENVIRONMENTAL REMEDIATION

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Environmental pollution is a growing public concern worldwide. Numerous materials including nanoparticles are being investigated towards the development of technologies for cleaning up contaminated soil, water, and air. Many of these technologies hold significant bottlenecks for widespread industrial uptake due to prohibitive costs and low performance.

Natural materials such as clay minerals are inexpensive, highly adsorptive, and available abundantly throughout the world. They hold great potential as materials useful in remediation of environmental contamination, both with and without modification. Many clay minerals occur naturally in particles with one or more nanoscale dimensions. For example, the average diameter of halloysite and palygorskite tubes can be <50 nm and <10 nm, respectively. The diameter of a spherical allophane particle can be as small as 3 nm. Additionally, deposition or grafting of reactive nanoparticles on clay minerals can impart additional adsorptive and catalytic properties to clean up target contaminants in the environment. Major groups of such clay-nanocomposite materials include nanoscale zero valent iron (nZVI) grafted clays, clay-polymer composites, clay-carbon composites, etc. Through physical attraction mechanisms (e.g., van der Waals interaction) the clay minerals serve as a host for the synthetic nanoparticles, and thus reduce their unwanted mobility in the environment.

This paper highlights recent advances in cross-disciplinary research in clay science and nanotechnology to find efficient technologies for cleaning up environmental contaminants. It demonstrates several successful examples of treating diverse contaminants in soil, water, and air environments using clay-based nanomaterials. These include degradation of warfare chemical analogues by clay-nZVI nanomaterials, adsorption of heavy metals (such as lead) and toxic gases (ammonia and chlorine) by clay-polymer nanocomposites, adsorption of organic dye compounds by clay-carbon nanocomposites, and enhanced bacterial degradation of polycyclic aromatic hydrocarbon compounds by biocompatible organoclays. The paper also introduces the scope for synthesizing high end nanomaterials (e.g., carbon nanotubes) using clay minerals. The results indicate a highly promising future for research in this interdisciplinary area, which potentially can deliver a cost-effective and green solution to the ever increasing environmental contamination issue.
DEEP REGOLITH BULK MINERALOGY OF THE CALHOUN CRITICAL ZONE OBSERVATORY USING X-RAY POWDER DIFRACTOMETRY

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Deep coring into the regolith beyond several meters is common practice in engineering disciplines, but it has not been traditionally performed in the soil and earth sciences. Critical zone science now recognizes that biogeochemical weathering fronts propagate 10s of meters below the land surface and this collective zone is a key link to understanding the long term cycling of elements. Quantifying the changes in mineral composition throughout these deep profiles is paramount to mass-balance studies, which further lead to understanding landscape denudation and chemical effluxes in, out, and across this zone. Using X-ray powder diffractometry (XRD) we studied a 60 m deep core taken at the Calhoun Critical Zone Observatory (CCZO) located on Paleozoic granitic gneiss in the Piedmont of South Carolina (Bacon et al., 2012).

Aliquots were ground in 10 ml of ethyl alcohol using a McCrone® mill with corundum pucks. Zincite (ZnO) was added at ~9% by weight. Samples were air-dried and back-fill mounted using 200 psi to minimize sample transparency. A Bruker D8 Advance® with Co radiation was used for XRD experiments. Bruker Topas® software was used for Rietveld refinement (Young, 1993). Crystallographic Information Files (.cif) containing structure data were mostly retrieved from the American Minerologist Crystal Structure Database. Patterns were initially best fit for quantitative abundance using initial structural data values. Unit cell parameters were then refined sequentially to allow for controlled convergence on the minimized solution. Phyllosilicates and feldspars that exhibited perfect cleavage had a preferred orientation factor entered into the refinement process. Full pattern refinements were conducted over the range of 5° to 75° 2θ with weighted profile R-factors minimizing on values between 14 and 20. No complete .cif structure file existed for hydrobiotite, therefore a one-dimensional pattern was simulated using the data of Brindley et al., (1983). Ideal mineral compositions were used to calculate the bulk chemistry from bulk mineralogy. These data compare favorably to mass loss values (tau) calculated from independent chemical analyses of the same samples. Chemical alteration indices (CAI) were also determined, revealing good correlation with other independent geophysical measures.


USING THE SCIENTIFIC UNDERSTANDING OF BENTONITE TO DEVELOP TECHNICAL DESIGN REQUIREMENTS FOR A NUCLEAR WASTE BARRIER

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The strategy for direct disposal of spent nuclear fuel in a KBS-3 repository is similar in Sweden and Finland. In both countries license applications for a final repository have been submitted and these are currently in a review process.

A KBS-3 repository consists of the rock at the repository site, the canisters containing spent nuclear fuel, buffer, backfill and closures as well as engineered and residual materials that remain in the rock once the underground openings have been backfilled and closed. The buffer surrounds the canister and fills the space between the canister and the bedrock. The buffer consists of clay containing a swelling material (bentonite). The primary safety function of the buffer is to provide predictable mechanical, geochemical, and hydrological conditions that support the containment function of the canister. Secondly, in case of loss of the containment provided by the canister the buffer is to prevent and retard the dispersion of radioactive substances from the canister to the bedrock.

Based on the understanding of the properties of the components and the long-term evolution of the system, a number of safety functions subordinate to containment and retardation can be identified. In this context, a safety function is defined as a role through which a repository component contributes to safety. The defined safety functions for the bentonite buffer are to:

- limit advective transport
- limit microbial activity
- keep the canister in position
- prevent damp rock shear
- be compatible with the other barrier

The design cannot be directly determined from the required safety functions. The safety functions together with the identified conditions and stresses form the basis for the development of a design with characteristics that are potentially capable of maintaining the safety functions in a long time perspective. The technical design requirements need to be based on properties that can be measured, controlled, and verified during manufacturing and installation of the components. Most of the properties needed to fulfill the safety functions are related to the dry density, which is a function of the installed mass and the excavated volume and can be controlled during installation. This also means that specific relations between the desired properties—hydraulic conductivity, swelling pressure, microbial survival, and shear strength—and the dry density have to be derived for all bentonite materials of interest. However, these tests are generally time-consuming and can therefore not be used directly for the quality control of large shipments of bentonite. Other tests, such as CEC measurements, will therefore be used to confirm an even quality of a given material.
DRILLING INTO NEW DEPTHS OF CLAY SCIENCE

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Over the past decades, advanced analytical techniques, especially those involving synchrotron-based radiation, have provided clay scientists important tools to investigate biogeochemical reactivity at mineral interfaces at small spatial and temporal scales. In my career, these tools have been applied to enhance understanding of sorption and desorption, precipitation, and redox processes involving clay minerals, metal oxides, and complex soils. Emphasis in this presentation will be placed on studies involving the formation and reactivity of mixed metal–Al layered double hydroxides, oxidation of metal(loid)s on manganese oxides, and carbon-mineral complexation mechanisms.
EDIAACARAN CLAYS OF THE EAST EUROPEAN CRATON – A UNIQUE RECORD OF THE PALEOENVIRONMENT

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Discoveries of the first multi-cellular forms of life during Ediacaran time (635-542 Ma) inspired intensive research on the Ediacaran rocks, to reconstruct the Earth surface conditions during this period. The major difficulty of such studies is the diagenetic or metamorphic overprint that affected all well-known and widely studied Ediacaran profiles. The Ediacaran rocks cover a major portion of the East European Craton. In the NW part of the craton, selected for this study, the Ediacaran rocks were not affected by major diagenetic alterations, as indicated by several lines of evidence. Over 1600 samples of Ediacaran rocks were collected from Russia, Estonia, Lithuania, Belarus, Poland, and Ukraine and studied first by quantitative XRD to establish mineral composition. These preliminary results are reported here.

The section begins with a series of tillites and fluvioglacial deposits (Vilchanskya Series) of unconstrained age, deposited over sandstones (Orshanskaya Series) and locally over dolomites (Lapickaya Series). The clay fraction of these continental glacial deposits (kaolinite, illite, illite-smectite and fine-grained hematite) is identical to that of the older Penskaya Series, indicating glacial transport from the west. Kaolinite and hematite are clearly products of weathering prior to the glacial period.

The overlying Volynskaya Series, dated at 560-570 Ma, contains basalt flows, tuffs, and tuffites. A pure dioctahedral smectite was identified in the bottom tuffites, indicating a smectite-type weathering in this period. The main body of basalts and tuffs contains zeolites, saponite, chlorite, mixed-layered chlorite-saponite and aluminoceladonite, interpreted as products of hydrothermal alteration. In the weathering profiles, developed on the top basalt flow, a transition from saponite or chlorite into dioctahedral smectite and then towards kaolinite+hematite was detected. The transition is complete if the exposure to weathering lasted sufficiently long. Such composition of the weathering crusts is indicative of a wet and hot climate. The weathering products are identical to those of the Recent.

The Redkino and overlying Kotlin Series are sediments of marine transgression. They contain abundant kaolinite and fine-grained hematite, implying that the nature of weathering did not change since the pre-Ediacaran times. In a broad range of sedimentary environments from fluvial to marine, hematite is reduced and kaolinite is altered into berthierine, which is indicative of a hot, equatorial climate.

Acknowledgment: The authors acknowledge financial support from the Polish National Science Centre MAESTRO grant 2013/10/A/ST10/00050.
ABSTRACTS

SWELLING OF MONTMORILLONITE WITH Divalent Interlayer Cations in Liquid Water – Effect by Cation, Layer Charge, and Temperature

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Most montmorillonites with divalent interlayer cations such as Ca are known to form a 19 Å basal spacing (three water layers; W3) when placed into water, but have been observed to sometimes swell and partly form a 21 Å basal spacing (W4) upon cooling [1]. The current study aimed at investigating this effect further using synchrotron X-ray diffraction and three montmorillonites with different layer charges, ion-exchanged with divalent Ca, Cu, Mg, Sr, and Zn (Wyoming, USA) or with Ca, Mg, and Zn (Milos, Greece; Kutch, India). The temperature was cycled between 20 and −50 ºC, or between 20 and 90 ºC, and the solid/water mass ratio was kept constant at 30% solid. It was observed that Ca and Sr Wyoming montmorillonite formed W4 during cooling, while Mg, Cu, and Zn Wyoming montmorillonite partly formed W4 already at 20 ºC and at lower temperature the W4/W3 intensity ratio increased further until ice was formed. After ice formation the smectites were dehydrated to 16 Å (W2). Neither the Milos nor Kutch montmorillonites (Ca, Mg, Zn) were found to form the W4 phase during cooling. Lower charged montmorillonite (Wyoming) expanded further compared to montmorillonites with higher charge (Milos and Kutch). Lower temperature caused the montmorillonites to expand to different extents until ice was formed. Higher Gibbs hydration energy of the interlayer cation allowed further hydration and expansion (Sr < Ca < Mg < Zn < Cu). The results contribute to an improved understanding of the crystalline swelling of smectites with divalent interlayer cations in complex applications and may be input for future model calculations.

ABSTRACTS

THE SETO-TONO KAOLIN FIELD, THE LARGEST SEDIMENTARY KAOLIN CLAY DEPOSIT IN THE JAPAN ARC

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The Seto-Tono district is the largest kaolin field in the Japan Arc. The kaolin products have been used mostly for ceramic industries, and the production of chinaware in the district accounts for more than 70 percent of the domestic market. The kaolin clay-bearing formations (lower Seto Group) comprise late Miocene to Pliocene fluvial and lacustrine sediments. The formations occur as small sedimentary basins 1 km$^2$ to 10 km$^2$ in area, and about 20 sedimentary basins are closely distributed in an area 20 × 50 km. The lower Seto Group unconformably overlies Paleozoic to early Miocene basement rocks, and is conformably overlain by the thick, coarse sediments of the upper Seto Group (e.g., Fujii 1968, Rep. Geol. Surv. Japan, 230, 56p; Nakayama 1991, Jour. Geol. Soc. Japan, 97, 945-958).

The kaolin clay deposits can largely be classified into three types; 1) gaerome, 2) kibushi, and 3) silica sand. Gaerome (frog eye) clay comprises arkose sandstone beds up to 10 m thick and suffered intense kaolinization. Granite-derived minerals except for quartz were mostly altered to kaolin clay or leached out; gaerome clay simply consists of kaolin clay and quartz sand. Kibushi (lignitic) clay comprises fine-grained kaolin clay and organic materials with ligneous fragments, showing chocolate-like texture. Kibushi clay occurs as well-stratified beds 0.5 to 6 m thick. Silica sand occurs as beds 1 to 30 m thick, comprising quartz sand and pebbles with small amounts of kaolin clay. In general, kibushi clay tends to be abundant northeastward and silica sand beds are thickened southwestward in the Seto-Tono district.

Kaolin clay of the deposits is basically composed of kaolinite with subordinate halloysite and trace amounts of smectite and illite. The parent materials of the kaolin clay should have been feldspars and mica derived mostly from Cretaceous granitic rocks distributed in the east of the district. The following occurrences suggest that most kaolin clay is not detrital in origin but authigenic: 1) homogeneous gaerome clay beds without sorting, 2) kaolinized tuff beds in the deposits, and 3) kaolinized weathering crusts of basement granite beneath the deposits.
GEOCHEMICAL EVALUATION PREVENTS PRODUCTIVITY LOSS IN THE GORGON FIELD, OFFSHORE WESTERN AUSTRALIA

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Gorgon’s eight gas wells contain completions that range in temperature from 144°C to 163°C (291°F to 325°F), cover 900 meters of section, and have top depths ranging from 3500 m to 4000 m tvdss. Reservoir sands vary in thickness from 5 to 65 meters. In Gorgon, Triassic Mungaroo Formation sands contain abundant authigenic kaolins as pore fillings and grain replacements. Prior to completion operations, formation integrity was questioned because of expected completion brine losses, high interval temperature, brine chemistry, and multi-year stand time after batch completion. Native kaolin minerals were speculated to be capable of dissolving and back-precipitating zeolites because initial completion brine pH was designed at 9.8. Zeolite growth can be a porosity-loss process if zeolite precipitates at the expense of higher-density parent minerals. This near-wellbore formation damage risk was thought to warrant further investigation.

Laboratory experiments were designed and run at 160°C, and SEM analyses were conducted before and after the experiments. Experiments were modelled with Geochem Workbench. All eight flow-through experiments were run with brine made up from Gorgon supplier materials, and pH was varied from 9.8 to near neutral. Zeolite growth was confirmed in high pH laboratory tests and shown to be viable by chemical modelling. Measured post-flood permeability ranges from 100% to 72% of initial. Although permeability loss was not correlated specifically to observed zeolite growth (analcime produced in only one of eight tests), the laboratory tests were conducted in only 4 weeks, which is 4% of actual Gorgon soak time. Zeolite morphology and chemistry are consistent with analcime, a Na zeolite type.

Laboratory tests were finished in time to consider results before Gorgon wells were completed. Completion brine pH, viewed as a critical factor in formation reactivity, was changed to a near neutral pH as a result of this testing. Field procedures were modified further to allow the neutral pH fluid in the 7” liner and 7 5/8” tubing during perforation, while the pH 9.8 brine remained above the production packer for corrosion control. Completion perforation operations were conducted successfully, and post-completion flowbacks produced as expected.

In summary, this set of geochemical experiments illustrated a downside risk for the field clearly enough that completion plans were altered. We believe that the integrity of the gas-producing formation and the revenue stream were maintained through thoughtful characterization and geochemical planning, execution, and knowledge sharing.
ANALYSIS OF NANO-PARTICLES IN CLAYS WITH A SMALL-ANGLE X-RAY SCATTERING METHOD

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Clays have high small-angle X-ray scattering intensities. The X-ray scattering intensities of clays at 1.0 degree in 2θ are 10 to 100 times higher than that of quartz. We consider that these high-intensity small-angle scatterings may come from nano-particles in clays. Therefore, we have tried to fit calculated scattering intensities with the observed ones assuming that small-angle scatterings of clays are from spherical nano-particles in the clays.

Figure 1 shows the observed and calculated small-angle intensities of hard kaolin from Georgia. We have successfully fitted the calculated intensities with the observed ones. In this calculation, we assumed that the average diameter of nano-particles is 7.2 nm and the standard deviation of the diameter distribution is 2.3 nm. We also assumed that the distribution of the distance between the centers of two spheres has a structure (Figure 2). A first peak appears at 7.0 nm in Figure 2, which corresponds to the distance between the centers of two spheres in contact with each other. A second peak appears at 13.3 nm, but it is unclear why the second peak appears at this position. At distances larger than 15 nm, the occupancy decreases with increasing distance, which may be due to the presence of secondary particles.

Figure 1. Small-angle scattering intensities

Figure 2. Distribution of distances between the centers of two spheres
ION ADSORPTION AT SMECTITE CLAY MINERAL SURFACES: THE HOFMEISTER SERIES FOR HYDRATED SMECTITE MINERALS

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Many important properties of anionic clay minerals are dictated by the species of charge-balancing cation. Phenomena such as clay swelling and cation exchange are heavily dependent upon the character of such cations, and it is therefore important to understand at a fundamental level how the cations bind with the mineral surface.

In this study, the binding affinities of several cations at the surfaces of smectite clay minerals have been calculated using the well-tempered metadynamics algorithm. The results follow a Hofmeister series of preferred ion adsorption to the smectite basal surfaces of the form: K⁺ > Na⁺ > Ba²⁺ > Ca²⁺ > Cs⁺. Furthermore, the results elucidate the energetically favorable positions of the ions above the clay basal planes, whilst simple Boltzmann population analysis of the free-energy profiles is shown to describe the key features of ionic density profiles surrounding the clay surfaces, Figure 1. It is also shown that the key features of the free energy profiles can be described as due to the overlap of the hydration layers of the ion and the mineral surface [1].

Ultimately, the results provide insight into the mechanisms of adsorption of several ionic species upon smectite clay minerals and are relevant to many phenomena thought to be affected by cation exchange, such as nuclear waste disposal, herbicide and pesticide–soil interactions, and enhanced oil recovery.

MOLECULAR DYNAMICS SIMULATIONS OF LOW-SALINITY ENHANCED OIL RECOVERY

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The aim of this research is to bring clarity to the fundamental mechanisms of clay-oil-brine interfaces that underpin low-salinity enhanced oil recovery (EOR), a technique whereby sea water, partially desalinated, is used and will be used in the future to push increasing amounts of crude oil from oil reservoirs, increasing the reservoir lifetime and overall production. The phenomenon of low-salinity EOR is thought to be due to the complex interactions between the organic oil compounds, the clay particles, and the salt ions within the reservoir.

Using large-scale molecular dynamics simulations to model the interactions of several different clays (montmorillonite, kaolinite, and illite) interacting with various model oil compounds, we have been able to analyze the phenomena of low-salinity EOR at the molecular level, Figure 1.

Our work presents an increasingly high-resolution picture of low-salinity EOR, whereby it is observed that the effects of double layer expansion cannot explain the phenomenon of low-salinity enhanced oil recovery. Rather, the results show that it is the pH level surrounding the clay in conjunction with the presence of divalent cations that is the determining factor driving the titular effect [1, 2]. The research highlights several key conditions required for a low-salinity EOR flood to function, and successfully presents how nanoscale simulations can help describe macroscopic phenomena.

FATE AND TRANSPORT OF SOLUTES IN ASTEROIDAL AQUIFERS - OR - SERPENTINE TELLS US (SOME OF) WHAT WAS IN THE WATER ON THE PARENT BOD(Y/IES) OF CM CARBONACEOUS CHONDRITES

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Previous work has established that the abundances of scientifically important organic compounds in carbonaceous chondrites increase with increased extent of aqueous alteration of the chondrites. The degree of aqueous alteration of CM and CI chondrites is widely understood to be measurable (albeit with limited resolution) in the abundances and Mg/Fe systematics of the volumetrically abundant phyllosilicates of these chondrites.

Dissolved Mg increased, and dissolved Fe decreased, with time in transient pore fluids of CM chondrites. Dissolved Fe dominated early, released from fast-reacting Fe-rich metal, sulfides, and Fe-rich primary anhydrous silicates. Fe-rich fines formed by alteration early in solute evolution. With continued alteration, Fe-rich reactants were progressively consumed and coarser, slower-reacting, Mg-rich reactant crystals (e.g., olivine and pyroxene in chondrules and isolated fragments) continued to react with transient pore fluids. More Mg-rich, nearly homogenous, ferroan serpentine (serpentine-greenalite solid solution) partially replaced olivines of diverse compositions during commonly incomplete and arrested alteration of coarse olivine in chondrules. The excess Mg and Si exported during formation of serpentine partial pseudomorphs after Mg-rich olivine and pyroxene dominated the more extensively evolved aqueous solutions, and were available to be incorporated into other phases spatially separate from the coarse chondrule-hosted reactants, including matrix Mg-rich serpentine. Mg-rich ferroan serpentines of similar compositions in the fine-grained rims and matrix and in pseudomorphically partially replaced olivines likely formed concurrently. The relative proportions of Fe(II) and Fe(III) in the serpentine-group minerals can be estimated from EPMA, charge balance, and site occupancy. Fine-grained and early-altered matrix and rim phyllosilicates are Fe-rich (e.g., cronstedtite), containing both Fe(II) and Fe(III). The dominance of Fe(II) in late-stage serpentine-greenalite (relative to the earlier, cronstedtite-forming alteration) indicates that the transient aqueous solutions became more reducing with overall reaction progress. These abundant ferroan Mg-phyllosilicates may be the dominant host phases for organic compounds in CM chondrites.

Variations in the apparent (bulk-sample) degree of aqueous alteration, according to a variety of different alteration metrics and scales, exhibit trends that may be partially explained by mechanical volumetric mixing of clasts with different degrees of alteration, in proportions that vary among individual CM chondrites. In selection of sample sites on the CM- and CI-like target asteroids of the Hayabusa 2 and OSIRIS-REx sample return missions, consideration of the overall degree of aqueous alteration of the regolith clast population will be required if samples with the largest proportion of highly altered, phyllosilicate-rich clasts are to be collected.
THE “IDDINGSITE” OF MARS

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Much of what is identified as clay minerals in Mars meteorites is classified on the basis of composition (by EPMA or EDS) and association. Among Mars meteorites, only nakhlites (clinopyroxenite meteorites from Mars) contain noteworthy abundances of phyllosilicate-like materials. The material called iddingsite in Mars meteorites resembles its terrestrial counterpart (a smectite-hydroxide assemblage) in its elemental composition and in being associated exclusively with olivine, but differs in being volumetrically dominated by amorphous material lacking the systematic crystallographic relationships with the reactant olivine that are common among terrestrial iddingsites examined by optical petrography.

Some structural data from TEM SAED exist for the material called iddingsite in nakhlites. Most iddingsite in nakhlites lacks crystal structure at TEM scale. TEM lattice-fringe images from the phyllosilicate component of nakhlite “iddingsite” indicate \( d(001) = 1.1 \pm 0.2 \) nm (consistent with collapsed smectite-group clay minerals) in almost half (four) of the presently known nakhlites, associated in two of the nakhlites with a phyllosilicate with \( d(001) = 0.7 \) nm (consistent with serpentine-group minerals). The occurrence of smectite-group phyllosilicates has been inferred from Fourier transform infrared spectroscopy in one nakhlite and from electron probe microanalysis in another, in which stilpnomelane has been inferred from Raman spectroscopy. In general, structural data are sparse from the dominantly amorphous material in nakhlites, and most occurrences of such materials would be more accurately described on compositional and textural evidence as clay mineraloids (following Gooding, 1986a,b).

Non-crystalline Fe-Mg-Al-Si material with smectite- and serpentine-like compositions occurs as a volumetrically dominant part of the “iddingsite” vein assemblage in the majority of the presently known nakhlites. Small parts of the community have taken to referring to the iddingsite veins in nakhlites as “gels.” However, the IUPAC definition of “gel,” “Non-fluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid” is accompanied by the note: “A gel has a finite, usually rather small, yield stress.” Rheology that varies with fluid content is a defining attribute of a gel. The mineral- or glass-like polish taken by iddingsite veins in nakhlite polished thin sections militates against the characterization of nakhlite iddingsite as a “gel.” No evidence has been presented from nakhlite iddingsite of cracking (syneresis) or volume loss (shrinking) caused by exudation of fluid or other volatile loss at near-ambient conditions. Such vesiculation as has been observed near the meteorite’s fusion crust (the last remnant of meteoritic rock melted and ablated by frictional heating during high-velocity passage through Earth’s atmosphere) is consistent with loss of structural OH from a solid clay mineraloid rather than evolved, formerly fluid, \( \text{H}_2\text{O} \) from a gel. Textural and compositional variations in nakhlite iddingsite with thermal metamorphism near the fusion crust in nakhlite MIL 03346 will be presented.
Charles E. Weaver, Clay Scientist and Founding Director of Georgia Tech’s School of Earth and Atmospheric Sciences

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In the fall of 1963, the last of the Clay Minerals Conferences organized by the Clay Minerals Committee of the U.S. National Academy of Science–National Research Council was held at Georgia Institute of Technology and was chaired by Willis E. Moody of Tech’s School of Ceramic Engineering. At the end of this transitional meeting, responsibility for future clay conferences passed to the nascent Clay Minerals Society (Rowland, 1968). Not long before that meeting, Charles E. (Chuck) Weaver had joined the Tech faculty with a mandate to establish a program of graduate study in the earth sciences. It surely was no coincidence that an accomplished clay scientist (the 7th recipient of the Mineralogical Society of America Award) was chosen for that task, for the new program was born and fostered within the School of Ceramic Engineering, in the State that led the world in kaolin production. Lane Mitchell, Director of the Ceramic Engineering School, and Jesse Mason, Dean of the Engineering College were leading advocates for the new program. Chuck set up his own clay mineralogy laboratory and organized an NSF-sponsored conference on “The Changing Identity of Graduate Earth Science Education,” held at Georgia Tech in January 1965. He recruited young scientists to help plan and to become part of the new program. The School of Geophysical Sciences was established in 1970 with Charles Weaver as Director and five other faculty members (one adjunct) offering graduate study in geochemistry, geophysics, mineralogy, sedimentology, marine geology, and oceanography.

Even while the fledgling program was housed in the School of Ceramic Engineering, Chuck maintained a productive research program, following up on concepts he had developed when he was employed in the petroleum industry and engaging his new colleagues in these and other research initiatives. It is noteworthy that the first steps toward a graduate program in atmospheric sciences were taken before 1970, although a decade was to pass before initiation of the strong atmospheric science component of the School, now known as the School of Earth and Atmospheric Sciences.

During the 1970s, graduate students who entered the new program mostly opted for the M.S. degree because of strong employment opportunities for persons with that level of training. A strong geophysics graduate program, bolstered by a long-standing geophysics option for undergraduates in the School of Physics, sent many graduates to successful careers in exploration geophysics. Demand was so great in the late 1970s that even geochemistry graduates were hired to work in petroleum exploration. Graduate study in oceanography, in cooperation with the new Skidaway Institute of Oceanography was also popular.

Around 1980, a large group of senior faculty was brought into the School for a new program in atmospheric sciences. With very strong outside support for research in that field, the School changed rather rapidly into one where doctoral study was predominant. Chuck Weaver was able to focus again on his own research and to write Clays, Muds, and Shales (1989) as a comprehensive capstone to his scientific work.

ABSTRACTS

TESTING EDGE EFFECTS IN POTASSIUM-ARGON DATING OF ILLITE

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Argon atoms are not chemically bonded in silicates. Radiogenic Ar atoms are held in illite because they are ‘caged’—surrounded by O atoms chemically bonded within a relatively compact mineral structure. It is generally understood that Ar atoms formed by decay of $^{40}$K atoms on the surfaces of crystals and within the expanded interlayers of illite-smectite are not retained. The fate of Ar atoms formed from $^{40}$K atoms that were just inside the edges of illite particles remains uncertain, however, because the character of the illite structure there is modified by edge effects. If such radiogenic argon is lost but K ions at the same distance from the edge are retained, the K-Ar age value of very fine illite crystallites may be smaller than the age value for coeval larger crystallites by a substantial percentage (Szczerba et al., 2015).

One way to test the importance of edge effects in K-Ar dating of illite would be to determine with the highest possible precision K-Ar age values for appropriate size fractions of K-bentonites formed during locally brief episodes of illitization, such as the K-bentonites in the Disturbed Belt of Montana (Osborn et al., 2014). Precision in K-Ar age values of ±1% (2σ) should be possible by repeated determinations, using for each determination one test portion for both K and Ar measurement to eliminate the effect of weighing error. A more direct test would use ion exchange to progressively remove K ions from peripheral areas of very fine illite particles (<0.02 µm) in a way that ensures removal of any radiogenic Ar atoms from corresponding peripheral sites. Information about the removed K and Ar could then be obtained by difference, using K-Ar measurements on the residual solids (Aronson and Douthitt, 1986), or directly by measuring the K and Ar released into solution that had previously been completely degassed.

Very fine muscovite remnants within hydroxy-interlayered vermiculite grains in coastal plain soils of South Carolina hold K, Rb, and Cs in interlayer wedge sites that correspond in some respects to the edge-interlayer sites of illite (Goto et al., 2014). Experiments on room-temperature dilute-acid extraction of the large-ion alkali metals from these soils show prompt removal of K ions from ordinary cation exchange sites followed by slow removal interpreted as exchange of hydronium ions for interlayer K ions in peripheral areas. The experiments also point the way to ensuring concomitant removal of Ar atoms from those peripheral areas.

RIETVELD REFINEMENT OF SELECTED STRUCTURAL PARAMETERS OF DIOCTAHEDRAL SMECTITES

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Turbostratically disordered structures like smectites may be treated within the Rietveld method by a supercell approach.¹ However, the refinement of important structural features, such as proportions of trans- or cis-vacant layers, the occupancy of iron at octahedral positions, and interlayer site occupation as a measure for layer charge density has not been tried yet. A structural model containing the atomic coordinates of TOT layers and mixed layering of cis- and trans-vacant layers was chosen. Mixed layering was approximated by an averaging of partial structure factors. The Rietveld refinement was primarily carried out on the simulated patterns with different starting values to test the structural parameters and their relevance. The same model was tested to refine parameters using measured data of pure dioctahedral smectites samples (<0.2 µm) covering a broad range of composition and structure. All samples were exchanged with Cu-triethylenetetramine to avoid the problems of unknown cation species and hydration stage in the interlayer.² Refinement of simulated data starting with incorrect values of structure parameters led to similar results. The diffraction peaks could be matched well. The incorrect starting values yield slightly wrong results, indicating some serial correlation. The refinement of real purified samples showed satisfying results. The refined octahedral iron content, P(Fe), and interlayer occupation, P(trien), corresponded quite well; only the percentage of cis-vacant layers, Pcv, was always overestimated and reached the refinement limits (Figure 1). The test and application of the structural model on the raw bentonite samples showed that it is possible to refine some structure parameters of dioctahedral smectites on Cu-trien exchanged samples with natural impurities by the Rietveld method and the results were reasonable (Figure 2).


Figure 1. Measured and refined diffraction patterns of purified Cu-trien exchanged sample XL_06 and corresponding structural parameters.

Figure 2. Measured and refined diffraction patterns of Cu-trien exchanged sample XL_09 with natural impurities and corresponding structural parameters.
HOW TO IDENTIFY ANTIBACTERIAL CLAYS

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A decade of research on clays that kill human pathogens, including antibiotic resistant bacteria, allows classification of their common characteristics to aid in identifying these potentially economic resources. Testing of ‘healing clays’ worldwide, finds ~5% are antibacterial when hydrated. None have been identified that kill bacteria by physical disruption, but rather antibacterial clays kill by chemical exchange. Most are from hydrothermal deposits, where volcanogenic fluids produced minerals containing reduced metals. Ferruginous illite-smectite (I-S) is the most common such clay mineral, although kaolins dominate some samples. Bactericidal clays may contain soluble Fe phases (e.g., pyrite) or other reduced metals that drive production of reactive oxygen species (H₂O₂, •OH, •O₂⁻), which damage cell membranes and intracellular proteins. Ion exchange with metals leads to loss of membrane-bound Ca²⁺ and Mg²⁺ and promotes bacterial oxidation.

Critically important is the role of the clay mineral assemblage in buffering the water pH to <4 or >10, where Al is soluble. Nanometric particle sizes (<200 nm) are a characteristic feature of antibacterial clays, suggesting that a high surface area aids solubility on the time scale of topical applications (~24 hrs). Smectite interlayers, and possibly halloysite lumens, can absorb reduced transition metals and act as a barrier to oxidation. However, when the clays are mixed with deionized water, cation exchange may release those metals and depending on the aqueous speciation may lead to mineral solubility.

Clay mineral assemblages that produce toxic levels of metals may inhibit or completely kill human pathogens. Table 1 summarizes the general ranges of pH and Eh of waters equilibrated (24 hrs) with the antibacterial clays we have tested, and shows significant minerals in the assemblage that can be used as field indicators for identifying potential antibacterial clays.

Table 1. Characteristics of antibacterial clays compared with non-antibacterial clays.

<table>
<thead>
<tr>
<th>Clays equilibrated with DI water (100mg/ml) for 24 hrs.</th>
<th>Bacterial effect*</th>
<th>Geologic Indicators</th>
<th>Identifying Mineral Assemblage **</th>
<th>pH</th>
<th>Eh (mV)***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bactericidal (kills 100%)</td>
<td>Hydrothermal</td>
<td>I-S, chlorite, pyrite, jarosite, magnetite</td>
<td>&lt;4</td>
<td>&gt;450</td>
<td></td>
</tr>
<tr>
<td>Growth Inhibition (reduces growth &gt;10⁻³)</td>
<td>Hydrothermal or Lacustrine</td>
<td>kaolins, I-S</td>
<td>&gt;10</td>
<td>300 - 450</td>
<td></td>
</tr>
<tr>
<td>Non-Antibacterial (No effect on growth)</td>
<td>Carbonate Oxidized</td>
<td>calcite, dolomite, goethite</td>
<td>5 - 8</td>
<td>100 - 300</td>
<td></td>
</tr>
<tr>
<td>Nutrient (increases growth)</td>
<td>Marine</td>
<td>Ca, Na-smectite, I-S</td>
<td>8 - 10</td>
<td>&lt;300</td>
<td></td>
</tr>
</tbody>
</table>

*relative to a control population of E.coli or S.aureus grown without clay
** may contain quartz, feldspars, other non-reactive phases
***potential relative to standard hydrogen electrode
Carbonates are key minerals for understanding ancient Martian environments because they represent a key component of the planetary carbon cycle, and they could be an important reservoir for paleo-atmospheric CO$_2$. Like clay minerals, they also typically indicate potentially habitable, neutral-to-alkaline waters. Indeed, the carbonate-bearing rocks identified on Mars to date almost invariably co-occur with clay minerals (often smectites), with the notable exception of the one carbonate-rich outcrop investigated in situ, Comanche in Gusev crater.

All other carbonate-bearing rocks have been identified remotely, based on infrared spectra acquired by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on board NASA’s Mars Reconnaissance Orbiter, which has been active at Mars since 2006.

Whereas CRISM has mapped tens of thousands of clay mineral occurrences, the number of carbonate outcrops confirmed to date numbers only in the dozens. However, clay minerals co-occurring with carbonates can dominate key portions of the spectrum even if their actual abundances are lower than those of the carbonates (Figure 1), implying that carbonates could be more widespread among the clay-bearing rocks on Mars than is currently appreciated.

Here we will describe recent CRISM-based discoveries of formerly buried, ancient carbonate-bearing rocks occurring in several regions across the planet. By evaluating their global distribution relative to major regional features such as giant impact basins and anomalous chemical provinces, we provide new insights into what conditions may have allowed formation and preservation of Martian carbonates.
ABSTRACTS

MID-INFRARED SPECTROSCOPY TO IDENTIFY ICY MOON SURFACE COMPOSITIONS: EVIDENCE FOR PHYLLOSILICATES?

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Previous spectroscopy work on icy moons has focused primarily on the visible portion of the spectrum owing to challenges presented by a low signal-to-noise ratio at the longer wavelengths. However, the mid-IR is the region of the strongest fundamental vibrations of many important types of molecules (e.g., organics) and has the potential to reveal unique compositional information [1]. We use the wealth of data that is now available from Cassini’s Composite Infrared Spectrometer (CIRS) to average spectra over similar regions to reduce the signal-to-noise issue, helping to reveal spectral features never before observed.

Our initial work has already led to the detection and tentative laboratory identification of the first spectral features observed for any icy moon in the mid-IR [2]. On Iapetus’ dark terrain, we found an emissivity feature at ~855 cm^{-1} and a possible doublet at 660 cm^{-1} and 690 cm^{-1} that does not correspond to any known instrument artifacts. We attributed the 855 cm^{-1} feature to fine-grained silicates, similar to those found in dust on Mars and in meteorites, which are nearly featureless at shorter wavelengths [3]. Silicates on the dark terrains of Saturn’s icy moons, possibly delivered meteoritically, have been suspected for decades, but there have been no definitive detections until now. Because peaks can shift depending on temperature, pressure, and grain size, measurements at Iapetus-like conditions are necessary for more positive feature identifications [e.g., 4].

We measured the vacuum and low temperature mid-infrared spectra of various fine-grained powdered silicates, including Mg-rich serpentines. We found that some of these materials do have emissivity features near 855 cm^{-1} and match the doublet. Identifying a specific silicate would provide clues into the origin and implications of the dark material in the Saturnian system. Presently, we are continuing to comb the CIRS icy moon database for spectral features (particularly focusing on the warmer surfaces in the Saturn System) and are performing further vacuum chamber measurements (to experiment with more silicate types and ice-silicate mixtures to determine the impacts of changing conditions in the chamber on features) at JPL’s Icy Worlds Simulation Lab.

CHARACTERISTICS AND ORIGIN OF A WHITE SMECTITIC KAOLIN FROM GEORGIA, USA

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A white smectitic kaolin commercially well-known as #6 Tile Kaolin was investigated by field geological work and by analytical methods of X-ray diffractometry, X-ray fluorescence spectrometry, inductively coupled plasma – atomic emission spectrometry, and scanning electron microscopy coupled with energy dispersive X-ray spectrometry. Analytical results indicate that there is a continuum of mineralogical and chemical characteristics from almost pure kaolin to smectitic kaolin to kaolinitic fuller’s earth and to bauxitic clay. It is postulated that this smectitic kaolin was formed through a process of aggregation from an initially rather pure kaolin, where favorable overlying sediments, bioturbation, and ground water movement provided the necessary elements for montmorillonite to grow at the expense of kaolinite on the edge of kaolin particles.
BRIEF DISCUSSION OF THE PALY-MONT DEPOSIT IN MINGGUANG, ANHUI PROVINCE, P.R. CHINA

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Fuller’s earth is used generally to refer to clays or earthy materials that are suitable for bleaching and sorptive uses, and it could include attapulgite, sepiolite, and smectite clays that have natural bleaching and/or sorptive capabilities (Murray, 2007). Paly-Mont refers specifically to a natural mixture of palygorskite and montmorillonite minerals and it has sorptive properties. Compared to palygorskite or montmorillonite, Paly-Mont is rarer and is truly a unique clay. There are only two known locations, southeastern US and central eastern China. In the patent # 5008226, Taylor and Ungermann (1991) used the following description of this unique clay mixture: naturally occurring mixtures of calcium bentonite and attapulgite clay. The mixtures can be treated with a low level of activating acid to make acid-activated bleaching earth for oil purification purposes. The deposit of Paly-Mont in central eastern China is at the Qingmingshan mine, Mingguang City, Anhui Province and is owned by Anhui Mingmei MinChem Minerals Co., Ltd.

The major minerals in the Qingmingshan mine are the two main components of the natural mixture of palygorskite, which varies from around 25% to more than 50%, and montmorillonite, which ranges from less than 50% to about 75%. Other minerals that occur in minor amounts include quartz, sepiolite, illite, dolomite, and opal. Both major and trace elements found in a related study imply that the source material was basalt, or basaltic volcanic ash. The overall depositional system was fluvial-lacustrine, in which normal sedimentation was interrupted by volcanic events. The originally deposited volcanic ash has undergone alteration or transformation. The Paly-Mont in this deposit can be processed to bleaching clay with low dosage acid or without. It is also an excellent source clay for use as a mycotoxin binder, with a high rate of adsorption of mycotoxins and very low adsorption of nutrients compared to montmorillonite.

SIMULTANEOUS ADSORPTION OF PHENOL, PHOSPHATE, AND CADMIUM ON INORGANIC-ORGANIC MONTMORILLONITE

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Organic contaminants, heavy metals, and oxyanions are the typical contaminants in the environment. Many organic contaminants (e.g. aromatic compounds) and heavy metals (e.g. cadmium) are potential carcinogens and/or mutagens. Adsorption is considered to be one of the most common processes for the removal of these pollutants from water, and many types of adsorbents have been developed accordingly. However, few adsorbents are available to simultaneously remove all of these contaminants in one step. As cost effective, efficient, and sustainable adsorption materials, naturally occurring clay minerals have been recognized as practical and versatile template materials to treat a wide range of contaminants. Inorganic-organic montmorillonites (IOMts), intercalated by both surfactant and hydroxyl-metal, have been developed to remove both organic and inorganic contaminants. The adsorption capacities of IOMts toward organic contaminants and phosphate or organic contaminants and heavy metal cations have received a lot of attention. Little attention, however, has been paid to the simultaneous adsorption of all three contaminants on IOMts. In the environment, organic contaminants, phosphate, and heavy metal cations often coexist in soil and wastewater, thus their transport and fate may be significantly influenced by mutual effects among them. Therefore, the adsorption behavior of organic contaminants, phosphate, and heavy metal cations on IOMts is worth studying.

In this study, IOMts obtained by modifying polyhydroxy-aluminum (Al13)-pillared montmorillonite (AlPMt) with the cationic surfactant C16 or the zwitterionic surfactant Z16 were investigated with the aim to remove phenol, phosphate, and Cd(II) simultaneously. The structures of IOMts prepared using different surfactant doses (0.4 and 1.0 CEC) strongly depended on the types and doses of the surfactants. The Al13 content of C16 modified AlPMts decreased with increasing C16 loading while that of Z16 modified AlPMt did not. In the single adsorption system, all IOMts could efficiently remove phenol and phosphate, but not Cd(II). IOMts, however, could efficiently remove all three contaminants simultaneously in the multi-contaminant adsorption system. The adsorption of phenol on IOMts was not affected by the two inorganic components and vice versa. The adsorption of both phosphate and Cd(II) was significantly enhanced in the multi-contaminant system, and the adsorption of one increased with increasing initial concentration of the other one, especially the adsorption of Cd(II). The enhancements of adsorption of phosphate and Cd(II) on the IOMts with higher Al13 content were much larger than that on IOMts with lower Al13 content. The adsorption mechanism for phosphate and Cd(II) uptake in the multi-contaminant system possibly involves the formation of phosphate-bridged ternary complexes.
BiVO₄/FeOOH/Mt for Visible-Light-Driven Degradation of Acid Dye

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Hydroxy-metal pillared montmorillonite (Mt) has been considered as a suitable catalyst support because of its low cost and its structural characteristics, such as nano-sized layered structure, large specific surface area, and abundant surface reactive sites. Moreover, some pillared Mts can be used directly as catalysts for the degradation of organic contaminants.

Hydroxy-iron intercalated Mt (FeOOH/Mt) has been used as a heterogeneous photo-Fenton catalyst for the degradation of organic contaminants under UV light irradiation; but its catalytic efficiency is far lower under visible light irradiation. Consequently, developing new approaches to enhance the catalytic degradation efficiency of FeOOH/Mt under visible light irradiation is of high importance for its pollution control applications. On the other hand, several studies showed that iron oxide can act as an electron-transfer channel and an electron acceptor in iron oxide–semiconductor composites, which thus can suppress the recombination of photogenerated electron holes.

In the present work, we developed a strategy for loading BiVO₄ on FeOOH/Mt, in which vanadate and bismuth were successively loaded on FeOOH/Mt, to synthesize BiVO₄/FeOOH/Mt composite with high photo-Fenton catalytic activity. The results indicated that BiVO₄ loaded not only on the outer surface but also into the interlayers of FeOOH/Mt. The BiVO₄/FeOOH/Mt composite exhibited high photocatalytic activity. The decolorization efficiency, TOC removal efficiency for AR18, and the production of •OH by BiVO₄/FeOOH/Mt were higher than those by FeOOH/Mt. The high removal efficiency for AR18 and remarkable •OH generation performance by BiVO₄/FeOOH/Mt could be attributed to the presence of BiVO₄, which can accelerate the reduction of Fe³⁺ to Fe²⁺ by providing photo-induced electrons from BiVO₄. In addition, the leached amount of Fe from BiVO₄/FeOOH/Mt was 0.32 mg/L after a 180 min reaction, much smaller than that from FeOOH/Mt (0.66 mg/L). The results of this work suggest that the introduction of semiconductor materials may be a feasible way for enhancing the photo-Fenton catalytic activity of heterogeneous photo-Fenton catalysts.
COMPARATIVE STUDY OF THE STRUCTURES AND RHEOLOGY OF ORGANO-MONTMORILLONITE AND ORGANO-PALYGORSKITE IN OIL-BASED DRILLING FLUIDS

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Organoclays are important rheological additives in oil-based drilling fluids. The structures and properties of montmorillonite (Mt) and palygorskite (Pal) are very different. Thus the influence of the structure and properties of these clays on their rheological properties and thermal stabilities in oil-based drilling fluids is a critical issue. Mt and Pal were organically modified by cationic surfactants. Organic surfactants intercalated into the interlayer space of Mt while surfactants only coated the Pal surface. However, the polar heads of surfactants might intercalate into the channels of Pal. This possibility depended on the scale of surfactants. SEM images indicated that OMt particles became small and more laminas emerged. Surface modification decreased the particle size of OPal and loosened the arrangement of nanofibers. Thermal analysis testified that interlayer surfactants in OMt were protected and their decomposition temperature increased. On the contrary, the surface surfactants in OMt and OPal decomposed at lower temperatures than pure surfactants. The structure of OMt in oil went through four stages with the temperature rising: swelling → continuous swelling → exfoliation → shrinking. Exfoliation of OMt in oil led to the best rheological properties. The structure of OPal in oil changed with the temperature rising as follows: particle dispersion → fiber dispersion → decomposition of surfactants. OMt and OPal formed networks in different ways. The structural changes resulted in rheological changes. The rheological behavior of OMt fluids was in accord with the Bingham plastic model while that of OPal fluids deviated. The rheological properties of organoclay fluids were influenced by the surfactant’s nature (polar head scale, HLB value, molecular conformation), loading level, and temperature.
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