

**PROGRAM &
ABSTRACTS**

55TH ANNUAL MEETING



The Clay Minerals Society

**UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN
JUNE 11-14, 2018**



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55TH ANNUAL MEETING



The Clay Minerals Society

HELD ON THE CAMPUS OF
THE UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN
JUNE 11-14, 2018

ORGANIZING COMMITTEE

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Joseph W. Stucki, Social Program Chair
Stephen Guggenheim, Program Chair
Stephen P. Altaner, Field Trips Chair
Martin Pentrak, Technology Chair
Jin-Ho Choy, Workshop Chair
Lynda Williams, Assistant Workshop Chair
Scott Randall, Conference Program Coordinator
Nancy Simpson, Conference Program Associate
Gretchen Wieshuber, Graphic Design

THE CLAY MINERALS SOCIETY ADMINISTRATION

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

Executive Committee

President:	Douglas K. McCarty, Chevron, Inc. (Retired)
Vice President:	Lynda B. Williams, Arizona State University
Secretary:	Warren Huff, University of Cincinnati
Treasurer:	Paul Schroeder, University of Georgia
Vice-President Elect:	Andrey Kalinichev, University of Nantes, France
Past President:	Jan Śródoń, Institute of Geological Sciences, Krakow, Poland
Editor-in-Chief:	Joseph W. Stucki, University of Illinois

Council

Thomas Bristow
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Eric Ferrage
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Shane Butler
Youjun Deng
Carolyn Olson
Javiera Cervini-Silva

Arek Derkowski
Stephen J. Hillier
Timothy Fischer
Ana Luisa Barrientos Velazquez

PAST PRESIDENTS

Chairmen of the Interdivisional Committee on Clay Minerals of the National Academy of Sciences—National Research Council

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

Presidents

1963–1964	Richards A. Rowland	1987–1988	Necip Guven
1964–1965	James W. Earley	1988–1989	William F. Moll
1965–1966	Haydn H. Murray	1989–1990	Brij L. Sawhney
1966–1967	Marion L. Jackson	1990–1991	Thomas J. Pinnavaia
1967–1968	Charles E. Weaver	1991–1992	Robert C. Reynolds, Jr.
1968–1969	Paul G. Nahin	1992–1993	David R. Pevear
1969–1970	George W. Brindley, Katherine Mather	1993–1994	Dennis D. Eberl
1970–1971	John F. Burst	1994–1995	Rossman F. Giese, Jr.
1971–1972	Sturges W. Bailey	1995–1996	Kenneth M. Towe
1972–1973	William F. Bradley	1996–1997	Stephen Guggenheim
1973–1974	John W. Jordan	1997–1998	Joseph W. Stucki
1974–1975	John C. Hathaway	1998–1999	David L. Bish
1975–1976	Stanley B. McCaleb	1999–2000	Patricia M. Costanzo
1976–1977	John Hower	2000–2001	Darrell G. Schultze
1977–1978	John B. Hayes	2001–2002	Blair F. Jones
1978–1979	Max M. Mortland	2002–2003	Jessica Elzea Kogel
1979–1980	Finis Turner	2003–2004	Kathry L. Nagy
1980–1981	R. Torrence Martin	2004–2005	Duane M. Moore
1981–1982	Joe B. Dixon	2005–2006	Cliff T. Johnston
1982–1983	William D. Johns	2006–2007	Richard K. Brown
1983–1984	Wayne Hower	2007–2008	Ray E. Ferrell, Jr.
1984–1985	Wayne M. Bundy	2008–2009	Andrew R. Thomas
1985–1986	Marion G. Reed	2009–2010	Derek C. Bain
1986–1987	Sam H. Patterson	2010–2011	Paul A. Schroeder
		2011–2012	David A. Laird

2012–2013	Peter Komadel	2016–2017	Jan Środoń
2013–2014	Michael A. Velbel	2017–2018	Douglas K. McCarty
2014–2015	W. Crawford Elliott	2018–2019	Lynda B. Williams
2015–2016	Prakash B. Malla		

SUSTAINING CONTRIBUTORS OF THE SOCIETY

Oil-Dri Corporation of America

Individual Sustaining Members

Leslie Baker	Stephen Guggenheim	Joseph W. Stucki
John D. Bloch	James Matthews	Michael A. Velbel
Richard W. Brown	Carolyn G. Olson	Lynda B. Williams
Randall T. Cygan	Paul A. Schroeder	

SPONSORS OF THE CMS 2018 CONFERENCE

National Science Foundation	Oil-Dri Corporation
College of ACES, University of Illinois	Thiele Kaolin Company
Department of NRES, University of Illinois	IMERYS
School of SESE, University of Illinois	Minerals
Geology Department, University of Illinois	Fisher Scientific
Illinois State Geological Survey	

AWARDS

Marilyn and Sturges W. Bailey Distinguished Member Award

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

<i>Distinguished Members</i>		1980	Haydn H. Murray	1996	Victor A. Drits
1968	Ralph E. Grim	1984	C. Edmund Marshall	1997	Udo Schwertmann
1969	Clarence S. Ross	1985	Charles E. Weaver	1998	Brij L. Sawhney
1970	Paul F. Kerr	1988	Max M. Mortland	<i>Bailey Distinguished Members</i>	
1971	Walter D. Keller	1989	Robert C. Reynolds, Jr.	2000	Boris Zvyagin
1972	George W. Brindley	1990	Joe L. White	2001	Keith Norrish
1975	Sturges W. Bailey	1990	John Hower	2002	Gerhard Lagaly
1975	William F. Bradley	1991	Joe B. Dixon	2004	Benny K. G. Theng
1975	José J. Fripiat	1992	Philip F. Low	2005	M. Jeff Wilson
1977	Marion L. Jackson	1993	Thomas J. Pinnavaia	2006	Frederick J. Wicks
1979	Toshio Sudo	1995	William D. Johns		

2008	Norbert Clauer	2011	Sridhar Komarneni	2015	R. James Kirkpatrick
2009	Joseph W. Stucki	2012	Akahiko Yamagishi	2016	Lisa Heller-Kallai
2010	José M. Serratos	2013	Stephen Guggenheim	2018	G. Jock Churchman

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

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

Jackson Awardees

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

George W. Brindley Lecture Award

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

Brindley Lecturers

		1993	Dennis D. Eberl	2003	Alain Manceau
1984	Walter D. Keller	1994	Robert C. Reynolds, Jr.	2005	Maria F. Brigatti
1985	José J. Fripiat	1995	Gerhard Lagaly	2008	Robert J. Gilkes
1986	Ralph E. Grim	1996	Samuel M. Savin	2009	Michael F. Hochella, Jr.
1987	Sturges W. Bailey	1997	Paul H. Nadeau	2010	Randall T. Cygan
1988	Marion L. Jackson	1998	Bruce Velde	2013	Andrey G. Kalinichev
1989	William D. Johns	1999	Richard Eggleton	2017	Sridhar Komarneni
1990	Alain Baronnet	2000	Duane M. Moore	2018	Cliff T. Johnston
1991	Thomas J. Pinnavaia	2001	Robert Schoonheydt		
1992	Philip F. Low	2002	David L. Bish		

Pioneer In Clay Science Award

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

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

CITATION OF SPECIAL RECOGNITION

1984	Richards A. Rowland	2013	Haydn H. Murray
1984	Ada Swineford	2014	Warren D. Huff
1991	Frederick A. Mumpton	2015	Stephen J. Hillier
1994	Kenneth M. Towe	2016	J. Reed Glasmann
1996	Don Scafe	2018	Duane M. Moore
2003	William D. Johns		

EDITORS OF CLAYS AND CLAY MINERALS

1952	J. A. Pash and M. D. Turner	1975–1978	Richards A. Rowland
1953	Ada Swineford and Norman Plummer	1979–1990	Frederick A. Mumpton
1954	W. O. Milligan	1990–1991	Kenneth M. Towe
1955–1961	Ada Swineford	1991–1995	Ray E. Ferrell, Jr.
1962–1964	William F. Bradley	1995–1998	Wayne H. Hudnall
1964–1969	Sturges W. Bailey	1999–2000	Stephen Guggenheim
1970–1972	Max M. Mortland	2000–2007	Derek C. Bain
1973–1974	William T. Granquist	2008–Present	Joseph W. Stucki

WELCOME

THE 55TH ANNUAL MEETING OF THE CLAY MINERALS SOCIETY, HELD JUNE 11-14, 2018, AT THE UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN, ILLINOIS, USA

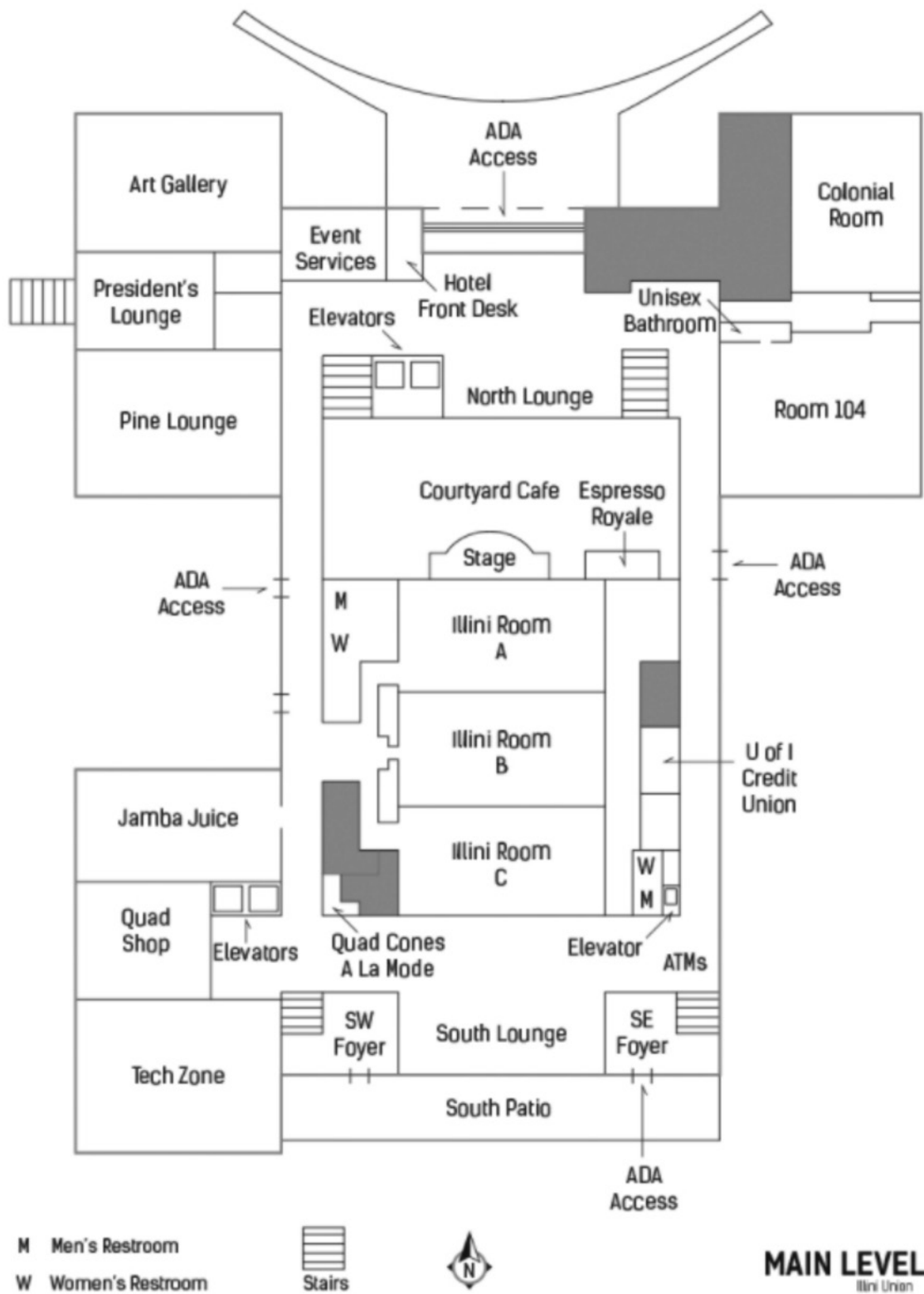
The Clay Mineral Society (CMS) began in 1952 as the Interdivisional Committee on Clay Minerals of the National Academy of Sciences-National Research Council. By 1962, the Clay Mineral Society was established as own its society. The primary purpose of CMS is to stimulate research and education and to disseminate information relating to all aspects of clay science and technology. Through its conference and publications (*Clays and Clay Minerals* and *CMS Workshop Lectures Series*) the society provides numerous opportunities for the information exchange and interdisciplinary research collaborations. The society welcomes colleagues from all branches of clay sciences and from many countries in the world to the CMS conferences and to our society journal, *Clays and Clay Minerals*, to disseminate their valuable work.

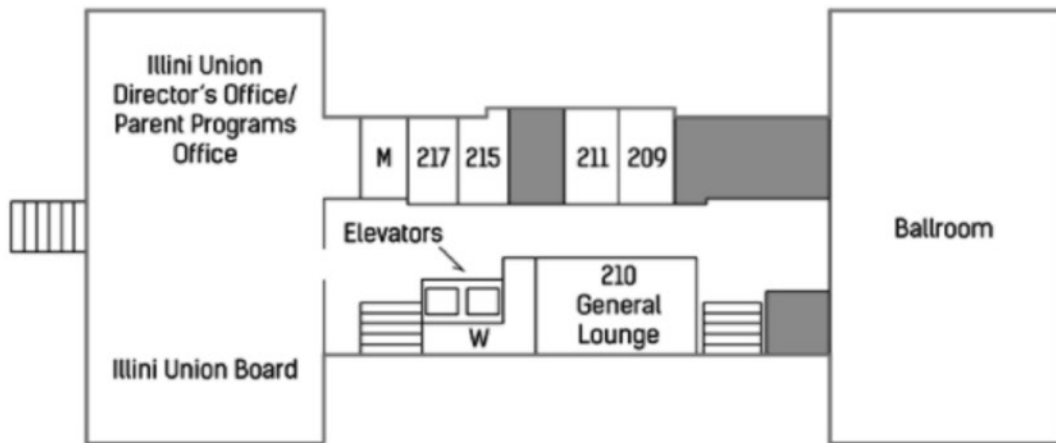
The program of the 55th annual meeting of The Clay Minerals Society (Theme: *New Visions of Clay Science*) consists of a workshop on Medicinal Applications of Clay Minerals organized by Professor Jin-ho Choy, Ewha Womans University, Korea and four days of technical sessions. Each technical session starts with an Award Lecture (Jackson Award recipient Stephen Hillier, Bailey Award recipient Jock Churchman, Brindley Award recipient Cliff Johnston, and Pioneer Award recipient Jan Środoń) that will be followed by thematic sessions. Nineteen thematic sessions that cover a broad range of clay sciences: clay mineralogy, crystallography, petrology, material science, nanoscience, bio-nanoclays in medicine, environmental engineering, soil science, biogeochemistry, industrial technology, isotope geochemistry, cosmogeochemistry, advanced spectroscopies, and education have attracted 240 abstracts. The Reynolds Cup competition award, NSF and CMS student travel grant awards, and students' best presentation awards will also be presented. Several field trips (Starved Rock and Matthiessen State Parks, Kaolinite in the Keokuk Geodes, Critical Zone Observatory, Fithian Illite, and Morrow Plots) and the social programs (Amish Tour, Arthur, Illinois; Abraham Lincoln Sites, Springfield, Illinois) are also offered to accommodate the participants' interest in the clay science, culture, and history in the State of Illinois. Enjoy the meeting at the University of Illinois at Urbana-Champaign. We hope that your interaction with international colleagues and students will further enhance research and education in clay sciences.

Yuji Arai

General Chairman of the 55th Annual Meeting of The Clay Minerals Society

ILLINI UNION



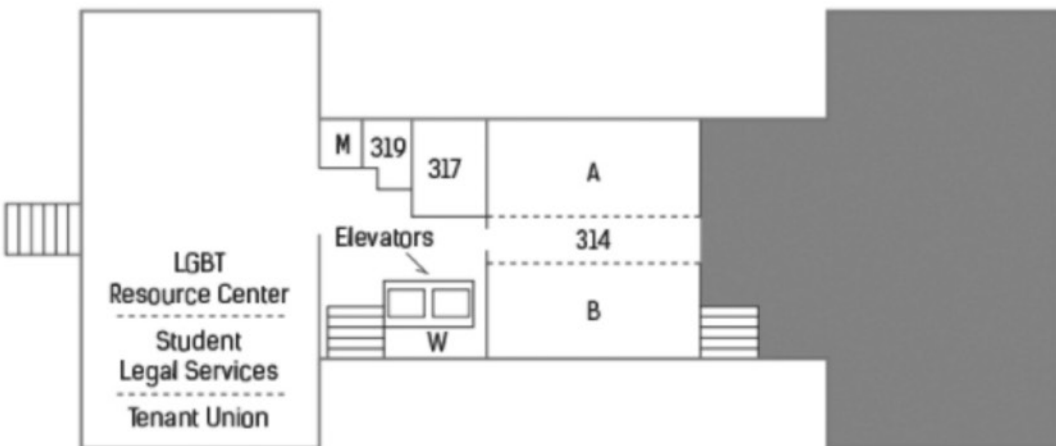


M Men's Restroom
 W Women's Restroom

 Stairs



2ND (NORTH)
 Illini Union

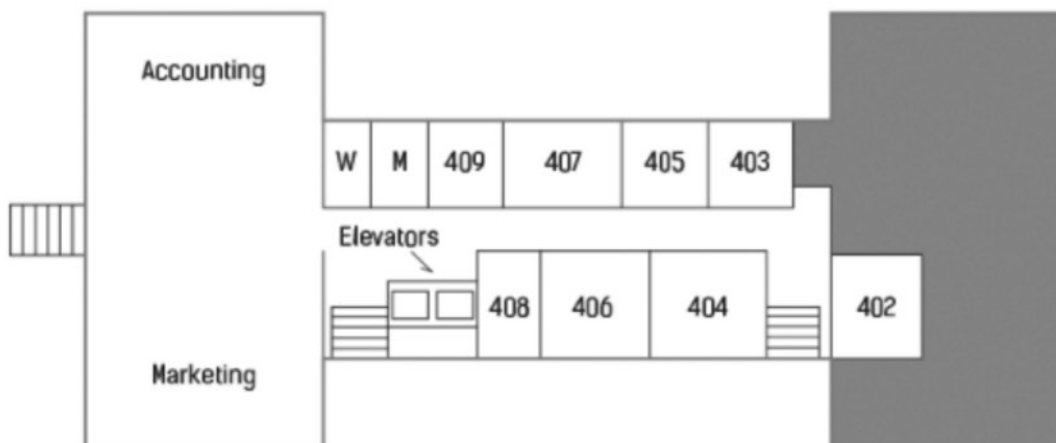


M Men's Restroom
 W Women's Restroom

 Stairs



3RD (NORTH)
 Illini Union



M Men's Restroom
 W Women's Restroom

 Stairs



4TH (NORTH)
 Illini Union

PROGRAM AT-A-GLANCE

	Day 1	Day 2			Day 3		Day 4					
	Friday	Saturday			Sunday		Monday					
Time/ Room	210	314	314/210	210	S. Lounge	Field Trips	Social Program	Illini A	Illini B	Illini C	210	Pine
8:00		Council Meeting	Breaks	Work- shop		(1) Starved Rock (2) Keokuk Geode	Amish Country Tour	Welcome + Special Award + Jackson Award Lecture				
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6:00	Exec. Comm. Meeting and Dinner	Informal BBQ at Stucki’s home. Bus leaves front of Illini Union at 5:30 PM.			Welcome Recep- tion & Student Welcome	Editorial Board Dinner at Biaggis—Bus leaves the front of the Illini Union at 5:45 pm					Authors Present: Poster Session and Recep- tion	
6:20												
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Day 5					Day 6					Day 7											
Tuesday					Wednesday					Thursday											
Field Trip	Illini A	Illini B	Illini C	Pine	Social Program	Illini A	Illini B	Illini C	Pine	314	210	Pine	Time/ Room								
	Pioneer Lecture				Lincoln Sites	Bailey Award Lecture				Brindley Lecture			8:00								
													8:10								
													8:20								
													8:30								
	Illite II	NMR	Palygorsk	Posters		HC	S&W	MD	Posters	Teaching	S&W	Posters	9:05								
													9:20								
													9:40								
				Break					Break			Break	10:00								
	Enviro	NMR	Palygorsk	Posters		HC	S&W	MD	Posters	Teaching	S&W	Posters	10:20								
										Zeolite			10:40								
													11:00								
													11:20								
11:40																					
Lunch On Your Own (CMS Past Presidents' Luncheon Room 314)													Lunch On Your Own					12:00			
Critical Zone Observatory	Enviro	EET	Palygorsk	Posters	HC	S&W	MD	Posters	Fithian and Morrow Plots Field Trips			1:00									
							Barrier					Life	1:20								
			Solar										1:40								
								Break							Break	2:20					
	Enviro	EET	Barrier	Posters	Solar	S&W	Isotopes	Posters				3:00									
							RC								3:40						
															4:00						
Conference Banquet at the Memorial Stadium Colonanades Club—Buses leave the front of the Illini Union at 5:30 pm						CMS Business Meeting and Student Presentation Awards in Illini Room A					Informal BBQ at Stucki's home. Bus leaves front of Illini Union at 5:30 PM.			4:20							
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KEY FOR SESSION ABBREVIATIONS

Abiotic: Abiotic Redox Processes Related to Clays and Clay Minerals

Barrier: Bentonite Barrier

Bio-nano: New Visions in Clay Science: Bio-nanoclays in Medicine

Critical Zone: Intensively Managed Clays in the Critical Zone

EET: EET (ExtMicrobial Oxidation and Reduction of Insoluble Fe Oxides and Phyllosilicates in Soil and Sedimentary Environments)

Enviro: Clay Interactions with Contaminants and Radionuclides: From Molecular Mechanisms to Environmental Fate

General: General Session

HC: The Role of Clay Minerals in Controlling the Properties and Geochemical Processes Associated with Hydrocarbon Systems

Illite: Illite-smectite Group in Geological Systems Soils Laboratory and Computer: The Complete Picture

IR: Applications of Infrared Spectroscopy to Clay Mineral Systems

Isotopes: The Isotopy of Clay Minerals—Mysteries in the Sheets

Life: Role of Clay Minerals in the Events Leading to the Origin of Life

MD: Molecular Studies of Clay Minerals and Related Structures

NMR: Applications of NMR Spectroscopy to Clays and Clay Mineral Systems

Palygorsk: Palygorskite: From Fundamental Research to Functional Materials

RC: Reynolds Cup Award and Presentation **Solar:** Phyllosilicates Throughout the Solar System

S&W: Structures and Reactivity of Clays and Nanoparticles in Soils and Water

Teaching: Teaching and History of Clay Sciences

Zeolite: Volcanic Ash as Source Material for Clay and Zeolite Mineral Formation

PROGRAM

MONDAY MORNING

Poster Presentation Setup in the Pine Room from 7:30 AM to 5:00 PM today.

Authors will be present this afternoon from 5:40–8:00 PM in the Pine Room.

PLENARY SESSION

ILLINI ROOM A

8:00–8:10	Introductory remarks, Yuji Arai, General Chair
8:10–8:20	Welcoming remarks, UIUC Provost Andreas C. Cangellaris
8:20–8:30	Introductory remarks, CMS President, D. McCarty
8:30–8:45	Special Recognition Award to Dewey Moore Introduction by Georg Grathoff, Ernst-Moritz-Arndt, Universitat, Greifswald
8:45–8:55	Introduction of the 2018 Marion L. and Chrystie M. Jackson Mid-Career Clay Scientist Award recipient, Kevin Murphy, Managing Editor, <i>Clays and Clay Minerals</i>
8:55–9:35	Acceptance and Presentation Stephen Hillier: DIGITAL SOIL MINERALOGY (JACKSON AWARD LECTURE)
9:40–10:00	Break

TECHNICAL SESSIONS

ILLINI ROOM A

Abiotic Redox Processes Related to Clays and Clay Minerals

Organizers: Yuanzhi Tang and Xiancai Lu

10:00–10:20	Alan Stone*, Xiaomeng Xia, and Weichen Liao: ADDING HYDRATION, TAUTOMERIZATION, AND NUCLEOPHILIC ATTACK TO OUR CONCEPTUALIZATION OF REDOX REACTIONS AT OXYHYDROXIDE MINERAL SURFACES TO IMPROVE REACTIVITY PREDICTIONS
10:20–10:40	Jeffrey Catalano*, Elaine D. Flynn, and Margaret A. G. Hinkle: REDUCTION OF PHYLLOMANGANATES BY ORGANIC ACIDS: EFFECTS ON MINERAL STRUCTURE AND TRACE METAL FATE
10:40–11:00	Matthew Ginder-Vogel and Lily Schacht: LIMITATIONS OF OBSERVED FIRST ORDER RATE CONSTANTS: A CASE STUDY ON As(III) DEPLETION BY Mn OXIDES

11:00–11:20	Mengqiang Zhu* and Qian Wang: DYNAMIC STRUCTURAL AND COMPOSITIONAL CHANGES OF BIRNESSITE DURING REDUCTIVE DISSOLUTION
11:20–11:40	Ao Qian, Chao Pan, Daniel E. Giammar, Songhu Yuan, and Zimeng Wang*: AQUEOUS COMPLEXATION AND DISPROPORTIONATION OF Mn(III) IN THE PRESENCE OF PYROPHOSPHATE: IMPLICATIONS FOR ITS ROLE AS A GEOCHEMICAL OXIDANT
11:40–12:00	Martial Taillefert: ROLE OF SOLUBLE Fe(III) COMPLEXES IN IRON REDOX REACTIONS
12:00–1:20	Lunch

ILLINI ROOM B

Applications of Infrared Spectroscopy to Clay Mineral Systems

Organizers: Sabine Petit and Jana Madejova

10:00–10:20	Nicolas Mangold*, John Carter, Fabien Baron, Erwin Dehouck, Anne Gaudin, Damien Loizeau, and François Poulet: IMPORTANCE AND DIVERSITY OF GEOLOGICAL SETTINGS OF ALUMINUM-RICH CLAY MINERALS ON MARS
10:20–10:40	John Carter*, Jean-Pierre Bibring, Nicolas Mangold, and the OMEGA1 and CRISM3 teams: THE CLAY STORY OF ANCIENT MARS, AN UPDATE
10:40–11:00	Sabine Petit*, Jan Środoń, Daniel Beaufort, and Małgorzata Lempart: STUDY OF BASALTIC PIECES OF ROCKS BY ATTENUATED TOTAL REFLECTANCE SPECTROSCOPY (ATR) AND NEAR INFRARED (NIR) SPECTROSCOPY
11:00–11:20	Michal Ritz*, and Lenka Vaculíková: QUANTIFICATION OF PREDOMINANT MINERALS IN SEDIMENTARY ROCKS BY CHEMOMETRIC ANALYSIS OF INFRARED SPECTRA
11:20–11:40	Stephan Kaufhold*, K. Ufer, and R. Dohrmann: HOW WE USED IR-SPECTROSCOPY IN THE REYNOLDS CUP
11:40–12:00	Bella B. Zviagina*, Victor A. Drits, and Olga V. Dorzhieva: DISTINGUISHING FEATURES AND IDENTIFICATION CRITERIA FOR K- DIOCTAHEDRAL MICAS (ILLITE-ALUMINOCELADONITE AND ILLITE-GLAUCONITE-CELADONITE SERIES) FROM MIDDLE-INFRARED SPECTROSCOPY DATA
12:00–1:20	Lunch

ILLINI ROOM C

New Visions in Clay Science: Bio-nanoclays in Medicine*Organizers: Jin-Ho Choy and Lynda B. Williams*

10:00–10:20	Ray Ferrell*: EXPANDED USE OF CLAYS IN MEDICINE LINKED TO MODERN CHARACTERIZATION METHODS AND IN VITRO AND IN VIVO INVESTIGATIONS
10:20–10:40	Robert Finkelman*: THE INFLUENCE OF CLAYS ON HUMAN HEALTH: A MEDICAL GEOLOGY PERSPECTIVE
10:40–11:00	Soo-Jin Choi*: TOXICITY MECHANISM, TOXICOKINETICS, AND IN VIVO TOXICITY OF CLAY MINERALS
11:00–11:20	Jin Yu*, and Soo Jin Choi: TOXICITY MECHANISM OF LAYERED DOUBLE HYDROXIDE NANOPARTICLE-INDUCED OXIDATIVE STRESS AND INFLAMMATION IN HUMAN LUNG EPITHELIAL CELLS
11:20–11:40	Keith Morrison* and Lynda B. Williams: THE ANATOMY OF AN ANTIBACTERIAL CLAY DEPOSIT
1:40–12:00	Suzannah Schmidt-Malan*, K.M. Caffisch, J.N. Mandrekar, and L.B. Williams, and R. Patel: ACTIVITY OF ANTIBACTERIAL CLAY AGAINST DRUG-RESISTANT BACTERIA
12:00–1:20	Lunch

ROOM 210

General Session*Organizer: Martin Pentrak and Linda Pentrakova*

10:00–10:20	Paolo Andre Benavides*, Jacqueline Kowalik, Stephen Guggenheim, and August F. Koster van Groos: EFFECT OF CO ₂ PRESSURE, TEMPERATURE, AND BRINE COMPOSITION ON THE INTERLAYER SPACING OF Na- AND Ca-EXCHANGED MONTOMORILLONITE
10:20–10:40	Mark Raven*, and Stephen Hillier: DIFFERENTIATING DEHYDRATED HALLOYSITE FROM KAOLINITE USING X RAY DIFFRACTION METHODS
10:40–11:00	Mohammed A. Gondal* and A.M. Ilyas: SYNTHESIS OF QUATERNARY (ZnO/TiO ₂ /CdS/SiC) NANO-COMPOSITES USING ADVANCED PULSED LASER ABLATION TECHNIQUE
11:00–11:20	Wei-Hsiang Hung* and Bing-Sheng Yu: OPTIMIZATION OF ORGANO-MODIFIED SMECTITE OF HYDROTHERMAL SYNTHESIS SMECTITE BY TAGUCHI METHOD
11:20–11:40	Sanda Maicaneanu* and Horea Bedelea: MONTMORILLONITIC CLAY APPLICATIONS IN WASTE WATER TREATMENT
11:40–12:00	Martin Pentrak*: INVESTIGATION OF CLAY MINERALS AT THE ILLINOIS STATE GEOLOGICAL SURVEY
12:00–1:20	Lunch

MONDAY AFTERNOON

TECHNICAL SESSIONS

ILLINI ROOM A

Abiotic Redox Processes Related to Clays and Clay Minerals

Organizers: Yuanzhi Tang and Xiancai Lu

1:20–1:40	Peng Yang*, Seungyeol Lee, Jeffrey E. Post, Huifang Xu, Qian Wang, Wenqian Xu, and Mengqiang Zhu: RAPID TRANSFORMATION OF LAYERED TO TUNNELED MANGANESE OXIDES TRIGGERED BY TRIVALENT MANGANESE ADSORBED ON VACANCIES
1:40–2:00	Michael E. Bishop, Hailiang Dong*, Paul Glasser, Brandon R. Briggs, Martin Pentrak, and Joseph W. Stucki: IRON REDOX CYCLING OF SUBSURFACE SEDIMENTS FROM HANFORD SITE, WASHINGTON STATE, USA
2:00–2:20	Young-Shin Jun* and Lijie Zhang: REDOX DEGRADITION OF PHOSPHONATE WITH Fe-BEARING CLAY MINERALS UNDER SUBSURFACE RELEVANT CONDITIONS
2:20–2:40	Dong Ma* and Mengqiang Zhu: COUPLED REDOX CYCLING OF MANGANESE AND CARBON ON IRON OXIDE SURFACES
2:40–3:00	Aaron Betts*, Matthew Siebecker, and Donald L. Sparks: OXIDATION STATUS OF SUBSOIL CLAY DURING Fe(II) SORPTION ALTERS THE COMPOSITION OF PRECIPITATED Fe(II)-BEARING LAYERED DOUBLE HYDROXIDES
3:00–3:20	Malgorzata Lempart*, Arkadiusz Derkowski, Katarzyna Luberd-Durnaś, and Artur Błachowski: THE CONTRIBUTION OF DEHYDROGENATION IN THERMAL DECOMPOSITION OF Fe(II)-CONTAINING CHLORITES
3:20–3:40	Break
3:40–4:00	Linda Pentrakova*, Martin Pentrak, and Joseph W. Stucki: THE INFLUENCE OF TETRAHEDRAL AND OCTAHEDRAL IRON IN SMECTITES ON THEIR REDOX ACTIVITY IN NITRATE REMOVAL
4:00–4:20	Qiang Zeng*, Hailiang Dong, and Xi Wang: EFFECT OF LIGANDS ON THE OXIDANT PRODUCTION FROM OXYGENATION OF REDUCED NONTRONITE

Illite-smectite Group in Geological Systems Soils Laboratory and Computer: The Complete Picture

Organizers: W. Crawford Elliott and Jan Środoń

4:20–4:40	Georg Grathoff*, Jared Freiburg, Kevin Henkel, and Klaus Wemmer: COMPARING ILLIIZATION IN LOWER PALEOZOIC SHALES AND SANDSTONES OF THE ILLINOIS BASIN: IMPLICATIONS FOR CARBON DIOXIDE STORAGE
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- 4:40–5:00 Arkadiusz Derkowski* and Douglas K. McCarty: RETENTION ON ILLITE CRYSTALLITE EDGES CONTRIBUTES TO CESIUM CYCLING IN THE UPPER CONTINENTAL CRUST
- 5:00–5:20 Artur Kuligiewicz, Arkadiusz Derkowski*, Jan Środoń, Vassilis Gionis, and Georgios D. Chrysikos: POLARITY OF ILLITESMECTITE FUNDAMENTAL PARTICLES REVISITED: NEW EVIDENCE FROM VIBRATIONAL SPECTROSCOPY MEASUREMENTS

ILLINI ROOM B

Applications of Infrared Spectroscopy to Clay Mineral Systems

Organizers: Sabine Petit and Jana Madejova

- 1:20–1:40 Fabien Baron*, Anne Gaudin, Nicolas Mangold, and Sabine Petit: A DETAILED INTERPRETATION OF THE NEAR-INFRARED SPECTRUM OF KAOLINITE
- 1:40–2:00 Lenka Vaculikova*, Eva Plevova, Vera Valovicova, Michal Ritz, and Lenka Blahova: COMPARISON OF INFRARED AND RAMAN SPECTRA FOR STRUCTURAL CHARACTERIZATION OF MONTMORILLONITES
- 2:00–2:20 Will Gates*, Heloisa N. Bordallo, Laurie P. Aldridge, Sylvia M. Mutisya, José E.M. Pereira, Caetano R. Miranda, and Anton P.J. Stampfl: GENERALIZED (VIBRATIONAL) DENSITY OF STATES OF WATER IN SODIUM MONTMORILLONITE
- 2:20–2:40 Brian Gregoire*, Eric Ferrage, Fabien Hubert, Thomas Dabat, and Sabine Petit: WHAT POLARIZED ATR-FTIR SPECTROSCOPY CAN TELL US ABOUT CLAY MINERALS?
- 2:40–3:00 Giora Rytwo*: FTIR BASED QUANTIFICATION OF ADSORBED COMPOUNDS ON CLAYS
- 3:00–3:20 Jana Madejová*, Michal Slaný, and Ľuboš Jankovič: CONFORMATION OF ALKYLAMMONIUM CATIONS IN MONTMORILLONITE INTERLAYERS AS REVEALED BY NEAR-INFRARED SPECTROSCOPY
- 3:20–3:40 Break
- 3:40–4:00 Runliang Zhu*, Hongping He, and Jianxi Zhu: EFFECT OF SURFACTANT PACKING DENSITY ON THE SORPTION OF HYDROPHOBIC ORGANIC CONTAMINANTS ON ORGANOCLAYS
- 4:00–4:20 Helena Pálková*, Martin Barlog, Lukáš Petra, Jana Madejová, Peter Bilik, Erik Šimon, and Juraj Bujdák: VERSATILITY OF INFRARED SPECTROSCOPY IN THE INVESTIGATION OF CLAY MINERALS EXPOSED TO VARIOUS MODIFICATIONS
- 4:20–4:40 Anna Koteja* and Jakub Matusik: MONITORING THE AZOBENZENE ISOMERIZATION IN LAYERED INTERCALATION COMPOUNDS USING THE INFRARED SPECTROSCOPY
- 4:40–5:00 Malgorzata Zimowska*, Helena Pálková, Jana Madejová, and Robert P. Socha: FTIR SPECTROSCOPY TO STUDY FORMATION AND FUNCTIONALISATION OF POROUS CLAY HETEROSTRUCTURES DERIVED FROM LAPONITE

5:00–5:20 Ana Barrientos* and Youjun Deng: RE-EVALUATE THE STRETCHING INFRARED BANDS OF INTERLAYER WATER IN SMECTITE AND THEIR IMPORTANCE IN INTERPRETING THE SMECTITE-ORGANIC BONDING MECHANISMS

ILLINI ROOM C

New Visions in Clay Science: Bio-nanoclays in Medicine

Organizers: Jin-Ho Choy and Lynda Williams

1:20–1:40	Shekooh Behroozian*, Sarah L. Svensson, Wanjing Xu, Mariko Ikehata, Slade Loutet, Loretta Li, Michael E.P. Murphy, and Julian Davies: ANTIMICROBIAL PROPERTIES OF KISAMEET CLAY, A NATURAL CLAY MINERAL FROM BRITISH COLUMBIA, CANADA
1:40–2:00	Xi Wang, Hailiang Dong*, Qiang Zeng, Qingyin Xia, Limin Zhang, and Ziqi Zhou: REDUCED IRON-CONTAINING CLAY MINERALS AS ANTIBACTERIAL AGENTS AND FACTORS THAT INFLUENCE ITS EFFICIENCY
2:00–2:20	Mark Peterman* and Larry A. Hanson: BACTERICIDAL EFFICACY OF SELECT CLAY MINERALS UPON A VIRULENT STRAIN OF AEROMONAS HYDROPHILA
2:20–2:40	Andrei Barkovskii*, Rachel Brineman, and Terrell Scott Johnson: REMOVAL OF MICROORGANISMS FROM AQUEOUS SOLUTIONS WITH CALCINED KAOLIN AND DIATOMACEOUS EARTH
2:40–3:00	Jin-Ho Choy*: 10B-CARBORATE-CLAY HYBRID SYSTEMS FOR BORON NEUTRON CAPTURE THERAPY
3:00–3:20	César Viseras*, Esperanza Carazo, Ana Borrego-Sánchez, Fátima García-Villén, Rita Sánchez-Espejo, Pilar Cerezo, and Carola Aguzzi: MONTMORILLONITE AS VEHICLE OF TUBERCULOSTATIC ISONIAZID
3:20–3:40	Break
3:40–4:00	Goeun Choi* and Jin-Ho Choy: TUMOR TARGETING DRUG-CLAY HYBRID DELIVERY SYSTEM IN THE ORTHOTOPIC CERVICAL CANCER MODEL
4:00–4:20	Pilar Aranda*, Ediana P. Rebitski, Margarita Darder, Raffaele Carraro, and Eduardo Ruiz-Hitzky: MONTMORILLONITE BASED HYBRIDS FOR METFORMIN CONTROLLING DELIVERY
4:20–4:40	Zhi Ping Xu*, and Weiyu Chen: CLAY NANOPARTICLES AS EFFICIENT VACCINE ADJUVANTS FOR ANIMAL AND HUMAN HEALTH
4:40–5:00	Youjun Deng*, Chun-Chun Hsu, and Maria Tenorio Arvide: ADSORPTION OF FUMONISIN B1 ON SMECTITE AND SYNTHETIC LAYERED DOUBLE HYDROXIDES
5:00–5:20	Jae-Min Oh*: SIZE AND MORPHOLOGY CONTROLLED LAYERED DOUBLE HYDROXIDES FOR ANTICANCER DRUG DELIVERY AND TUMOR TRACER

ROOM 210

General Session*Organizer: Martin Pentrak and Linda Pentrakova*

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| 1:20–1:40 | Mary Arenberg* and Yuji Arai: IMMOBILIZATION OF AGRICULTURAL PHOSPHORUS IN CLAYEY FLOODPLAIN SOILS |
| 1:40–2:00 | Iqra Zubair Awan*, Giada Beltrami, Annalisa Martucci, Stefania Albonetti, Fabrizio Cavani, Didier Tichit and Francesco Di Renzo: STUDY OF THE FIELD OF SYNTHESIS OF Cu-Ni-Fe LAMELLAR DOUBLE HYDROXIDES AND THEIR TRANSFORMATION INTO MIXED OXIDES FOR CATALYTIC APPLICATIONS |
| 2:00–2:20 | Ahmed Radwan*, A.M. Abudeif, M.M. Attia, M. A. Elkhawaga, and Wael K. Abdelghany: SMECTITE TO ILLITE TRANSFORMATION AS A GEOPRESSURE GENERATION MECHANISM, GULF OF SUEZ—MUD ROCK: A CASE STUDY |
| 2:20–3:40 | Break |
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Intensively Managed Clays in the Critical Zone*Organizers: Paul Schroeder, Kumar Praveen, and Thanos Papanicolao*

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| 3:40–4:00 | Jason Austin*, Amelia Perry, Daniel deB. Richter, and Paul A. Schroeder: MODIFICATIONS OF 2:1 CLAY MINERALS IN A KAOLINITE DOMINATED ULTISOL UNDER CHANGING LAND-USE REGIMES AT THE CALHOUN CRITICAL ZONE OBSERVATORY, SOUTH CAROLINA, USA. |
| 4:00–4:20 | Bruno Lanson*, Eleanor Bakker, Michelle M. Wander, and Fabien Hubert: MINERALOGICAL EVOLUTION IN A TEMPERATE CULTIVATED SOIL ARISING FROM DIFFERENT AGRONOMIC PROCESSES AND K-UPTAKE BY PLANTS: INSIGHTS FROM THE MORROW PLOTS EXPERIMENTAL FIELDS |
| 4:20–4:40 | Maximilien Mathian*, Julie Aufort, Jean-Jacques Braun, Jean Riotte, Madeleine Selo, Etienne Balan, Emmanuel Fritsch, Shrema Bhattacharya, and Thierry Allard: EPR DATING OF INDIAN REGOLITHS (KARNATAKA PLATEAU): RECORD OF THE ASIATIC MONSOON EVOLUTION |
| 4:40–5:00 | Mohammadhasan Sasar*, Marika Santagata, Cliff Johnston, Antonio Bobet, and Heather Kaminsky: STRUCTURE CHANGE IN OIL SANDS FLUID FINE TAILINGS DUE TO FLOCCULATION WITH A HIGH MOLECULAR WEIGHT ANIONIC POLYACRYLAMIDE |
| 5:00–5:20 | Paul Schroeder*, Jason C. Austin, and Daniel deB. Richter: LANDSHED POSITION AND MANAGEMENT AND THEIR RELATION TO MINERAL AND CHEMICAL WEATHERING AS ASSESSED BY HIERARCHICAL CLUSTER ANALYSIS OF REGOLITH ELEMENTAL DATA |

MONDAY EVENING

PINE ROOM

5:40–8:00 Poster Session and Reception

Posters

Abiotic Redox Processes Related to Clays and Clay Minerals

Héloïse Verron*, Julien Bonnet, Jérôme Sterpenich, Franck Bourdelle, Régine Mosser-Ruck, Aurélien Randi, and Nicolas Michau: IRON/CEMENTIOUS BENTONITIC MATERIAL/CLAYSTONE INTERACTION UNDER HYDROTHERMAL CONDITIONS

Clay Interactions with Contaminants and Radionuclides: From Molecular Mechanisms to Environmental Fate

Hui Xu, Yong Chen*, Rongrong Hao, Xia Zhang, and Chengyu Huang: RAPID ADSORPTION AND REDUCTIVE DEGRADATION OF NAPHTHOL GREEN B FROM AQUEOUS SOLUTION BY POLYPYRROLE/ATTAPULGITE COMPOSITES SUPPORTED NANOSCALE ZERO-VALENT ION

Xiaolei Liu and Hailiang Dong*: EFFECTS OF ORGANIC LIGANDS ON HEXAVALENT CHROMIUM REDUCTION BY STRUCTURAL IRON IN NONTRONITE

Yong Chen, Hui Xu*, Zeting Zhao, and Jing Tang: POLYANILINE/ATTAPULGITE-SUPPORTED NANOSCALE-VALENT IRON FOR THE RIVAL REMOVAL OF AZO DYES IN AQUEOUS SOLUTION

Victoria V. Krupskaya, Olga V. Dorzhieva*, Sergey V. Zakusin, Ekaterina A. Tyupina, Petr S. Belousov, Yana Yu. Ershova, Victoria O. Zharkova, Elena V. Zakharova: STRUCTURAL FEATURES OF MONTMORILLONITES FROM RUSSIAN DEPOSITS AND THEIR INFLUENCE ON SORPTION CHARACTERISTICS TOWARDS RADIONUCLIDES ^{90}Sr , ^{137}Cs , ^{233}U , ^{241}Am

EET (Extracellular electron transfer) goes AC/DC: Microbial Oxidation and Reduction of Insoluble Fe Oxides and Phyllosilicates in Soil and Sedimentary Environments

Jingyu Ma, Hailiang Dong*, and Qiang Zeng: DYNAMICS OF MINERAL-ORGANIC MATTER COMPLEXES DURING MINCROBIAL Fe REDUCTION

Simin Zhao* and Hailiang Dong: THE EFFECT OF ORGANIC LIGANDS ON BIOTIC OXIDATION OF STRUCTURAL Fe(II) IN REDUCED NONTRONITE BY PSEUDOGULBENKIANIA SP. STRAIN 2002

Hongyan Zuo*, Hailiang Dong, Zihua Zhu, Ravi Kukkadapu, and Liuqin Huang: EFFECTS OF MICROBIAL ACTIVITIES ON ORGANIC MATTER-CLAY MINERAL ASSOCIATIONS

General Session

Ryan Bowman*, and L. Lefticariu: CHARACTERIZATION OF MIXED- MINERAL SYSTEMS INVOLVING CLAY AND IRON OXYHYDROXIDE MINERALS UNDER ACIDIC CONDITIONS

Lingya Ma*, Jianxi Zhu, Yunfei Xi, Runliang Zhu, Hongping He, and Xiaoliang Liang: ADSORPTION OF PHENOL, PHOSPHATE AND Cd(II) BY INORGANIC-ORGANIC MONTMORILLONITES: A COMPARATIVE STUDY OF SINGLE AND MULTIPLE SOLUTE

Ahmed Radwan*, A.M. Abudeif, M.M. Attia, M. A. Elkhawaga, and Wael K. Abdelghany: EFFECT OF THE CLAY MINERALS CHEMICAL STABILITY ON THE PORE PRESSURE MODEL CALIBRATION, GULF OF SUEZ, EGYPT

Aakriti Sharma*, Dean Hesterberg, Amanda Muyskens, Matthew L. Polizzotto, Joseph Guinness, Montserrat Fuentes, Juergen Thieme, and Garth Williams: MODELING MICROSCALE ARSENATE ACCUMULATION IN COMPLEX SOIL MINERAL ASSEMBLAGES

Slawomir Zimowski*, Małgorzata Zimowska, and Helena Pálková: MICROMECHANICAL PROPERTIES OF CLAY POLYMER NANOCOMPOSITE COATINGS

Intensively Managed Clays in the Critical Zone

Suwei Xu* and Yuji Arai: DEPTH SEQUENCE PHOSPHORUS DISTRIBUTION AND SPECIATION IN INTENSIVELY MANAGED CLAYEY AGRICULTURAL SOILS IN CENTRAL ILLINOIS

New Visions in Clay Science: Bio-nanoclays in Medicine

Margarita Bobadilla*, Maria G. Silva-Valenzuela, Lilian Gregory, and Francisco R. Valenzuela: TETRACYCLINE INCORPORATION INTO BENTONITE FOR CONTROLLED DRUG DELIVERY APPLICATIONS

Goeun Choi*, Ie-Rang Jeon, Huiyan Piao, and Jin-Ho Choy: BOROCAPTATE-CLAY HYBRID FOR BORON NEUTRON CAPTURE THERAPY

Goeun Choi*, Yeon-Ji Oh, Huiyan Piao, and Jin-Ho Choy: A NEW ANTIDEPRESSANT CLAY HYBRID DRUG; ARIPIPRAZOLE-MONTMORILLONITE

Sairan Eom*, Goeun Choi, and Jin-Ho Choy: 64CU-DOPED ANIONIC NANOCCLAY FOR IN-VIVO PET IMAGING

Sairan Eom*, Goeun Choi, and Jin-Ho Choy: INDUCED POLARIZATION AND PIEZOELECTRIC EFFECT BY NON-POLAR HYDROTALCITE-LIKE CLAY MINERAL

JiSoo Hwang* and Soo-Jin Choi: SYNTHESIS, CHARACTERIZATION, BIOAVAILABILITY, AND TOXICITY OF MONTMORILLONITE INTERCALATED WITH GLUTATHIONE

Hyoung-Jun Kim*, Sung Hoon Kim, Yoon Suk Kim, and Jae-Min Oh: CELLULAR UPTAKE BEHAVIOR OF LAYERED DOUBLE HYDROXIDE BASED HYBRIDS WITH DIFFERENT SURFACE ROUGHNESS

Ji Yeong Kim*, Goeun Choi, and Jin-Ho Choy: NOVEL ANTIMALARIAL DRUG-CLAY NANOHYBRID; ORAL AND INTRAVENOUS ADMINISTRATION ROUTES

Ji Yeong Kim*, Goeun Choi, and Jin-Ho Choy: PARACELLULAR TRANSPORT OF ANIONIC CLAY VIA IN-VITRO FOLLICLE-ASSOCIATED EPITHELIAL MODEL

Huiyan Piao*, Goeun Choi, and Jin-Ho Choy: GRAPHITIC CARBON NITRIDE INCORPORATED IN 2D NANOCLAY AS A NOVEL UV SCREENING AGENT

Jinseop Shin*, Tae-Hyun Kim, Hyun-Jin Choi, Yeoung-Seuk Bae, and Jae-Min Oh: STABILIZATION OF NEUTRAL MOLECULES INTO INTERLAYER MODIFIED LAYERED DOUBLE HYDROXIDES THROUGH π - π ATTRACTION

Palygorskite: From Fundamental Research to Functional Materials

Qingguo Tang*, Shuang Yang, Jianfeng Sun, Zishuai Xu, Lei Wang, and Jinsheng Liang: STUDY ON THE ADSORPTION OF NANO-FIBER REINFORCED POROUS CARBON ON EMULSIFIED OIL IN WASTEWATER

Wenbo Wang, Guangyan Tian, Qin Wang, Li Zong, Junping Zhang, and Aiqin Wang*: NOVEL ENVIRONMENT-FRIENDLY RED HYBRID PIGMENT FABRICATED FROM NATURAL NANOCLAY

Yujie Zhang*, Shouyong Zhou, Yijiang Zhao, Junping Zhang, and Aiqin Wang: LEARNING FROM ANCIENT MAYA: FACILE PREPARATION OF STABLE PALYGORSKITE/ASTROZON BRILLIANT RED 4G@SiO₂ MAYA-BLUE LIKE PIGMENT

Li Zong, Jie Tang, and Aiqin Wang*: AGING OF BIOCHAR/ATTAPULGITE COMPOSITES AND ITS APPLICATION FOR Pb(II) REMOVAL

Phyllosilicates Throughout the Solar System

Laura Fackrell*: DEVELOPMENT OF MARTIAN REGOLITH SIMULANTS FOR EXPLORATION OF IN SITU RESOURCE AVAILABILITY AND POTENTIAL: PHYLLOSILICATES AND SULFATES ON MARS

Thomas Jeute*, Leslie L. Baker, Janice L. Bishop, Zaenal Abidin, and Elizabeth B. Rampe: CHARACTERIZING NANOPHASE MATERIALS ON MARS: SPECTROSCOPIC STUDIES OF ALLOPHANE AND IMOGOLITE

Anne Gaudin*, Nicolas Mangold, Erwin Dehouck, and Olivier Grauby: FORMATION OF CLAY MINERALS ON MARS: INSIGHTS FROM LONG-TERM EXPERIMENTAL WEATHERING OF OLIVINE

Brad Sutter*, Amanda M. Ostwald, Angela H. Garcia, Tanya S. Peretyazhko, and Douglas W. Ming: IRON/MAGNESIUM SMECTITE FORMATION UNDER ACIDIC CONDITIONS ON EARLY MARS: AN EXPERIMENTAL FLOW-THROUGH ASSESSMENT

Erin Gibbons*, Richard Léveillé, and William Rapin: CLAY-RICH FRACTURE-FILLING CEMENTS IN YELLOWKNIFE BAY, GALE CRATER, MARS: RECOGNIZING CLAY-RICH ROCKS WITH LASER-INDUCED BREAKDOWN SPECTROSCOPY

Structures and Reactivity of Clays and Nanoparticles in Soils and Water

Xiaoqian Jiang, Yuji Arai*, and Lowell Gentry: CHARACTERIZATION OF PARTICULATE PHOSPHORUS IN TILE WATERS FROM INTENSIVELY MANAGED AGRICULTURAL FIELDS IN THE MIDWESTERN U.S.

Yuan Ding, Paul Schwab, M. Aurora Armienta, and Youjun Deng*: PHASE TRANSFORMATION AND CRYSTALLINITY CHANGE OF IRON OXIDE NANOPARTICLES AND THEIR RETENTION OF As, Cu, AND Zn IN SIMULATED ACID MINE DRAINAGE NEUTRALIZATION BY CALCITE AND DOLOMITE

Jing Liu* and Runliang Zhu: Co-ADSORPTION OF PHOSPHATE AND Cd(II) ON IRON (OXYHY)OXIDES: A COMPARATIVE STUDY ON FERRIHYDRITE, GOETHITE, AND HEMATITE

Katarzyna Luberda-Durnaś*, Marek Szczerba, Małgorzata Lempart, and Arkadiusz Derkowski: DISORDER IN Mg-Fe CHLORITES WITH SEMI-RANDOM STACKING AND POLYTYPES' INTERSTRATIFICATION STUDIED WITH POWDER X-RAY DIFFRACTION

Karolina Rybka* and Jakub Matusik: THE QUALITY OF Mg-Fe LAYERED DOUBLE HYDROXIDE DERIVED FROM MAGNESITE AND HEMATITE

Magdalena Skoneczna*, Michał Skiba, Katarzyna Maj-Szeliga, Wojciech Szymański, and Marta Kisiel: APPLICATION OF HIGH GRADIENT MAGNETIC SEPARATION FOR CHARACTERIZATION OF GLAUCONITE WEATHERING PRODUCTS FORMED IN SOILS UNDER DIFFERENT pH CONDITIONS

Qi Tao*, Manyou Chen, Hongping He, and Sridhar Komarneni: HYDROTHERMAL REACTIVITY OF MIXED METAL OXIDES WITH SILICATE ANIONS UNDER ALKALINE CONDITIONS

The Isotopy of Clay Minerals—Mysteries in the Sheets

Skylar Chauvin*, Fred Longstaffe, and Ian Clark: INVESTIGATING THE H-ISOTOPE COMPOSITION OF BOUND WATER IN VERY LOW PERMEABILITY CLAY-RICH SEDIMENTARY ROCKS

Zebadiah Teichert*, Lynda B. Williams, and Maitrayee Bose: A STUDY OF LITHIUM ISOTOPE ALTERATION IN METEORITIC ORGANICS

The Role of Clay Minerals in Controlling the Properties and Geochemical Processes Associated with Hydrocarbon Systems

Jack Fekete*, Timothy Henderson, Cliff Johnston, Nate Schultheiss, Ken Ridgway, and Bryan Clayton: INTEGRATIVE RESERVOIR CHARACTERIZATION FOR CHEMICAL ENHANCED OIL RECOVERY, TAR SPRINGS FORMATION, ILLINOIS BASIN, UNITED STATES OF AMERICA

Jared Freiburg*, Markus Peltz, and Georg H. Grathoff: HIGH-RESOLUTION PORE NETWORK AND MINERALOGICAL MODELING OF SEALING SHALES AT THE ILLINOIS BASIN-DECATUR PROJECT

TUESDAY MORNING

PLENARY SESSION

ILLINI ROOM A

8:00–8:05	Introductory announcements, Yuji Arai, General Chair
8:05–8:15	Introduction of the 2018 Pioneer in Clay Science recipient, Warren D. Huff, University of Cincinnati
8:15–8:55	Acceptance and Presentation Jan Środoń MY LIFE WITH ILLITE-SMECTITE (PIONEER IN CLAY SCIENCE LECTURE)

TECHNICAL SESSIONS

ILLINI ROOM A

Illite-smectite Group in Geological Systems Soils Laboratory and Computer: The Complete Picture

Organizers: W. Crawford Elliott and Jan Środoń

9:00–9:20	Olga Dorzhieva*, Victoria V. Krupskaya, Boris A. Sakharov, Sergey V. Zakusin, Svetlana A. Garanina, and Olga V. Andreeva: STRUCTURAL FEATURES OF HYDROTHERMAL ILLITE-SMECTITES IN METASOMATITES AT THE ANTEI-STRELTISOVSKOE URANIUM DEPOSIT (RUSSIA)
9:20–9:40	Mingyong Du*, Jishan Liu, and Yee-Kwong Leong: TRIPOLYPHOSPHATE EFFECT ON THE RHEOLOGY AND MICROSTRUCTURE OF MAGNESIUM CHLORIDE LOADED BENTONITE GELS
9:40–10:00	Ahmed Radwan*, A.M. Abudeif, M.M. Attia, A. A. Kassem, and W. Said: EFFECT OF CLAY MINERALS IN OIL AND GAS FORMATION DAMAGE PROBLEMS: A CASE STUDY, GULF OF SUEZ, EGYPT
10:00–10:20	Break

Clay Interactions with Contaminants and Radionuclides: From Molecular Mechanisms to Environmental Fate

Organizers: Jeff Catalano and Nik Qafoku

10:20–10:40	Carolyn Pearce*, Kirk J. Cantrell, Sarah A. Saslow, Elsa A. Cordova, Whitney L. Garcia, Adam P. Sims, Steve M. Heald, and Vicky L. Freedman: ROLE OF CLAY STRUCTURE, COMPOSITION AND REDOX CHEMISTRY IN IMMOBILIZATION OF CATIONIC AND ANIONIC RADIONUCLIDES
10:40–11:00	Daniel Kaplan*, Dien Li, Shan Huang, Peter R. Jaffé, John C. Seaman, Chen Xu, Peter H. Santschi, Alice C. Dohnalkova, and Nikola Tolic: IMPACT OF THE UNIQUE MINERALOGY AND ORGANIC MATTER COMPOSITION OF THE RHIZOSPHERE ON URANIUM IMMOBILIZATION

11:00–11:20	Itamar Shabtai* and Yael G Mishael: POLYCYCLODEXTRIN-MONTMORILLONITE COMPOSITES: REGENERABLE DUAL-SITE SORBENTS FOR REMOVAL OF BISPHENOL A FROM WASTEWATER
11:20–11:40	Samuel Perry*, Stuart J. Mills, and Peter C. Burns: URANYL PEROXIDE NANOCLUSTER INTERCALATION INTO SYNTHETIC HYDROTALCITE
11:40–12:00	Sang Soo Lee* and Paul Fenter: EVOLUTION OF ADSORBED METAL CATION SPECIATION DURING ION EXCHANGE AT THE MUSCOVITE (001)–WATER INTERFACE
12:00–1:20	Lunch

ILLINI ROOM B

Applications of NMR Spectroscopy to Clays and Clay Mineral Systems

Organizers: Wei Li and Brian Phillips

9:00–9:20	Geoffrey Bowers* and R. James Kirkpatrick: BRINGING INTERFACIAL PROCESSES TO LIGHT (OR MAGNET): NMR OF SMECTITE-FLUID INTERFACES
9:20–9:40	William Casey*: SOLUTION NMR AT GEOCHEMICAL PRESSURES
9:40–10:00	Ren Chao*, Junfeng Ji, and Wei Li: APPLICATION OF SOLID STATE NMR AT MINERAL/WATER INTERFACE: A MOLECULAR LEVEL INVESTIGATION OF FLUORIDE REMOVAL BY NANO-SIZED HYDROXYAPATITE
10:00–10:20	Break
10:20–10:40	Jinlei Cui, David Olmsted, Mark D. Asta, Daniel E. Giammar, and Sophia E. Hayes*: SURPRISING FINDINGS FROM SOLID-STATE NMR OF ¹³ C IN CARBONATES: ON THE PATHWAY TO NMR CRYSTALLOGRAPHY
10:40–11:00	Rixiang Huang*, Biao Wan, Margot Hultz, Julia M. Diaz, and Yuanzhi Tang: APPLICATION OF ³¹ P NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY FOR UNDERSTANDING POLYPHOSPHATE DEGRADATION
11:00–11:20	Harris Mason*: PROBING THE MINERAL SURFACE REACTIONS OF RADIONUCLIDES WITH ADVANCED SOLID-STATE NMR TECHNIQUES
11:20–11:40	Nicholai Daugaard Jensen, Suraj S.C. Charan, Claude Forano, Yusuke Nishiyama, Nghia Dong, Ralph Bolanz, Dorthe B. Ravnsbæk, and Ulla Gro Nielsen: THE ATOMIC LEVEL STRUCTURE OF LAYERED DOUBLY HYDROXIDES AS SEEN BY SOLID STATE NMR SPECTROSCOPY AND OTHER TECHNIQUES
11:40–12:00	Brian Phillips*: QUANTIFYING HYDROLYSIS OF KEGGIN-BASED AL-CLUSTERS FROM NMR SPECTROSCOPY
12:00–1:20	Lunch

ILLINI ROOM C

Palygorskite: From Fundamental Research to Functional Materials

Organizers: Aiqin Wang and Junping Zhang

9:00–9:20	Atsushi Takahara*, Wei Ma, and Yuji Higaki: DESIGN AND CHARACTERIZATION OF NOVEL (POLYMER/CLAY NANOTUBE) HYBRIDS
9:20–9:40	Shouyong Zhou*, Ailian Xue, Yan Zhang, Meisheng Li, and Yijiang Zhao: POLYVINYLIDENE FLUORIDE ULTRAFILTRATION MEMBRANE BY INCORPORATION OF THERMO-RESPONSIVE PALYGORSKITE NANOFIBERS WITH ENHANCED FLUX AND ANTIFOULING PROPERTIES
9:40–10:00	Meisheng Li*, Yijiang Zhao, Shouyong Zhou, and Wen Zhang: HETEROGENEOUS POLY(IONIC LIQUIDS) CATALYST ON NANOFIBER-LIKE PALYGORSKITE SUPPORTS FOR BIODIESEL PRODUCTION
10:00–10:20	Break
10:20–10:40	Junping Zhang*, Bucheng Li, and Aiqin Wang: SUPERHYDROPHOBIC AND SUPERAMPHIPHOBIC COATINGS BASED ON PALYGORSKITE
10:40–11:00	Eduardo Ruiz-Hitzky*, Cristina Ruiz-García, Margarita Darder, and Pilar Aranda: CARBON-SILICATE COMPOSITES: THE ROLE OF FIBROUS CLAYS
11:00–11:20	Meng Fu*, Xiangming Li, and Zepeng Zhang: HIGHLY TUNABLE LIQUID CRYSTALLINE ASSEMBLIES OF SUPERPARAMAGNETIC ATTAPULGITE Fe_3O_4 NANORODS
11:20–11:40	Pilar Aranda*, Marwa Akkari, Ana C.S. Alcântara, Yorexis González, Margarita Darder, and Eduardo Ruiz-Hitzky: MAGNETIC NANOPLATFORMS BASED ON FIBROUS CLAYS FOR REMOVAL OF POLLUTANTS
11:40–12:00	Xuehua Zou*, Tianhu Chen, Haibo Liu, Ping Zhang, and Steven L. Suib: HIGH CATALYTIC PERFORMANCE OF Fe-Ni/PALYGORSKITE IN THE STEAM REFORMING OF TOLUENE FOR HYDROGEN PRODUCTION
12:00–1:20	Lunch

TUESDAY AFTERNOON

TECHNICAL SESSIONS

ILLINI ROOM A

Clay Interactions with Contaminants and Radionuclides: From Molecular Mechanisms to Environmental Fate*Organizers: Jeff Catalano and Nik Qafoku*

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| 1:20–1:40 | Tomasz Bajda*: OXYANIONS SORPTION BY ORGANO-SMECTITE |
| 1:40–2:00 | Anastasia Ilgen*, Ravi K. Kukkadapu, Rachel E. Washington, and Kevin Leung: REACTIVITY OF IRON IN NATURAL AND SYNTHETIC FERRIC NONTRONITES |
| 2:00–2:20 | Paulina Maziarz* and Jakub Matusik: MAGHEMITE PARTICLES SUPPORTED ON HALLOYSITE AS MAGNETICALLY RESPONSIVE COMPOSITES FOR EFFICIENT As(V) REMOVAL |
| 2:20–2:40 | Emily Saad, Shiliang Zhao, and Yuanzhi Tang*: MOLECULAR SCALE MECHANISM OF CHROMIUM INTERACTION WITH METAL OXIDES: MICROBIAL AND STRUCTURAL ASPECTS |
| 2:40–3:00 | Khalid Zakaria, Yang Ding, Lening Chen, and Anke Neumann: CONTAMINANT OXIDATION WITH Fe(II)-BEARING CLAY MINERALS |
| 3:00–3:20 | Ying Li*, Xiaoliang Liang, Hongping He, Joseph W. Stucki, Linda Pentrakova, and Martin Pentrak: HETEROGENEOUS REDUCTION OF 2-CHLORONITROBENZENE BY Co-SUBSTITUTED MAGNETITE COUPLED WITH AQUEOUS Fe(II): PERFORMANCE, CHARACTERIZATION AND MECHANISM |
| 3:20–3:40 | Break |
| 3:40–4:00 | Sergey V. Zakusin*, Yana V. Bychkova, Ekaterina A. Tyupina, Petr S. Belousov, and Victoria V. Krupskaya: SORPTION CHARACTERISTICS OF NATURAL AND ACID-TREATED BENTONITES FROM RUSSIAN DEPOSITS |
| 4:00–4:20 | Yayu Li* and Cristian P. Schulthess: STRICT ION-EXCHANGE MODELING FOR CATION SELECTIVE ADSORPTION ON Na- MONTMORILLONITE |
| 4:20–4:40 | Jesús I. Martínez-Costa, Roberto Leyva-Ramos*, Erika Padilla-Ortega, Antonio Aragón-Piña, and Damarys H. Carrales-Alvarado: COMPETITIVE SORPTION OF SULFAMETHOXAZOLE-TRIMETHOPRIM AND SULFAMETHOXAZOLE-CADMIUM (II) ON AN ORGANOCLAY |
| 4:40–5:00 | Liliana Lefticariu*, Stephen R. Sutton, Antonio Lanzirotti, Theodore M. Flynn, and Martin Pentrak: THE IMPACT OF DETRITAL CLAY MINERALS ON CONTAMINANT DYNAMICS IN AMD-IMPACTED SYSTEMS |

ILLINI ROOM B

EET (Extracellular electron transfer) goes AC/DC: Microbial Oxidation and Reduction of Insoluble Fe Oxides and Phyllosilicates in Soil and Sedimentary Environments

Organizers: Eric Roden and Jinwook Kim

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| 1:20–1:40 | Li Zhang*, Hailiang Dong, and Liang Shi: FUNCTION OF THE OUTER-MEMBRANE CYTOCHROMES IN REDUCTION OF NONTRONITE BY SHEWANELLA ONEIDENSIS MR-1 AND COMPARISON BETWEEN DIFFERENT ELECTRON SHUTTLES |
| 1:40–2:00 | Vincent Noël, Kristin Boye, Callum Bobb, Emily Cardarelli, Ravi Kukkadapu, Scott Fendorf, Kate Maher, Chris A. Francis, and John Bargar*: IRON-SULFUR REDOX CYCLING AND CONTAMINANT MOBILITY IN THE UPPER COLORADO RIVER BASIN |
| 2:00–2:20 | Luis Zarate-Reyes, Cynthia Lopez-Pacheco, Antonio Nieto-Camacho, Maria Teresa Ramirez Apán, Eduardo Palacios, Stephan Kaufhold, Kristian Ufer, Eduardo Garcia Zepeda, and Javiera Cervini-Silva*: NATURALLY OCCURRING LAYERED-MINERAL MAGNESIUM AS A BACTERICIDAL AGAINST ESCHERICHIA COLI |
| 2:20–2:40 | Bingjie Shi*, Philippe Van Cappellen, Chris T. Parsons, Christina M. Smeaton, Eric E. Roden, Clark M. Johnson, and Brian Kendall: DIFFERENT POOLS OF BIOAVAILABLE IRON IN NONTRONITE N _{Au} -1: INSIGHTS FROM IRON STABLE ISOTOPES |
| 2:40–3:00 | James Entwistle*, David Werner, Drew E. Latta, Michelle M. Scherer, and Anke Neumann: MICROBIALLY MEDIATED ABIOTIC REDUCTION OF CLAY MINERAL IRON: UNDERSTANDING THE ROLE OF SECONDARY PRECIPITATES FOR CONTAMINANT REMEDIATION |
| 3:00–3:20 | Jin-wook Kim*: MICROBE-MINERAL INTERACTION IN EXTREME ENVIRONMENTS |
| 3:20–3:40 | Break |
| 3:40–4:00 | Tae-hee Koo*, Gill Geseey, Kyeong Ryang Park, and Jin-wook Kim: BIOMINERALIZATION ASSOCIATED WITH MICROBIAL Fe/As REDOX REACTION IN EXTREME ENVIRONMENT: YELLOWSTONE NATIONAL PARK |
| 4:00–4:20 | Stephanie Napieralski*, H.L. Buss, S. He, and E.E. Roden: EXTRACELLULAR ELECTRON TRANSFER AS A MECHANISM OF BIOGEOCHEMICAL WEATHERING OF Fe(II) SILICATES BY LITHOTROPIC IRON OXIDIZING BACTERIA |
| 4:20–4:40 | Katherine A. Rothwell and Anke Neumann*: EFFECT OF MICROBIALLY PRODUCED ORGANIC COMPOUNDS ON THE REDOX REACTIVITY OF Fe-BEARING CLAY MINERALS |
| 4:40–5:00 | Eric Roden*, T. Wu, S. He, and E. Shelobolina: MICROBIAL REDUCTION AND OXIDATION OF Fe(III)-OXIDES AND Fe(III)-PHYLLOSILICATES IN SOIL AND SEDIMENTARY ENVIRONMENTS |

ILLINI ROOM C

Palygorskite: From Fundamental Research to Functional Materials*Organizers: Aiqin Wang and Junping Zhang*

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| 1:20–1:40 | Mercedes Suarez*, Emilia García-Romero, Juan Morales, and Esperanza San-Gregorio: THERMAL BEHAVIOR OF DIFFERENT TERMS OF THE SEPIOLITE-PALYGORSKITE POLYSOMATIC SERIES |
| 1:40–2:00 | Wenbo Wang*, Aiqin Wang, Li Zong, Qin Wang, and Yuru Kang: SIMULTANEOUS TRANSFORMATION OF PALYGORSKITE AND ASSOCIATED MINERALS TO FABRICATE HIGHLY EFFICIENT MESOPOROUS SILICATE ADSORBENT |
| 2:00–2:20 | Yijiang Zhao*, Ailian Xue, Yan Zhang, Shouyong Zhou, and Meisheng Li: THE CERAMIC MICROFILTRATION MEMBRANE WITH A SEPARATION LAYER OF PALYGORSKITE NANOFIBERS |
| 2:20–2:40 | Jinlong Jiang, Lingli Li*, and Yongkui Liu: GREEN SYNTHESIS OF ZEOLITE FROM NATURAL CLAY UNDER MICRO-AMOUNT OF SOLVENT CONDITIONS |
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Bentonite Barriers*Organizer: Georg Grathoff and Stephen Kanfhold*

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| 2:40–3:00 | Macarena Leal* and Thomas B. Scott: A STUDY OF GEOLOGICAL DISPOSAL FACILITIES ALTERATION PHENOMENA IN BENTONITE. |
| 3:00–3:20 | Carolyn Podlech*, Nicole Matschiavelli, Georg H. Grathoff, and Laurence N. Warr: BENTONITE ALTERATION IN AQUEOUS SOLUTIONS RELEVANT TO THE UNDERGROUND DISPOSAL OF RADIOACTIVE WASTE INCLUDING THE EFFECTS OF MICROBIAL ACTIVITY |
| 3:20–3:40 | Break |
| 3:40–4:00 | Patrik Sellin*: MECHANICAL PROPERTIES OF BENTONITE BARRIERS—THE BEACON PROJECT |
| 4:00–4:20 | Daniel Svensson*: DEVELOPMENT OF INDUSTRIAL SCALE QUALITY CONTROL OF BENTONITE FOR BUFFER IN A KBS-3 HIGH LEVEL RADIOACTIVE WASTE REPOSITORY |
| 4:20–4:40 | Paul Wersin*, Jebril Hadi, Andreas Jenni, Jean-Marc Grenèche, Daniel Svensson, Patrik Sellin, Olivier Leupin, and Florian Kober: WHAT CAN WE LEARN FROM IRON-BENTONITE INTERFACES WITH REGARD TO SAFETY ASSESSMENT OF HIGH-LEVEL WASTE REPOSITORIES? |
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**CONFERENCE BANQUET AT THE MEMORIAL STADIUM COLONNADES CLUB—
BUSES LEAVE THE FRONT OF THE ILLINI UNION AT 5:30 PM**

WEDNESDAY MORNING

PLENARY SESSION

ILLINI ROOM A

8:00–8:05	Introductory announcements, Yuji Arai, General Chair
8:05–8:15	Introduction of the 2018 Marilyn & Sturges W. Bailey Distinguished Member Award recipient, Will P. Gates, SmecTech Research Consulting
8:15–8:55	Acceptance and Presentation Jock Churchman: THE ENIGMA OF HALLOYSITE (BAILEY AWARD LECTURE)

TECHNICAL SESSIONS

ILLINI ROOM A

The Role of Clay Minerals in Controlling the Properties and Geochemical Processes Associated with Hydrocarbon Systems

Organizers: David Cole

9:00–9:20	Steve Chipera* and Leonardo Alcantar-Lopez: MEASUREMENT OF POROSITY SIZE AND DISTRIBUTION IN SHALES AND OTHER TIGHT-ROCK RESOURCES
9:20–9:40	Shane Butler*, Alexander Azenkeng, Kurt E. Eylands, Blaise A.F. Mibeck, and Bethany A. Kurz: PRELIMINARY CHARACTERIZATION OF CLAYS IN THE UNCONVENTIONAL BAKKEN OIL RESERVOIR
9:40–10:00	Heather Kaminsky*: CLAYS IN OIL SANDS: AN UPDATE AND CALL FOR COLLABORATION
10:00–10:20	Break
10:20–10:40	Ali Seiphoori*, Andrew J. Whittle, Paul Marschall, and Herbert H. Einstein: DIAGENETIC CEMENTATION EFFECTS ON THE PORE STRUCTURE AND MECHANICAL PROPERTIES OF OPALINUS CLAY-SHALE
10:40–11:00	Gernot Rother*, Michael Cheshire, and David R. Cole: NOBLE GAS AND LIGHT HYDROCARBON INTERACTIONS WITH MONTMORILLONITE: ACCESSIBILITY OF THE INTERLAYERS
11:00–11:20	Pan Liu* and Junfeng Ji: HYDROTHERMAL SYNTHESIS OF CHLORITE FROM SAPONITE: KINETICS AND MECHANISMS OF SMECTITE-CHLORITE CONVERSION
11:20–11:40	R. James Kirkpatrick*, Narasimhan Loganathan, Geoffrey M. Bowers, Ozgur O. Yazaydin, John S. Loring, H. Todd Schaefer, Eric D. Walter, Sarah D. Burton, and David W. Hoyt: CLAY MINERALS IN HYDROCARBON RESERVOIRS: COMPUTATIONAL AND EXPERIMENTAL STUDIES OF SMECTITE-H ₂ O-CO ₂ -CH ₄ INTERACTIONS

11:40–12:00	Jennifer A.R. Willemsen, Lydia Watt, Alex W. Byrnes, Alison O. Chang, and Ian Bourg*: NANOSCALE CONTROLS ON CLAY-ORGANIC INTERACTIONS
12:00–1:20	Lunch

ILLINI ROOM B

Structures and Reactivity of Clays and Nanoparticles in Soils and Water

Organizers: Youjun Deng, Mengqiang Zhu, and Yuji Arai

9:00–9:20	Donald L. Sparks*: MINERAL/WATER INTERFACIAL REACTIVITY IN A CHANGING ENVIRONMENT
9:20–9:40	Mengqiang Zhu*, Xiaoming Wang, and Chunhao Gu: IDENTIFICATION AND QUANTIFICATION OF SILICATE, PHOSPHATE AND SULFATE SPECIES ON IRON OXIDE SURFACES USING SPECTROSCOPIC AND ATOMIC PAIR DISTRIBUTION FUNCTION ANALYSES
9:40–10:00	Jakub Matusik*, Karolina Rybka, Joanna Kuzdro, and Bartosz Toboła: HALLOYSITE-BASED HYBRID COMPOSITES WITH SYNTHETIC LDH AND THEIR AFFINITY TO REMOVE ANIONS
10:00–10:20	Break
10:20–10:40	Anping Peng, Yi Wang, and Cheng Gu*,: TRANSFORMATION OF ORGANIC CONTAMINANTS ON MONTMORILLONITE CLAY MINERAL SURFACES
10:40–11:00	Hui Li*, Yingjie Zhang, Stephen A. Boyd, Brian J. Teppen, and James M. Tiedje: BIOAVAILABILITY OF TETRACYCLINE TO ANTIBIOTIC RESISTANT ESCHERICHIA COLI IN AQUEOUS CLAY SUSPENSIONS
11:00–11:20	Dongsheng Li*, Jaehun Chun, Hailong Wang, Ben Legg, Dongdong Xiao, Kevin M. Rosso, Christopher J. Mundy, Gregory K. Schenter, and James J. De Yoreo: INFLUENCE OF CRYSTAL ORIENTATION AND MOLECULAR DETAILS ON LONG-RANGE DISPERSION FORCES UNDERLYING AGGREGATION AND CO-ALIGNMENT BETWEEN CRYSTALS
11:20–11:40	Juan Liu*, Anxu Sheng, Yixiao Zhang, and Xiaoxu Li: SIZE-DEPENDENT AGGREGATION OF HEMATITE PARTICLES IN AQUATIC ENVIRONMENTS
11:40–12:00	Derek Peak*, David Hilger, and Jordan G. Hamilton: THE ROLE OF MAGNESIUM IN METASTABILITY OF CALCIUM PHOSPHATE MINERALS
12:00–1:20	Lunch

ILLINI ROOM C

Molecular Studies of Clay Minerals and Related Structures*Organizers: Jeff Greathouse*

9:00–9:20	Eric Ferrage*, Patrice Porion, Thomas Dabat, Fabien Hubert, Erwan Paineau, Emmanuel Tertre, and Alfred Delville: ANISOTROPIC FEATURES OF WATER DIFFUSION IN CLAY POROUS MEDIA: A COMBINATION OF COMPUTATIONAL AND EXPERIMENTAL METHODS
9:20–9:40	Jing Peng*, Guoping Zhang, and Don J. DeGroot: QUANTITATIVE TEXTURE ANALYSIS OF WET CLAYS DURING THIXOTROPIC HARDENING USING SYNCHROTRON X-RAY DIFFRACTION
9:40–10:00	Tuan Ho*, Louise Criscenti, Jeffery Greathouse, and Yifeng Wang: MOLECULAR STUDY OF THE EDGE EFFECT ON AQUEOUS CATION ADSORPTION ON GIBBSITE NANOPARTICLES
10:00–10:20	Break
10:20–10:40	Chi Zhang*, Andrey G. Kalinichev, and Xiandong Liu: MOLECULAR DYNAMICS SIMULATIONS OF HEAVY METALS ADSORPTION ON CLAY MINERALS
10:40–11:00	McNeill Bauer* and F. Marc Michel: FACTORS REGULATING SYNTHESIS AND FORMATION STAGES OF ALLOPHANE NANOPARTICLES
11:00–11:20	Javiera Cervini-Silva*, Eduardo Palacios, and Virginia Gómez- Vidales: NONTRONITE AS NATURAL SOURCE AND GROWTH TEMPLATE FOR (NANO) MAGHEMITE [γ -Fe ₂ O ₃] AND (NANO)WÜSTITE [Fe _{1-x} O]
11:20–11:40	Alena Kremleva*, Sven Krüger, and Notker Rösch: QUANTUM CHEMICAL MODELING OF Fe(III) IN 2:1 DIOCTAHEDRAL SMECTITES
11:40–12:00	Marek Szczerba* and Kristian Ufer: NEW MODEL OF ETHYLENE GLYCOL LAYERS INTERCALCATED IN SMECTITES FOR XRD MODELLING
12:00–1:20	Lunch

WEDNESDAY AFTERNOON

ILLINI ROOM A

The Role of Clay Minerals in Controlling the Properties and Geochemical Processes Associated with Hydrocarbon Systems*Organizers: David Cole*

1:20–1:40	Louise Criscenti*, Yifeng Wang, and Tuan Anh Ho: MOLECULAR MODELING OF KEROGEN AND NATURAL GAS SYSTEMS
1:40–2:00	Pawel Ziemianski*, Arkadiusz Derkowski, and Marek Szczerba: HIGH-PRESSURE METHANE ADSORPTION ON MONTMORILLONITE: EXPERIMENTS AND MONTE CARLO SIMULATIONS

- 2:00–2:20 Andrey Kalinichev*, Brice F. Ngouana-Wakou, and Iuliia Androniuk: INTERACTION OF NATURALLY OCCURRING RADIOACTIVE MATERIALS WITH CLAY MINERALS IN THE CONTEXT OF SHALE GAS EXPLORATION
- 2:20–2:40 David Cole* and Alberto Striolo: STRUCTURE, DYNAMICS AND REACTIVITY OF C-O-H FLUIDS IN NANOPOROUS REGIMES

Phyllosilicates Throughout the Solar System

Organizer: Michael Velbel

- 2:40–3:00 Thomas Bristow*, V. K. Fox, K. A. Bennett, E. B. Rampe, V. Z. Sun, and the MSL Science Team: A PRELUDE TO THE CLAY-BEARING UNIT OF MOUNT SHARP, GALE CRATER, MARS
- 3:00–3:20 Valerie Fox*, B. Ehlmann, J. G. Catalano, R. J. Kupper, R. D. Nickerson, S. M. Katz, and A. A. White: SPECTRAL AND OPTICAL PROPERTIES OF $\text{Fe}^{3+}/\text{Fe}^{2+}$, Mg, Al SMECTITES TO IMPROVE PLANETARY REMOTE SENSING
- 3:20–3:40 Break
- 3:40–4:00 Tanya Peretyazhko*, Brad Sutter, Paul B. Niles, Richard V. Morris, David G. Agresti, Joanna V. Hogancamp, and Douglas W. Ming: SMECTITE FORMATION IN ACID SULFATE ENVIRONMENTS ON MARS
- 4:00–4:20 Jeffrey Catalano*, Steven M. Chemtob, Ryan D. Nickerson, Richard V. Morris, and David G. Agresti: FORMATION AND OXIDATION OF Fe(II) -Mg TRIOCTAHEDRAL SMECTITES ON EARLY MARS
- 4:20–4:40 Leslie Baker*: MAGNESIAN CLAYS IN COLUMBIA RIVER BASALTS: A NEW POSSIBLE MARS ANALOG FOR EARLY WEATHERING
- 4:40–5:00 Rebecca Smith*, Briony Horgan, Elizabeth Rampe, and Erwin Dehouck: ARE AMORPHOUS PHASES ON MARS PRECURSORS TO CLAY MINERALS?
- 5:00–5:20 Michael Velbel*: FATE AND TRANSPORT OF SOLUTES IN MICROPOROUS CHONDRITIC ASTEROIDAL AQUIFERS—AND CORES OF OCEAN WORLDS?
- 5:20–5:40 **Reynolds Cup**
Rieko Adriaens: REYNOLDS CUP 2018 WINNER AND PRESENTATION
- 5:40–6:40 CMS Business Meeting, all welcome, in Illini Room A

ILLINI ROOM B

Structures and Reactivity of Clays and Nanoparticles in Soils and Water

Organizers: Youjun Deng, Mengqiang Zhu, and Yuji Arai

- 1:20–1:40 Javier Ramiro Chaparro Barajas*, Carolina Pazos, Lisette D. Ruiz, Esperanza Pavón, María D. Alba, Agustín Cota, and Francisco J. Osuna: Al/Fe PILLARED FROM SYNTHETIC HIGH CHARGED Na-2-MICA

1:40–2:00	Shiliang Zhao, Chenning Li, Mengqiang Zhu, Shuo Chen, and Yuanzhi Tang*: EFFECTS OF METAL IMPURITIES ON THE STRUCTURE AND REACTIVITY OF Mn OXIDE NANOPARTICLES
2:00–2:20	Young-Shin Jun* and Haesung Jung: PHOTOCHEMICALLY-FORMED BIRNESSITE NANOSHEET LAYER STRUCTURES
2:20–2:40	Shichao Ji*, Hongping He, Jianxi Zhu, Qi Tao, Shangying Li, and Zangchao Qun: THE SOLID-STATE TRANSFORMATION FROM BRUCITE TO CLAY MINERALS
2:40–3:00	Wei Li*, Wenxian Gou, and Weiqiang Li: Zn ISOTOPE FRACTIONATION DURING SORPTION ONTO Al OXIDE: MOLECULAR LEVEL UNDERSTANDING FROM Zn EXAFS INVESTIGATION
3:00–3:20	Shupe Wu* and Yu Qingchun: EXPERIMENTAL INVESTIGATIONS ON WATER CONDENSATION IN SHALES
3:20–3:40	Break
3:40–4:00	Zhenqing Shi*, Lei Tian, Pei Wang, and Xionghan Feng: COUPLED KINETIC REACTIONS AT MINERAL-WATER INTERFACES: DEVELOPING QUANTITATIVE MODELS
4:00–4:20	Mingyong Du* and Yee-Kwong Leong: MORPHOLOGY STUDY ON MONTMORILLONITE GELS WITH DIFFERENT MICROSCOPY SCANNING METHODS
4:20–4:40	Jerome Labille*, Danielle Slomberg, Anne Pariat, Jonathan Brant, Patrick Ollivier, Olivier Radakovitch, Nicole Sani-Kast, Antonia Praetorius, and Martin Scheringer: ENVIRONMENTAL FATE OF MANUFACTURED NANOPARTICLES IN SURFACE WATER DRIVEN BY HETEROAGGREGATION WITH CLAY COLLOIDS
4:40–5:00	Kirk Scheckel*, Erica Donner, Ryo Sekine, Gianluca Brunetti, and Enzo Lombi: ENVIRONMENTAL TRANSFORMATIONS OF SILVER AND ZINC OXIDE NANOPARTICLES DRIVE RISK ASSESSMENT UNDERSTANDING
5:00–5:20	Dean Hesterberg* and James LeBeau: NANOSCALE STRUCTURAL COMPLEXITY AND REACTIVITY OF SOIL MINERAL ASSEMBLAGES
5:20–5:40	Taofeeq O. Salawudeen, Monsurat Jimoh*, Akeem O. Arinkoola, and Micheal O. Daramola: MODIFICATION AND CHARACTERIZATION OF A NIGERIAN CLAY FOR IMPROVED RHEOLOGY IN WATER-BASED DRILLING FLUID
5:40–6:40	CMS Business Meeting, all welcome, in Illini Room A

ILLINI ROOM C

Molecular Studies of Clay Minerals and Related Structures

Organizer: Jeff Greathouse

1:20–1:40	Jeffery Greathouse*, Jacob A. Harvey, Todd R. Zeitler, Louise J. Criscenti, Randall T. Cygan, Joanne T. Fredrich, Gary R. Jerauld, and Cliff T. Johnston: MOLECULAR MODELING OF VIBRATIONAL AND ADSORPTION PROPERTIES AT CLAY EDGES
1:40–2:00	Qi Rao and Yongsheng Leng*: MOLECULAR SIMULATION STUDIES OF CO ₂ -GEOLOGICAL FLUIDS IN SWELLING CLAYS

Role of Clay Minerals in the Events Leading to the Origin of Life

Organizers: Gözen Ertem

2:00–2:20	Gözen Ertem*: ROLE OF MINERALS IN THE EVENTS LEADING TO THE ORIGIN OF LIFE-BERNAL-II: PROTECTION OF BIO-ORGANIC MOLECULES BY MINERALS AGAINST RADIATION EFFECTS
2:20–2:40	Gözen Ertem*: CATALYTIC ROLE OF MINERALS FOR THE FORMATION OF RNA OLIGOMERS-BERNAL-I
2:40–3:00	Francisco de Assis Rodriguez, Thomas Georgelin, Jean-François Lambert, and Maguy Jaber*: CONSPIRATION OF MINERALS AND ORGANICS IN ORIGINS OF LIFE
3:00–3:20	Alex Kugler*, and Hailiang Dong: MICAS AS PROTECTIVE HABITATS OF CYANOBACTERIA AGAINST ULTRAVIOLET RADIATION
3:20–3:40	Break

The Isotopy of Clay Minerals—Mysteries in the Sheets

Organizers: Fred Longstaffe

3:40–4:00	Daniel Deocampo*, F. J. Longstaffe, D. Gebregiorgis, G. M. Ashley, E. Beverly, J. Delaney, and J. Cuadros: CHEMISTRY AND ISOTOPES OF PLEISTOCENE CLAYS, OLDUVAI GORGE, TANZANIA: ORBITAL CONTROL OF EAST AFRICAN PALEOCLIMATE
4:00–4:20	H. Albert Gilg* and Mathias Köster: ISOTOPE OF THE SHEETS: EMPERATURES, TIMING AND TRACING OF FLUIDS INVOLVED IN BENTONITE FORMATION
4:20–4:40	Itay Halevy*: THE OXYGEN ISOTOPE COMPOSITION OF SEAWATER THROUGH TIME: A PERSPECTIVE FROM IRON OXIDES AND CLAYS
4:40–5:00	Sarah Simpson*, Fred J. Longstaffe, and Gordon R. Osinski: SECONDARY CLAY MINERALIZATION IN THE CHICXULUB IMPACT CRATER PEAK-RING: AN ISOTOPIC PERSPECTIVE
5:00–5:20	Matthew Svensson*, Gordon R. Osinski, Fred J. Longstaffe, and Sarah L. Simpson: HYDROTHERMAL ALTERATION OF CRATER LAKE DEPOSITS AT THE RIES IMPACT STRUCTURE, GERMANY
5:20–5:40	Lynda Williams* and Maitrayee Bose: LITHIUM ISOTOPE HETEROGENEITY IN COALS AND KEROGEN: AN UNRECOGNIZED LITHIUM CONTRIBUTION TO THE GLOBAL GEOCHEMICAL CYCLE
5:40–6:40	CMS Business Meeting, all welcome, in Illini Room A

THURSDAY MORNING

PLENARY SESSION

ILLINI ROOM 314

8:00–8:05	Introductory announcements, Yuji Arai, General Chair
8:05–8:15	Introduction of the 2018 Brindley Lecture, Douglas McCarty, President of The Clay Minerals Society
8:15–8:55	Acceptance and Presentation Cliff T. Johnston: PROBING THE HYDROPHOBIC/HYDROPHILIC NATURE OF CLAY MINERALS AT THE MESOSCALE SCALE (BRINDLEY LECTURE)

TECHNICAL SESSIONS

ILLINI ROOM 314

Teaching and History of Clay Sciences

Organizers: Steve Altaner

9:00–9:20	Stephen Aja*: THE THERMODYNAMIC STABILITY OF CLAY MINERALS: A RETROSPECTIVE
9:20–9:40	Stephen Altaner*: TEACHING OF CLAY SCIENCE: THE IMPORTANCE OF EMPHASIZING IMPORTANCE
9:40–10:00	W. Crawford Elliott*: THE DERIVATION OF FORMULAS FOR SIMPLE PHYLLOSILICATE MINERALS
10:00–10:20	Break
10:20–10:40	Warren Huff*: TEACHING CLAY SCIENCE: FROM PAST TO PRESENT

Volcanic Ash as Source Material for Clay and Zeolite Mineral Formation

Organizers: Rona Donahoe and Kim Genareau

10:40–11:00	Rona Donahoe*: FORMATION OF ZEOLITE MINERALS FROM VOLCANIC ASH: AN OVERVIEW
11:00–11:20	W. Crawford Elliott*: CLAY GENESIS FROM VOLCANIC PARENT MATERIALS: DIFFRACTION TELLS ONLY PART OF THIS STORY
11:20–11:40	Briony Horgan*, Rebecca Smith, Oliver Chadwick, Greg Retallack, Eldar Noe Dobrea, and Phil Christensen: THE EFFECTS OF CLIMATE, ENVIRONMENT, AND DIAGENESIS ON THE SPECTRAL PROPERTIES OF VOLCANIC SOILS ON EARTH AND MARS

11:40–12:00 Elizabeth Rampe*, Richard V. Morris, Douglas W. Ming, Thomas F. Bristow, Cherie N. Achilles, Janice L. Bishop, Briony Horgan, Rebecca J. Smith, and Michael D. Kraft: ALTERATION OF VOLCANIC SEDIMENTS ON MARS AND THE FORMATION OF CLAY MINERALS AND X-RAY AMORPHOUS MATERIALS

ILLINI ROOM 210

Structures and Reactivity of Clays and Nanoparticles in Soils and Water

Organizers: Youjun Deng, Mengqiang Zhu, and Yuji Arai

9:00–9:20 Yongkang Wu*, Shengmin Luo, Jing Peng, Don J. DeGroot, and Guoping Zhang: FORMATION OF CONCRETIONS IN CONNECTICUT VALLEY VARVED CLAY

9:20–9:40 Fabien Hubert*, Shang Yao Guo, Pierre Barré, Claire Chenu, Eric Ferrage, Emmanuel Tertre, and Folkert van Oort: CLAY MINERALOGY FROM TEMPERATE SOILS: NEW INSIGHTS FROM THE 42 PLOTS LONG-TERM EXPERIMENTAL SITE OF VERSAILLES (FRANCE)

9:40–10:00 Shoeleh Assemi*, Partaksh Sidhu, Sugandha Sharma, Vishal Gupta, Jing Lliu, and Jan D. Miller: INVESTIGATION OF THE PROPERTIES OF CLAY MINERALS AT NANOSCALE

10:00–10:20 Break

10:20–10:40 Seungyeol Lee* and Huifang Xu: THE STRUCTURE, CHEMISTRY, AND TRANSFORMATION OF VERNADITE IN A FERROMANGANESE CRUST FROM A NORTH-WEST PACIFIC SEAMOUNT

10:40–11:00 Bruno Lanson* and Sylvain Grangeon: INFLUENCE OF VERNADITE CRYSTAL STRUCTURE ON ITS REACTIVITY: IMPLICATIONS FOR METAL SORPTION AND PHYLLO-TO-TECTOMANGANATE TRANSFORMATION

11:00–11:20 Huifang Xu*: SOLVING CRYSTAL STRUCTURES AND CONSTRUCTING SIZE-DEPENDENT PHASE MAPS FOR Fe(III)-OXIDE NANO-MINERALS

11:20–11:40 Hongping He*, Shichao Ji, Jianxi Zhu, and Qi Tao: CONVERSION OF 1:1 CLAY MINERALS TO SMECTITE UNDER HYDROTHERMAL CONDITION: IMPLICATION FOR SOLID STATE TRANSFORMATION

11:40–12:00 Xiancai Lu*, Huan Liu, Meng Li, Lijuan Zhang, Chao Pan, Juan Li, and Wanli Xiang: MINERALOGICAL PROPERTIES AND ENVIROMENTAL IMPLICATION OF Mn-SUBSTITUTED GOETHITE

ABSTRACTS

THE THERMODYNAMIC STABILITY OF CLAY MINERALS: A RETROSPECTIVE

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The thermodynamic stabilities of clay minerals have been largely unresolved despite the wealth of thermodynamic data that have become available over the past fifty years; in fact, thermodynamic models of illite stability still routinely use muscovite as a proxy for illite. This stems partly from persistent questions on the validity of solubility measurements under the physicochemical conditions in which clay minerals form. Nonetheless, an assessment of available experimental studies suggests that the evidence for the attainment of equilibrium in certain studies with clay minerals is rather compelling.

Yates & Rosenberg (1996, 1998) equilibrated mixtures of kaolinite (or microcline) with a 2M₁ Brazilian muscovite and with two San Juan sericites (RM30, SG4) in hydrothermal solutions; they assessed reversal of equilibrium in terms of the location of univariant phase boundaries and compositions of the solubility-controlling phases. The solubility-controlling phases they observed were largely identical with phases inferred in prior studies with natural illites (Aja et al., 1991; Aja, 1991; Sass et al. 1987); that is, in studies conducted by several investigators with one natural muscovite and six different natural illites of contrasting lithogeochemistry (SH, GL, BB, MH, SG4, RM30), only four illitic solubility-controlling phases were repeatedly observed. In addition, Illite(I) rather than muscovite formed in the muscovite equilibration experiments suggesting that muscovite is not stable under these diagenetic conditions.

The presumption that the multiplicity of these solubility-controlling phases implies the operation of Ostwald ripening processes is questionable. In that these solubility-controlling phases have the same basic structural motif but different crystal thicknesses and compositions, their occurrences is more likely to have been a consequence of entropy production rather than Ostwald ripening.

Experimental studies of chlorite-kaolinite equilibria under low temperature conditions (25–200 °C) have shown that: 1) chlorite-kaolinite-fluid equilibrium is attainable in low temperature conditions; 2) the law of mass action is applicable to these hydrothermal reactions of chlorite with kaolinite; and 3) chlorite compositions constrain the magnitudes of the slopes of univariant phase boundaries in chemical potential diagrams. Furthermore, in these chlorite equilibration studies, solubility was controlled by a phase having the same composition as the starting Fe-Mg chlorites attesting to the stability of chlorites within the temperature range typical of diagenesis and/or hydrothermal alteration.

TEACHING OF CLAY SCIENCE: THE IMPORTANCE OF EMPHASIZING IMPORTANCE

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Effective teaching begins with capturing the attention of students. This can be done successfully by describing the many ways that clay minerals are important to society and science at the very beginning of the course. As most clay scientists already know, clay minerals are enormously beneficial to society as a natural resource in terms of soil fertility; discovery, recovery and catalysis of oil; discovery of ore deposits; and the clay mineral industry including bentonite, kaolin, ball clay, and common clay. Engineered clay liners can help keep pollution in landfills; clay minerals in soil and rock can naturally remediate polluted groundwater. On the other hand, clays can cause death and destruction due to their role in landslides and earthquake-induced liquefaction. Additional damaging clay-related hazards include swelling clay, quick clay, and weak and compressible clay that can cause construction problems and subsidence.

Geologists study clay-rich sediment and rock to understand the Earth's geologic history including sediment provenance, depositional and diagenetic conditions, paleoclimates, and plate tectonic reconstructions. Diagenetic reactions of clay minerals impact mineral cements, groundwater composition, geopressure development, and oil maturation and migration. Soil scientists study clay minerals in soil to address its formation, fertility, and degradation by erosion, pollution, and salinity. Archeologists examine clay minerals in artifacts to determine its source, local vs. externally derived. Clay minerals are the original nanoparticles, which are generating intense interest due to their unique surface properties resulting in their use in healthcare including pharmaceuticals, drug delivery, diagnosis, and biosensors. It's hard to imagine life without clay minerals. In fact, clay minerals may have played a critical role in the origin of life itself.

It's easy to get students excited about studying clay minerals by emphasizing their diverse and critical importance.

MONTMORILLONITE BASED HYBRIDS FOR METFORMIN CONTROLLING DELIVERY

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Metformin hydrochloride (MF) is the most extensively used oral antidiabetic drug for treatment of type 2 diabetes. Some of the problems related to its administration refer to the necessity of using elevated dosages for keeping an optimal therapeutic effect, which often is accompanied by diverse gastrointestinal side effects. In this context, it is of great interest to produce formulations that allow for a controlled and prolonged release of MF. There are examples in the literature on the association of MF with ion-exchange resins and other substrates which have been explored in the search of controlled drug delivery systems (CDDS) of this drug. In this context, we have evaluated the possibility of using layered clays, such as montmorillonite as substrate for MF in view to apply the resulting hybrids as drug reservoirs in CDDS (Rebitski et al., 2018). MF intercalates montmorillonite following an ion-exchange mechanism though it is possible to obtain materials with MF content up to three-fold the cation exchange capacity (CEC) of the clay mineral. The adsorbed excess can be easily removed just by washing with water, leading to an intercalation compound that contains 93 mEq of metformin per 100 g of montmorillonite (i.e., the clay CEC). In the intercalated hybrids the MF species are arranged in the interlayer space as a monolayer of mono-protonated molecules, remaining strongly entrapped within the solid. Evaluation of the drug delivery from hybrids containing different amounts of MF in simulated media with pH values that mimic the gastrointestinal tract show a rapid release at low pH values (i.e. typical of the stomach), pointing out the necessity to optimize the systems. Currently, we are exploring systems in which the hybrid is combined with biopolymers to produce convenient CDDS. In this way, bionanocomposites involving the association of MF-montmorillonite hybrids with chitosan and pectin polysaccharides were produced. The preparation of beads involving both biopolymers have proved effective to stabilize the system in acid media and the presence of chitosan may have additional advantages related to its mucoadhesive properties for increasing its permanence in the intestinal tract (Ribeiro et al., 2014). Preliminary results involving beads of pectin-chitosan/MMT-metformin formulation seem promising for proposing this type of systems as candidates for the oral administration of metformin regarding the treatment of type 2 diabetes as well as other applications of MF.

Acknowledgements: MINECO (Spain, project MAT2015-71117-R) and CNPQ (Brazil, fellowship 204360/2014-5).

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Ribeiro, L.N.M., Alcântara, A.C.S., Darder, M., Aranda, P., Araújo-Moreira, F.M., and Ruiz-Hitzky, E. (2014) Pectin-coated chitosan-LDH bionanocomposite beads as potential systems for colon-targeted drug delivery. *Int. J. Pharm.*, **463**, 1– 9.

MAGNETIC NANOPLATFORMS BASED ON FIBROUS CLAYS FOR REMOVAL OF POLLUTANTS

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Nowadays, there is an increasing interest on sepiolite and palygorskite fibrous clay minerals to develop a large variety of functional materials. Their relatively high specific surface area and the presence of numerous silanol groups present at the external surface of the fibers make them attractive as nanoplateforms for the assembly of many different types of nanoparticles (NP) for applications in environmental remediation amongst others (Aranda and Ruiz-Hitzky, 2018, *Chem. Rec. (on line)*. DOI: 10.1002/tcr.201700113). In this context, the development of materials immobilizing Fe₃O₄ NP are of special interest as the resulting systems may present magnetic properties that allow their easy recovering from aqueous media by using an external magnetic field. Within this perspective, the present communication will introduce two examples in which superparamagnetic nanoplateforms based on sepiolite immobilizing Fe₃O₄ NP are used to develop functional systems of interest in applications related to removal of pollutants in water. On the one side, ZnO NP have been assembled to sepiolite nanofibers that have been previously modified by in situ growing Fe₃O₄ NP. The resulting multifunctional materials show simultaneously magnetic and photoactive properties, acting as efficient and reusable photocatalysts in the removal of diverse pollutants in water (e.g., methylene blue dye, ibuprofen and other pharmaceuticals) (Akkari *et al.*, 2017, *J. Hazardous Mater.*, **340**:281–290). On the other side, Fe₃O₄ NP present in a ferrofluid can be also used to modify sepiolite and other porous inorganic solids for developing superparamagnetic adsorbents (González-Alfaro *et al.*, 2011, *Adv. Mater.*, **23**:5224–5228). Besides its use as adsorbent, Fe₃O₄-sepiolite materials can be used as nanofiller of polymers to incorporate magnetic properties to the resulting materials. Thus for instance, it has been used to produce bionanocomposite foams based on zein. The hydrophobic properties of this protein produce foams that remain very stable in water media and can be used as adsorbents of low water soluble organic compounds, as for instance herbicides and other pesticides. Preliminary assays using 4-chloro-2-methylphenoxyacetic acid as model pollutant confirm this point and show that these zein-sepiolite superparamagnetic bionanocomposite foams could be easily recovered from the aqueous media by just using a magnet, making them especially attractive for applications in open water areas.

Acknowledgements: MINECO (Spain, project MAT2015-71117-R).

IMMOBILIZATION OF AGRICULTURAL PHOSPHORUS IN CLAYEY FLOODPLAIN SOILS

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Nutrient losses from the Mississippi watershed are exacerbating the growth of the hypoxic zone in the Gulf of Mexico. Located within the highly agricultural Piatt County, IL, Allerton Park encompasses a riparian forest that receives an influx of phosphorus (P) via surface runoff and leaching during spring flooding. The purpose of this study is to investigate the ability of a poorly drained Sawmill silty clay loam (fine-silty, mixed, superactive, mesic Cumulic Endoaquolls) and a poorly drained Tice silty clay loam (fine-silty, mixed, superactive, mesic Fluvaquent Hapludolls), both with an average pH of 7.08, to buffer agricultural P losses through immobilization. Surface clays tend to be enriched with organic matter and, thus, may contain elevated fractions of organic P and microbial P biomass compared to coarser soils. Meanwhile, slower rates of mineralization have been observed in clayey soils.

The system's response to the seasonal flooding event was assessed by comparing P mineralization-immobilization dynamics within the silty clay loam bottomland and the surrounding upland, which is comprised of a well-drained Senachwine silt loam and a well-drained Russell silt loam. Specifically, organic P, microbial P, phosphatase activity, and total P were assessed. First, total P ranged from 338 to 819 mg kg⁻¹, averaging at 580 mg kg⁻¹, in the bottomland and from 113 to 533 mg kg⁻¹, averaging at 245 mg kg⁻¹, in the upland. Next, organic P spanned from 90 to 457 mg kg⁻¹ in the bottomland, comprising an average of 45% of total P, and ranged from 42 to 243 mg kg⁻¹ in the upland, comprising an average of 36% of total P. Furthermore, microbial P averaged 13.08 mg kg⁻¹ in the bottomland and 6.87 mg kg⁻¹ in the upland. Finally, acidic phosphatase activity averaged 13 µmol p-nitrophenyl phosphate (PNP)/g·hr in the bottomland and 11 µmol PNP/g·hr in the upland while alkaline phosphatase activity averaged 24 µmol PNP/g·hr in the bottomland and 8 µmol PNP/g·hr in the upland. Our preliminary assessment suggests that the concentrations of total P, organic P, and microbial P in the silty clay loam are greater than that of the silty loam. This suggests that the silty clay loam in the bottomland has been effectively immobilizing agricultural P. This observation is further evidenced by a higher organic P percentage in the silty clay loam. In this presentation, statistical assessment of the soil P characterization will also be presented.

INVESTIGATION OF THE PROPERTIES OF CLAY MINERALS AT NANOSCALE

Shoeleh Assemi*, Partaksh Sidhu, Sugandha Sharma, Vishal Gupta, Jing Liu, and Jan D. Miller

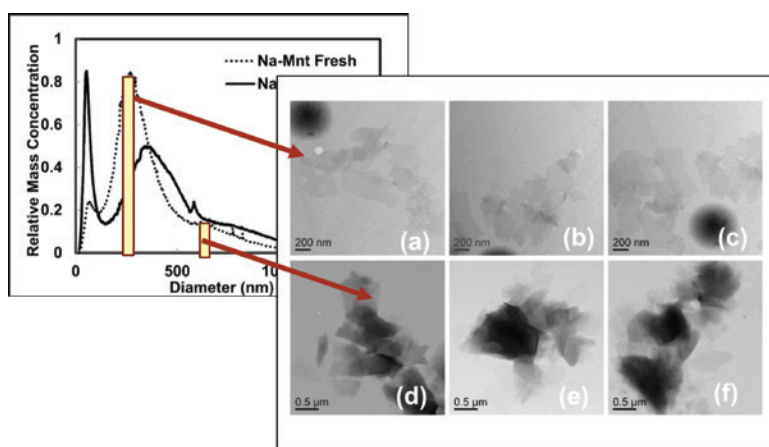
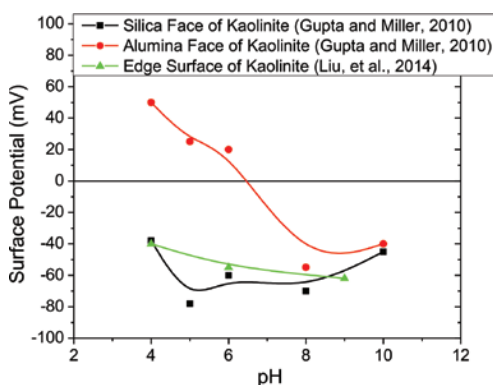
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The special mechanical and physical properties that make clay minerals such unique and versatile particles are governed by their crystal structure and surface chemistry. It is expected that clay particles would be more surface active at smaller sizes. In fact, the importance of size on the surface properties of clay minerals has been recognized since the 1960s, where it was demonstrated that the cation-exchange capacity of kaolinite increased after grinding. Recent advances in instrumentation and separation science can now be used to reveal interesting information about clay particles at the nano scale.

Several clay minerals such as montmorillonite, illite, kaolinite and halloysite were separated using sedimentation field-flow fractionation (SdFFF). Narrow-size fractions (within 30 nm size range) were obtained along the size distribution and were analyzed by various techniques to obtain information such as composition, isomorphous substitution, clay layer thickness, pore size and electrophoretic mobility. For all clay minerals, the smaller size particles ($d < 300$ nm), showed a more positive electrophoretic mobility. Elemental molar ratios obtained from SdFFF-ICP-OES revealed that the charge on smaller particles was influenced by the adsorption of cations such as Ca^{2+} and Mg^{2+} . A combination of SdFFF and electron microscopy analyses of Na-Mnt revealed that the swelling nano clay particles can have a layer thickness 14 times larger than the primary particle, under the condition of the analysis

Surface force measurements using AFM were used to calculate the surface charge of clay surfaces from DLVO theory. For example, with a silicon nitride tip, surface charges of the alumina face, silica face and edge of a single kaolinite particle were obtained. An IEP of 6.7 was estimated for the alumina face of kaolinite. The silica face and the kaolinite edge remained negatively charged down to pH 4. In a similar fashion, the wetting characteristics of clay surfaces have been examined by AFM using a hydrophobic DLC probe.



MODIFICATIONS OF 2:1 CLAY MINERALS IN A KAOLINITE DOMINATED ULTISOL UNDER CHANGING LAND-USE REGIMES AT THE CALHOUN CRITICAL ZONE OBSERVATORY, SOUTH CAROLINA, USA

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Chemical denudation and chemical weathering rates vary under climatic, bedrock, biotic, and topographic conditions. Constraints for landscape evolution models must consider changes in these factors on human and geologic time scales. Changes in nutrient dynamics, related to the storage and exchange of K⁺ in clay minerals as a response to land use change, can affect the rates of chemical weathering and denudation. Incorporation of these changes in landscape evolution models can add insight into how land use changes affect the thickness and erodibility of soil. In order to assess changes in soil clay mineralogy resulting from land-use differences, this study contrasts the clay mineral assemblages in three proximal sites managed differently over nearly the past two centuries in which contemporary vegetation is dominated by old hardwood forests, old-field pine, and cultivated biomes. X-ray diffraction (XRD) of the oriented clay fraction with the treatments of K-, Mg- and Na-saturation in the air-dried, ethylene glycol (EG), and heated (100°, 350, and 550°C) states was used to characterize the clay mineral assemblages. XRD patterns for degraded biotite (oxidized iron and expelled compensating interlayer potassium) exhibit coherent scattering characteristics similar to illite. XRD patterns of the Mg-EG samples were therefore accurately modeled with NEWMOD2®, using structure files for discrete illite, vermiculite, and kaolinite and mixed-layer kaolinite-smectite, illite-vermiculite, kaolinite-illite and hydroxy-interlayered vermiculite. The soil and upper saprolite profiles, situated on Neo-proterozoic gneiss in the Calhoun Experimental Forest, in South Carolina, USA, reveal a depth-dependence of deeply-weathered kaolinitic to shallowly-weathered illitic/vermiculitic assemblages that varied from the cultivated to pine and hardwood sites, respectively. Analysis of archived samples collected over a five-decade growth period from the pine site suggests an increase in illite-like layers at the surface within eight years. Historical management of the sites has resulted in different states of dynamic equilibrium, whereby deep rooting of the hardwood and pine site promotes nutrient uplift of potassium sourced from orthoclase and micas. Differences in denudation rates through time are reflected in changes in the clay mineralogy of the soil, specifically increased abundance of illite-like layers that can serve as a reservoir of K⁺ in the surface soil.

STUDY OF THE FIELD OF SYNTHESIS OF CU-NI-FE LAMELLAR DOUBLE HYDROXIDES AND THEIR TRANSFORMATION INTO MIXED OXIDES FOR CATALYTIC APPLICATIONS

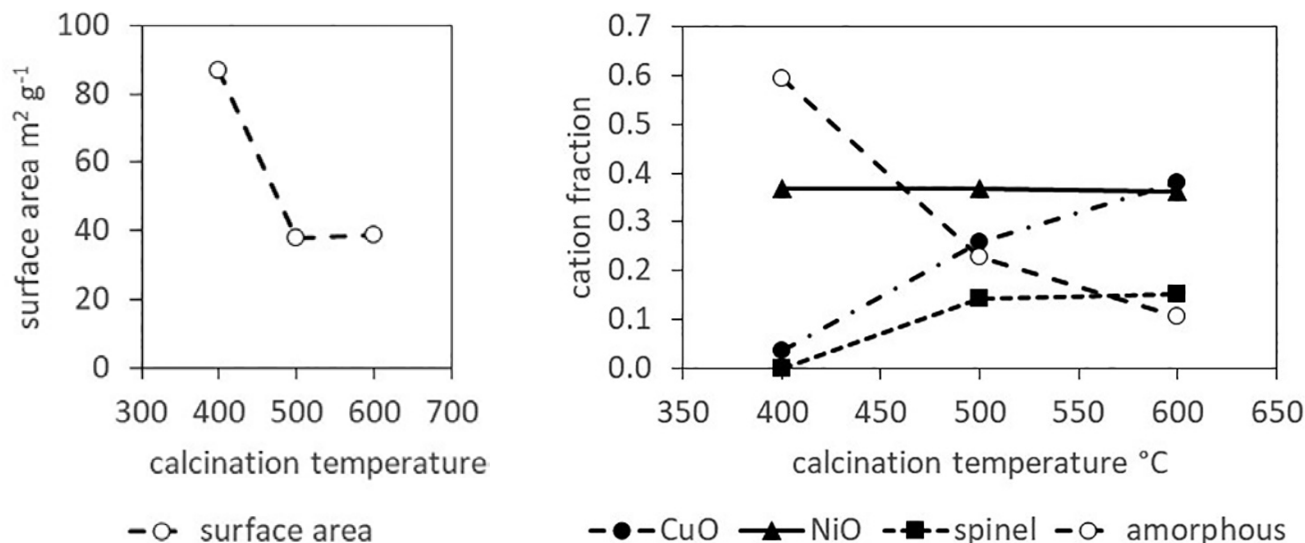
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Transition metal-bearing layered double hydroxides (LDHs) are effective precursors of mixed oxide catalysts. We synthesized series of LDH solid solutions in the systems Ni-Cu-Fe, Ni-Fe, Cu-Fe, Ni-Cu-Al and Cu-Al at varying pH by coprecipitation method to investigate the best suitable redox catalysts for the oxidative depolymerization of biomass. In Cu-Fe system, pure Cu-Fe LDHs were not formed and direct precipitation of CuO or $\text{Cu}_2(\text{OH})_3\text{NO}_3$ was instead observed. In mixed Cu-Ni systems, Fe-bearing LDHs were easily formed and crystallographic analysis allowed to measure a deformation of octahedra related to the Cu content. This deformation, attributed to Jahn-Teller effect, has often been cited to justify the difficult formation of Cu-Fe LDHs. However, the same mechanism seems not being operative in the Cu-Al system, in which pure Cu-Al LDHs are easily formed.

Nature and distribution of the oxide phases formed from the LDH precursors were extremely dependent on the calcination conditions. LDHs dehydration and decarboxylation produced amorphous materials from which individual oxide phases crystallized at different temperature. NiO was nearly completely segregated at 400°C and the following crystallization of CuO left trivalent-enriched amorphous materials, from which spinel phases crystallized at higher temperature. It is likely that most catalytic active surface is provided by trivalent-rich amorphous or nanospinel phases, as in the case of $\text{Cu}_3\text{Ni}_3\text{Fe}_2(\text{OH})_{16}\text{CO}_3 \cdot n\text{H}_2\text{O}$ LDH, which activation data are provided in the graphs below.



OXYANIONS SORPTION BY ORGANO-SMECTITE

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The surfactant-modified smectites have the ability to sorb inorganic oxyanions from aqueous solutions. Clays modified by cationic surfactant such as hexadecyltrimethylammonium cations (HDTMA⁺) to remove metal anions from liquid phases include smectite, kaolinite, illite, palygorskite and sepiolite. The aim of the work was to present the results of FT-IR and XRD studies of anions—chromates, vanadates, molybdates and tungstates—sorbed from aqueous solutions on smectite modified with HDTMA⁺. The used initial inputs of HDTMA correspond to 100% (1.0) and 200% (2.0) CEC of the mineral. Organo-modified sorbents were subsequently used to immobilization mentioned anions. The amounts of sorbed CrO₄²⁻, VO₄³⁻, MoO₄²⁻, WO₄²⁻ ions were calculated from the difference between their concentrations in solutions before (initial concentration) and after (equilibrium concentration) sorption experiments. It was proven that those anions' sorption causes changes in IR spectra and XRD patterns of the HDTMA-smectite. These alterations are dependent on the kind of anions that were sorbed. Variations in IR spectra are due to bands corresponding to the characteristic Si–O(Si,Al) vibrations (occurring in alumino- and silicoxygen tetrahedra building spatial framework of layer structure of smectite), OH group vibrations and alkylammonium surfactant vibrations have been observed. Observed differences can be divided into three groups which are connected with different vibration types occurring in the structure of the sorbents: (a) 3800–3100 cm⁻¹—OH⁻ groups stretching vibrations bands range; (b) 3040–2800 cm⁻¹—vibrations related to the presence of HDTMA⁺ in the structure; (c) 820–680 cm⁻¹—pseudolattice vibrations of aluminosilicate structure and vibrations characteristic for HDTMA. In the first range, connected with OH⁻ groups' vibrations, the band at about 3382 cm⁻¹ strongly depends on the anion type. It is possible to assume that it is caused by a creation of some kind of ordering in the arrangement of OH⁻ ions on the surface of sorbent. A significant increase in the intensity of the band at 2953 cm⁻¹, connected with the disappearance of the constituent band in the case of oxyanions was observed. As can be noticed, the changes in analyzed range pertain primarily to the bands of symmetrical vibrations. Their position shifts toward higher frequencies and the intensity drops. The changes on the spectra in the range of 2800–3050 cm⁻¹ depend on the amount of anions introduced into the sorbent structure. The bands in the third analyzed range, concern two groups of bonds. The first group is connected with HDTMA⁺ vibrations at ca. 719 and 730 cm⁻¹. Their integral intensity gradually decreases with the increase concentrate of initial solution. Other bands originate from pseudolattice vibrations realized in aluminosilicate structure of sorbents.

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MAGNESIAN CLAYS IN COLUMBIA RIVER BASALTS: A NEW POSSIBLE MARS ANALOG FOR EARLY WEATHERING

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Clay minerals detected on Mars by remote sensing contain information about the martian near-surface environment in the ancient past. Understanding how such clays form is key to interpreting these deposits and what they imply about early Mars. Many of the martian clays are of ferromagnesian composition; some or most of these may have formed by weathering of crustal rocks under pedogenic conditions. The Fe-Mg ratio of these clays may also hold information about the early martian weathering environment.

Previous studies of weathering of Columbia River Basalts (CRB) have observed high-Fe nontronites in saprolites, overlain by Al-smectites and kaolinite in paleosols. Mg-rich clays have not generally been observed in these studies or described in the CRB. Geochemical studies of saprolites have suggested that Mg is mobilized relatively early in weathering of CRB. For example, it has been suggested that most Mg could have been leached from the weathering basalt at Trinidad, WA prior to precipitation of nontronite, resulting in formation of a high-Fe clay.

Here I describe an occurrence of magnesian clays that occur as vesicle fillings in a low-elevation saprolite formed on Grande Ronde N2 basalts of the Columbia River Basalts (CRB). Vesicles in the saprolite are filled with magnesian clays that are surrounded by Fe (oxyhydr)oxides and a silica phase. No Fe-rich clays are present anywhere in the vesicle infillings. The overall degree of alteration of the samples appears to be low.

The stratigraphic position of this saprolite—paleosol sequence is comparable to other sequences that weathered at low elevation under relatively warm and dry conditions. Similar CRB paleosols have been described as forming under well-drained conditions resulting in extensive Fe oxidation, whereas high-Fe nontronite typically forms under conditions of poor drainage. Thus, climate and redox factors may have controlled clay chemistry in these samples.

The observation of Mg-rich clays formed by basalt alteration in the CC saprolite presents a different possible Mars analog from the Fe-rich clays that have been previously examined by other studies of CRB weathering. Further study of this site may help illuminate how physiochemical conditions during weathering control clay chemistry.

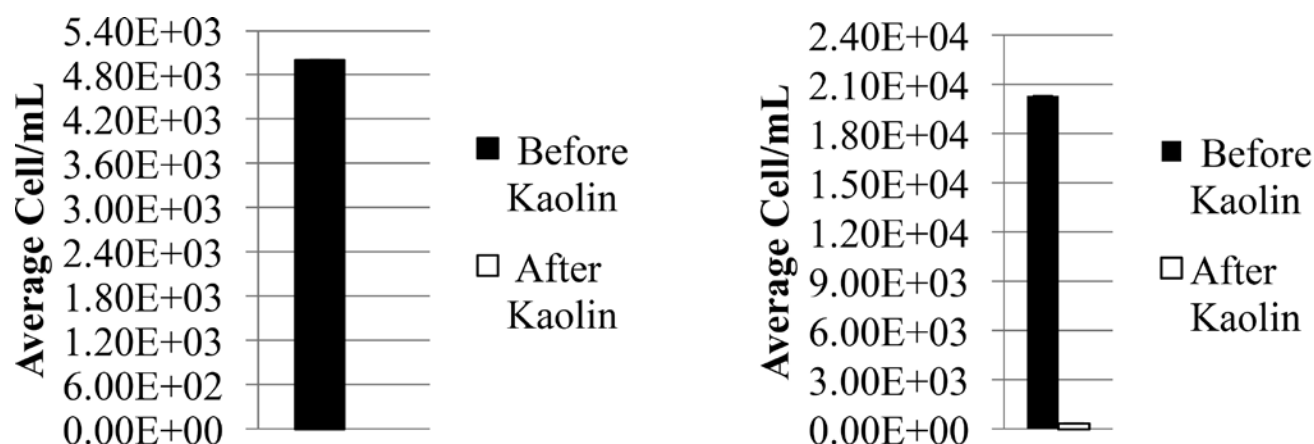
REMOVAL OF MICROORGANISMS FROM AQUEOUS SOLUTIONS WITH CALCINED KAOLIN AND DIATOMACEOUS EARTH

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Kaolin products and diatomaceous earth were evaluated for removal of microorganisms from aqueous media. Ten products have been evaluated against four bacteria, *Escherichia coli* ATCC 11775, *Pseudomonas aeruginosa* ATCC 27853, *Staphylococcus aureus* ATCC 27661 and *Bacillus megaterium* ATCC 14581; and two bacteriophages, T4 and MS2. Impacts of microbial concentration (10^2 - 10^9 range), pH (5-8 range), potassium phosphate buffer molarity (0.001-1 M range), and Al^{3+} cations were evaluated. Impacts of the above parameters on the removal of bacteria varied between the tested products. The best results were achieved for two diatomaceous earth products, KDE-1A and CA-2, and calcined kaolin at pH 5.0, 0.1M buffer concentration, and in the presence of Al^{3+} cations. Under the above conditions, the above products have removed 98-100% of the above bacteria from aquatic solutions in the entire range of their concentrations. Subsequently, two diatomaceous earth products were evaluated for the removal of viruses with the plaque assay technique using bacteriophages T4 (isoelectric point 4.0-5.0) and MS2 (isoelectric point 3.9) as models and *Escherichia coli* ATCC 11303-B4 and ATCC 15597 as their hosts. Preliminary data indicated that the tested products were also effective for the removal of the above bacteriophages. The efficacy of diatomaceous earth products against other viruses is to be investigated. Optimization of kaolin sorption capacities towards microorganisms may lead to new approaches in water treatment and related technologies.



Removal of *E. coli* (left) and *S. aureus* (right) with KDE-1A.

A DETAILED INTERPRETATION OF THE NEAR-INFRARED SPECTRUM OF KAOLINITE

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Near-infrared (NIR) spectroscopy is currently used to determine the mineralogy of rocks for many purposes (geology, mining, planetology, geomaterials). This spectroscopy is particularly efficient to study the hydroxylated-minerals and especially clay minerals. Kaolinite [$\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$] is one of the most abundant clay minerals in the Earth due to its wide range of geological formations. This mineral is also detected several times at the surface of Mars using imaging spectrometer (e.g. Carter *et al.*, 2015). Even if the NIR spectroscopy is used for decades to identify kaolinite, only few papers deal with a detailed interpretation of its NIR spectrum. Moreover, several parts of this kaolinite spectrum remain unexplained (see Madejová *et al.*, 2017). The aim of this study was to interpret in detail the spectral features of the NIR kaolinite spectrum of a natural reference kaolinite (KGa-1b from the Clay Minerals Society). The interpretation of the NIR spectrum of kaolinite was based on the procedure developed by Baron and Petit (2016).

A coherent and comprehensive interpretation of the first OH-overtone (2νOH) region of kaolinite spectrum was proposed. As previously observed for lizardite (Baron and Petit, 2016), the combination region results from the combination of the νOH and the OH-bending vibrations (δOH), and the combination of the νOH and lattice vibrations especially those linked to octahedrons. The very intense absorption classically attributed to (ν+δ) Al_2OH was revisited. This complex massif of bands results of the combination of the four main νOH and the two OH-bending vibrations (δOH). All the other bands that could be observed in the combination region were also attributed for the first time. The intense combination bands in these regions match well with the combination between νOH and lattice vibrations. From this study, the whole NIR spectrum of kaolinite KGa-1b could be totally interpreted.

Baron and Petit (2016) *Am Mineral*, **101**:423–430.

Carter *et al.* (2015) *Icarus*, **248**:373–382.

Madejová *et al.* (2017) in: *Developments in clay sciences*, **8**:107–149.

RE-EVALUATE THE STRETCHING INFRARED BANDS OF INTERLAYER WATER IN SMECTITE AND THEIR IMPORTANCE IN INTERPRETING THE SMECTITE-ORGANIC BONDING MECHANISMS

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Smectites are one group of the most reactive clay minerals in the environment and industry applications due to their small particle size, expandable layer structures, and permanent negative layer charge. Numerous organic compounds including contaminants, toxins, and biological molecules can access the interlayer spaces of smectites. The study on the interactions of the organic compounds with smectites revealed the importance of nanometer-scale differences of surface polarity on smectite in regulating the selectivity and affinity of the mineral for neutral and weakly polar organic compounds such as atrazine and aflatoxin. The nanometer-scale surface heterogeneity of the smectite, along with the interlayer cations, possibly contributed to the different properties of the interlayer water molecules. In turn, accurate interpretation of the spectroscopic differences of the interlayer water and their changes when smectites interact with interested organic compounds can offer more insight about the organic-smectite reactions. Accurate band assignments and vibration origins are critical before any attempt to interpret the meaning of the IR spectra. Interlayer water on smectites can have a sharp OH band at $\sim 3630\text{ cm}^{-1}$ and an overlap of the more broad bands in the range of $3000\text{--}3600\text{ cm}^{-1}$. The 3630 cm^{-1} is attributed to the weakly H-bonded interlayer water molecules, yet the interpretation of the origin of the weakly-H bonded water is still in debate and largely questionable. The role of these weakly-H bonded water molecules in organic-smectite interactions has not been addressed. The objectives of this study were to re-evaluate the infrared stretching 3630 cm^{-1} band of interlayer water and its responses in binding the weakly polar aflatoxin when water activity and the type of the interlayer cations were changed.

Two trioctahedral smectites (saponite and hectorite) were selected for this study. Their octahedral layer OH band occurs at 3677 cm^{-1} , which allowed the distinction of the interlayer water OH band at 3628 cm^{-1} on the IR spectra. The nearly perpendicular orientation of the OH group relative to the basal surface of the smectites also enabled the manipulation of the 3677 cm^{-1} band intensity and therefore further reduce the ambiguity in calculating the band shift and intensity changes of the interested interlayer water band at 3628 cm^{-1} . It was observed that the 3628 cm^{-1} band persisted when the interlayer cations are changed from Na to Ca, or Ba, and after adsorbing aflatoxin in the presence of these three types of cations. The 3628 cm^{-1} band position or intensity was much less responsive to humidity changes or to the interlayer gallery collapse at room temperature or during heating. These observations led us to assign the 3628 cm^{-1} band to the water in the hydration shell of the exchange cations. These water were more polarized than the water stayed in the non-polar regions of the interlayer space. The hydration shell water can get involved in the bonding to aflatoxin. The strong radiating orientation of water molecules around the exchange cation made them more difficult to form strong H-bonding with surround water or other molecules.

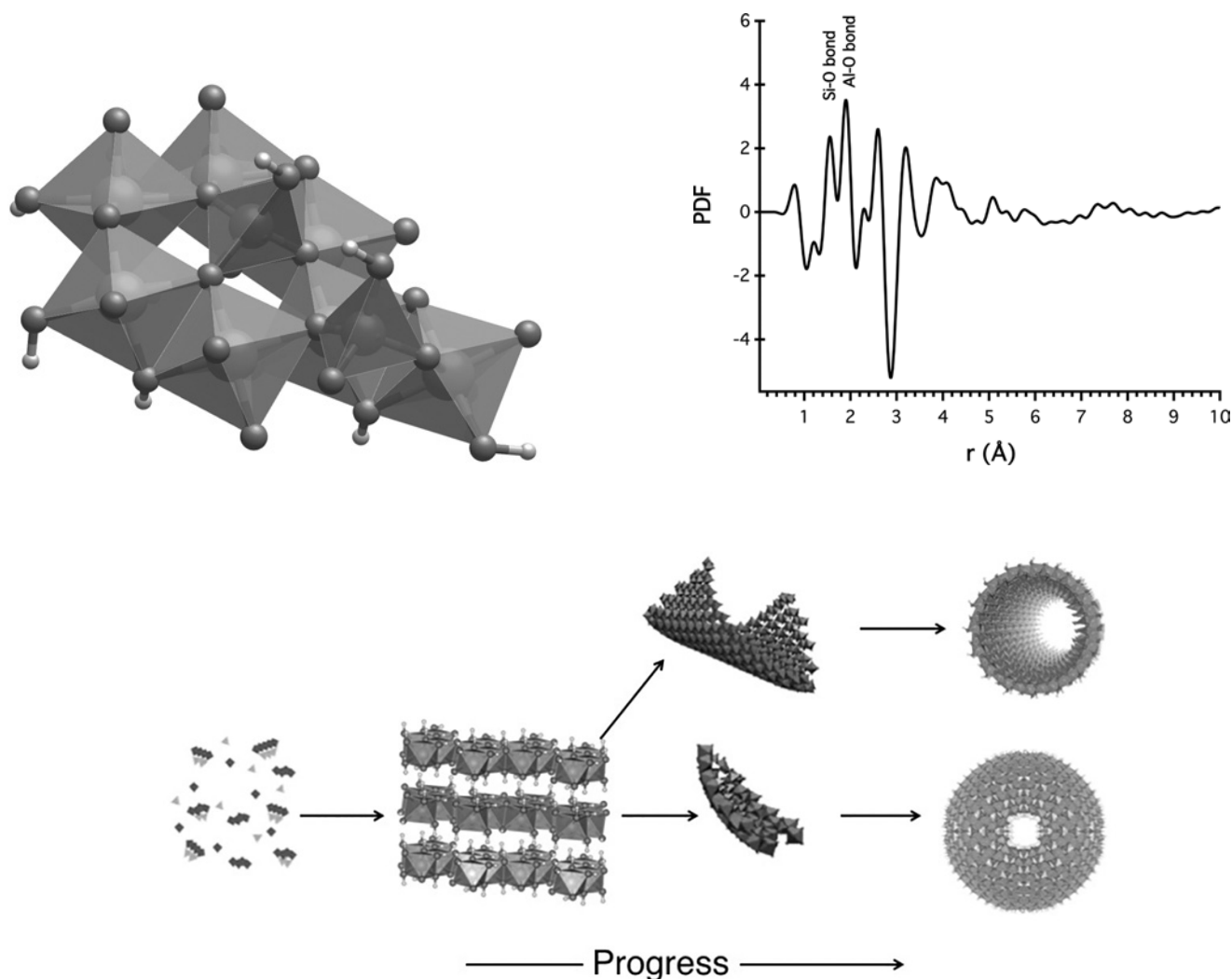
FACTORS REGULATING SYNTHESIS AND FORMATION STAGES OF ALLOPHANE NANOPARTICLES

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Formation mechanisms of nanosized aluminosilicates with tubular or hollow spherical morphologies are poorly understood. This study aims to observe the stages of allophane and imogolite formation in a native hydrated state. SAXS measurements during the first hour of synthesis suggests the presence of <1 nm precursors. In situ PDF analysis shows with time the development of an imogolite-like local structure. XRD measurements after heat treatment of the synthesized materials show broad peaks characteristic of allophane.



ANTIMICROBIAL PROPERTIES OF KISAMEET CLAY, A NATURAL CLAY MINERAL FROM BRITISH COLUMBIA, CANADA

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Natural clay minerals have a long history of biomedical and therapeutic applications resulting from specific properties provided by their complex nanostructure and geochemical characteristics. Recent studies have confirmed the potent antibacterial activity of some medicinal clays. Here, we present studies with Kisameet clay (KC), found in a natural clay deposit in British Columbia, Canada. KC has been used by the local First Nations people for its curative and medicinal properties and we have validated its antimicrobial activity against diverse human pathogens. In order to characterize the antimicrobial activity of KC and to define its active components, we have performed a series of integrated microbiological, chemical, and mineralogical studies. The inhibitory and microbicidal action of KC against multi-drug resistant (MDR) clinical bacterial isolates and two fungal pathogens was investigated. Chemical analysis of aqueous leachates was performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and its mineralogical composition was determined using X-ray diffraction methods. The potential role of pH and metal ions in the antibacterial activity was shown using metal solutions and also chelating agents. The effect of KC aqueous leachates on bacterial cell membrane integrity and permeability was also investigated. To elucidate any inhibition-related induction or suppression of cellular processes, a library of fluorescent transcriptional reporters in *E. coli* K12 was also used.

KC suspensions exhibited broad-spectrum antibacterial activity against the major nosocomial bacterial pathogens (ESKAPE), and also MDR clinical isolates of *Burkholderia cepacia* complex and *Pseudomonas aeruginosa* from patients suffering from cystic fibrosis. Moreover, KC exhibited activity against *Candida albicans* and *Cryptococcus neoformans*. KC aqueous leachates also eradicated Gram-negative and Gram-positive biofilms, and prevented their formation. The aqueous leachates showed a pH-dependent bactericidal activity. Studies with reporter clones revealed KC-related transcriptional modulations in stress responses (oxidative stress, envelope stress), DNA damage, and metal detoxification pathways.

Our results suggest that KC exhibits its antibacterial activity through a pH-dependent release of exchangeable transition metal ions, especially iron and aluminum. Better knowledge of KC activity may permit the formulation of defined, active preparations for a wide range of therapeutic applications.

EFFECT OF CO₂ PRESSURE, TEMPERATURE, AND BRINE COMPOSITION ON THE INTERLAYER SPACING OF NA- AND CA-EXCHANGED MONTMORILLONITE

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Carbon dioxide (CO₂) capture and storage (CCS) in deep geological reservoirs are considered an effective approach to curb the increase of anthropogenic CO₂ in the environment. The proposed method is to inject supercritical CO₂ in deep saline aquifers¹. To seal the aquifer, a clay-rich impermeable cap rock (shale) is required. A primary clay mineral constituent in both the aquifer and the cap rock is smectite. Smectite has the capability to control porosity and permeability because its molar volume changes in response to local parameters such as temperature (T), pressure (P), including the partial pressure of CO₂ [$P(\text{CO}_2)$], and activity of H₂O [$a(\text{H}_2\text{O})$], which is partly controlled by brine composition. Using a high-pressure X-ray environmental chamber², an increase in NaCl brine concentrations from 0.17 M to saturation at $P(\text{CO}_2) = 0$ bar and $T = 30^\circ\text{C}$ shows a decrease of $d(001)$ values of SWy-2 from 22.6 to 16.9 Å (25%). The effect of increase in $P(\text{CO}_2)$ to 500 bars at $T = 30^\circ\text{C}$ is more pronounced at lower brine concentrations. A substantial decrease with $d(001)$ value is observed at a brine concentration of 0.34 M, from 22.5 to 20.7 Å (8%), while the smallest decrease is observed with a saturated brine, from 16.9 to 16.7 Å (1%). A similar trend is observed when temperature was increased from 30 to 150 °C at $P(\text{CO}_2)$ at 500 bars. At 0.17-M brine concentration, $d(001)$ decreases from 21.5 to 20.8 Å (3%), and from 16.9 to 16.7 Å (1%) at saturated concentration. At brine composition 1.71 M, $d(001)$ decreases from 20.4 to 16.9 Å (17%) from $T = 50$ to 150 °C. At 1.37 M, $d(001)$ decreases by 10% (20.9 to 18.7 Å) for $T = 100$ to 150 °C. Ca-exchanged montmorillonite in CaCl₂ brine shows a similar trend as Na-exchanged montmorillonite in a NaCl brine. At $P(\text{CO}_2) = 0$ bar and $T = 30^\circ\text{C}$, decrease in $d(001)$ from 20.73 to 16.31 Å (21%) is observed with an increase in brine concentration from 0.17 M to saturation. Increase of $P(\text{CO}_2)$ to 500 bars shows a minimal decrease in $d(001)$ at 1% (20.86 to 20.64 Å) at 0.17 M. The effect of increasing $T = 30$ to 150 °C is more pronounced at lower (< 2.05 M) brine concentrations, where a maximum decrease of $d(001)$ occurs at 1.37 M, from 18.30 to 16.62 Å (9%). The largest difference in $d(001)$ between Na⁺ and Ca²⁺ is 20.7 (Na⁺) to 16.63 Å (Ca²⁺) at 1.71 M (20%). Experiments performed at He pressure show identical results with CO₂, within error, suggesting that CO₂ does not enter the interlayer.

Results show that brine composition and concentration, T , P , $P(\text{CO}_2)$, and interlayer cation composition are important parameters affecting interlayer H₂O content [$a(\text{H}_2\text{O})$] of montmorillonite. The loss or addition of interlayer H₂O in the smectite component of the reservoir and cap rock changes smectite's molar volume. This change may compromise the safety and integrity of reservoirs targeted for CO₂ sequestration because of volume changes (e.g. formation of fractures) of the cap rock.

¹ IPCC (2014) Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, IPCC, Geneva, Switzerland, 151 pp.

² Guggenheim, S. and Koster van Groos, A. F. (2014) An Integrated Experimental System for Solid-Gas-Liquid Environmental Cells. *Clays and Clay Minerals*, **62**:479-485.

OXIDATION STATUS OF SUBSOIL CLAY DURING Fe(II) SORPTION ALTERS THE COMPOSITION OF PRECIPITATED Fe(II)-BEARING LAYERED DOUBLE HYDROXIDES

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Reduction and oxidation reactions common to flooded soils can greatly affect iron (Fe) cycling and cause complex Fe dissolution and sorption processes. In suboxic, slightly alkaline (pH 7-8) conditions, dissolved ferrous iron (Fe(II)) will sorb to soils and clays and can coprecipitate as layered double hydroxides (LDH), which have unique properties that make them highly reactive sorbents. The LDH sheet structure makes them important anionic sorbents and the Fe(II) acts as an abiotic reducing agent for many inorganic and organic contaminants. However, the cation and Fe(II) content can greatly alter particle size, sorption and reductive ability so it is important to know how environmental conditions will affect the LDH composition. One such condition is the redox status of the clay as Fe(III) within clays can transfer electrons to sorbed Fe(II) and increase the Fe(III) content of the LDH. It is our goal to determine the effects of sorption conditions on the composition and reactivity of Fe(II) LDH precipitates following Fe(II) sorption to the clay minerals and advance the understanding of Fe(II) LDHs in natural systems.

Clay minerals were isolated from the Ap and Bt horizons of a Matapeake silt loam in Newark, Delaware. Sorption of Fe(II) to these clay minerals was studied as a function of pH (6.5-7.5), reaction time (2 hours-16 weeks), loading of Fe(II)(aq) (0.5-3 mM) and with dithionite-reduced or natural clay in sorption experiments. Sorption products were characterized by X-ray absorption spectroscopy, X-ray diffraction (XRD), Fe⁵⁷ Mössbauer spectroscopy, and microscopy. Our findings have the potential to advance the understanding of Fe(II) cycling in soils and sediments which influence the fate and transport of a variety of trace metals and clay minerals via both redox and sorption reactions.

IRON REDOX CYCLING OF SUBSURFACE SEDIMENTS FROM HANFORD SITE, WASHINGTON STATE, USA

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Iron-bearing clay minerals are predominant in soils and sediments, and they undergo oxidation-reduction cycle as a result of natural and artificial processes such as wetting/drying cycles and plant root respiration. However, the kinetics and mechanisms of multiple redox cycles of iron in clay-rich sediments and consequences of such cycling on their sediment properties are poorly understood. The objective of this study was to understand how multiple redox cycles of Fe in clay-rich sediment affect the rate and extent of Fe bioreduction and the physicochemical properties of the sediment. A natural sediment sample containing Fe(III)-bearing montmorillonite and illite from Hanford, Washington, USA was size-fractionated and redox cycled four times. Bioreduction was achieved utilizing *Geobacter sulfurreducens* and re-oxidization was performed with sparged air. Time-course change of Fe(II) was monitored to understand the rate and extent of bioreduction. Reaction products were characterized to monitor changes in physicochemical properties and mineralogy. Overall, both the initial rate and final extent of bioreduction decreased across the four redox cycles, but with variations depending on the presence/absence of electron shuttle AQDS and sediment size. This decreasing trend of bioreduction rate and extent was likely due to reductive dissolution and removal of small and poorly crystalline clay particles, as evidenced by aqueous chemistry and formation of secondary mineral (biogenic quartz and zeolite). Once these reactive particles were dissolved, the structural Fe in the residual larger and more crystalline clay particles was largely reversible across additional redox cycles, as evidenced by Mössbauer spectroscopy. In addition, redox-induced clay particle aggregation, as well as decreased surface area and cation exchange capacity (CEC), may have accounted for the diminished bioreduction rate and extent as well. This study has demonstrated that even ancient sediment still contains sufficient reducing power for possible bioremediation application, but with multiple redox cycles, the reducing power may decrease to a low level.

TETRACYCLINE INCORPORATION INTO BENTONITE FOR CONTROLLED DRUG DELIVERY APPLICATIONS

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Studies have shown that clays can interact with antibiotics, like tetracycline, and they can behave as drug carriers too. In this work different quantities of tetracycline were incorporated in 4% w/w aqueous clay dispersions. Fann's Viscosity was measured. X-ray Diffraction and thermogravimetry showed that there was an effective incorporation of the tetracycline. Antibioqram test using E. Coli showed a halo formation. Those results indicate that a bentonite-tetracycline system has a potential use in the controlled delivery of that antibiotic.

BRINGING INTERFACIAL PROCESSES TO LIGHT (OR MAGNET): NMR OF SMECTITE-FLUID INTERFACES

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The structure and dynamics of clay-fluid interfaces play crucial roles in an enormous variety of phenomena, from nuclear waste transport/remediation and nutrient cycling to catalysis and shale gas extraction. Smectite-fluid interfaces are particularly interesting since smectites have multiple types of external surfaces (basal vs. edge) as well as two-dimensional interlayer nanopores, all of which can interact with many types of fluid. In this talk, we examine the unique role of NMR in characterizing the structural and dynamical behavior of smectite-fluid interfaces over a range of temperatures, and thanks to new technology developed at Pacific Northwest National Laboratory, a range of fluid types and pressures. Both ¹H and particularly ²H variable temperature NMR are excellent probes of the dynamics and hydrogen bonding networks that form at smectite-H₂O interfaces. For example, variable temperature ²H NMR has shown that the H-bond strengths for H₂O within two monolayers (~5 Å) of smectite basal and interlayer surfaces is similar to H-bonds in ice-1h, yet this H₂O remains dynamically active to temperatures as low as 173 K. Variable temperature ²H NMR studies allow us to isolate different reorientation mechanisms for interfacial H₂O and, under appropriate conditions, provide insight into the activation energy associated with these reorientations. Likewise, ¹³C NMR studies of smectites interacting with variably wet hydrophobic fluids at elevated temperature and pressure are providing new insight into the partitioning of H₂O between the fluid and surface, the composition of the interfacial fluid, the types of adsorption environments, the dynamics of adsorbed fluid molecules at conditions relevant to the subsurface, and chemistry that can occur at these interfaces. High-resolution magic angle spinning (MAS) NMR studies at elevated temperatures and pressures have recently become feasible thanks to the development of special valving systems for NMR rotors that permit control over the bulk fluid composition of solid/fluid mixtures. Much of our recent work has examined variably wet supercritical carbon dioxide (scCO₂) and supercritical methane (scCH₄) fluids at smectite interfaces at 90 bar and 323 K; conditions relevant to subsurface CO₂ sequestration reservoirs and shale gas production. For scCO₂, NMR has identified key relationships between the identity of the charge balancing cation, the humidity of the scCO₂, and the intercalation of CO₂ into the interlayer galleries. It has also enabled us to characterize the molecular reorientation mechanisms of intercalated CO₂ and constrain the CO₂/H₂O ratio of the interlayer fluid, both as a function of the humidity and basal spacing. NMR has also helped identify multiple adsorption environments for CH₄, including direct evidence of CH₄ intercalation, and how the occupancy of these environments varies with the humidity of the scCH₄ fluid. Finally, ¹H and ²⁹Si NMR have played important roles in identifying a novel route to producing hydronium smectite catalysts without resorting to harsh acidic pH conditions and without damaging the smectite framework.

CHARACTERIZATION OF MIXED-MINERAL SYSTEMS INVOLVING CLAY AND IRON OXYHYDROXIDE MINERALS UNDER ACIDIC CONDITIONS.

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Clay minerals have been detected on Mars which provides important knowledge on water- rock interactions on the surface of Mars. Fe oxyhydroxide and iron oxyhydrosulfate deposits have been found in close proximity to sedimentary deposits pointing toward an aqueous history on the planet. Often, the formation and evolution of the clay-rich and Fe-rich formations are considered as separate geological events, in which no interaction occurred after their initial formation. However, clay minerals and acidic environments are known to interact rather than form as separate entities. In this study, we analyzed mixed-mineral systems involving clays and iron oxyhydroxides deposited in an acid mine drainage (AMD) system in Southern Illinois. The goal has been to better understand the evolution of such mineral systems under a wide range of pH and redox conditions. Particularly we seek to determine how the biologically-mediated iron oxidation and iron reduction processes influences the transformation of both iron oxyhydroxides and clay minerals in the chemically-complex, natural systems under low-pH conditions.

We found that detrital clays were relatively stable under low-pH conditions both in the AMD and in the AMD sediments, even though previous studies have showed that at low-pH clays could undergo extensive dissolution. At the microscale, the μ XRF maps for Fe (proxy for Fe oxyhydroxides) and Ga (proxy for clays) overlap and the high abundance of Fe in the sample suggest that this particle represents a clay platelet coated by Fe oxyhydroxides (Fig. 1). The spectral signature of the same sample shows two peaks and a trough between 500 and 1250 nm (Fig. 2).

Our study highlights the complexity of the mixed mineral systems that involves Al-rich clays and Fe oxyhydroxides. In AMD settings, both the Fe-rich and Al-rich minerals can coevolve and transform during complex biogeochemical and diagenetic processes. Such information can provide critical information in interpreting similar sedimentary formations on Mars.

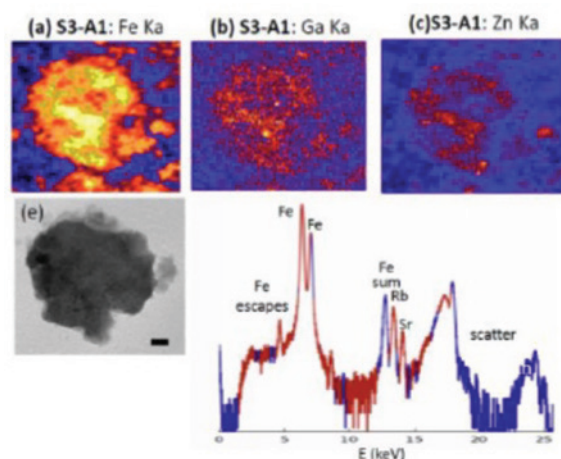


Fig. 1: (a)-(c) XRF maps for Fe, Ga, and Zn and (d) XRF spectrum collected from sample P11-3-25-30(cm). All images are $500 \times 500 \mu\text{m}$. (e) TEM image of a citrate-bicarbonate-dithionite (CBD)-treated clay mineral which shows crystal fragmentation and edge dissolution features.

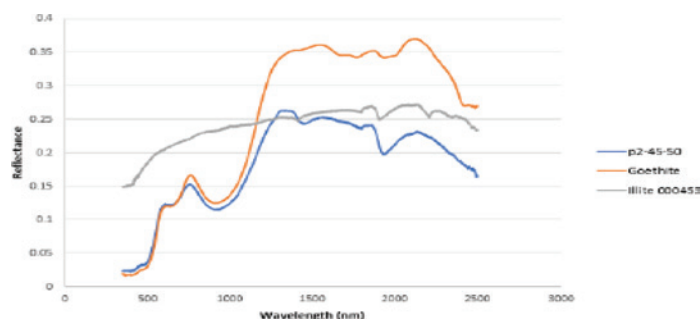


Fig. 2: Spectral signature of sample P11-3-25-30(cm).

A PRELUDE TO THE CLAY-BEARING UNIT OF MOUNT SHARP, GALE CRATER, MARS

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Phyllosilicates are common components of Noachian and Early Hesperian age (>3.5 Ga) terrains on Mars. Their occurrence is evidence of a larger water inventory and more vigorous hydrological cycle earlier in the planet's history. The demise of phyllosilicate formation appears to coincide with planetary aridification and acidification, also signaled by an increasing abundance of sulfate and Fe-oxide minerals. This mineralogical motif has been identified from orbital spectrometers in stratified deposits of Aeolis Mons (Mount Sharp), a 5 km tall mountain in the center of Gale crater, with distinct clay-bearing strata overlain by sulfate-bearing units. The Mars Science Laboratory (MSL) Rover, Curiosity, was sent to study these units and examine the possibility that they record a global change in environmental conditions. Since landing in 2012, MSL has documented almost 400 m of vertical stratigraphy consisting of fluvial-lacustrine sediments deposited ~3.7 Ga. Many of the drill samples collected by MSL and analyzed by the CheMin XRD instrument and SAM evolved gas analysis experiment contain clay minerals that comprise up to ~25 wt. % of the bulk rock. Smectite clay minerals are dominant in all the samples analyzed so far. The smectites show variable chemistry indicating a variety of aqueous alteration conditions. Detrital sources for the clays have been proposed, but coincidental changes in clay mineral chemistry with sedimentological, mineralogical and geochemical indicators of changing lacustrine conditions and processes support formation close to the time of deposition.

Although the clay minerals discovered by MSL were not originally observed by orbital spectroscopic studies of Gale, the next stratigraphic sequence to be explored by the rover is associated with orbital clay mineral signatures. One of the outstanding questions to be addressed by the mission is *if* and how clay-bearing materials identified by the rover so far are related to this clay-bearing unit visible from orbit. MSL is currently investigating the Vera Rubin Ridge (VRR), a resistant band of lacustrine sediments with strong orbital hematite signatures. The VRR is adjacent to the clay-bearing unit and MSL will soon embark on a campaign to investigate it. An important part of this campaign will be to document the nature, abundance and origin of clay minerals in the clay-bearing unit. This will help constrain stratigraphic models of sedimentary deposits at Gale, improve our understanding of how environmental conditions changed in Gale crater, and allow ancient habitability and organic preservation potential to be assessed. Combined with *in situ* examination of the terrain, mineralogical data will provide important ground-truth for orbital data and new information on the factors that influence the detectability of clay minerals from orbit.

PRELIMINARY CHARACTERIZATION OF CLAYS IN THE UNCONVENTIONAL BAKKEN OIL RESERVOIR

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Clay minerals strongly influence the rock fabric of many lithofacies comprising the Bakken formation in the Williston Basin, North Dakota. Yet, clay distributions and composition have not been widely studied across the Williston Basin. Basic clay mineralogy can strengthen the understanding of fracture networks, swelling potential, thermal maturity, available pore space, and permeability. Advanced characterization of clays in Bakken Formation samples is difficult because of the extremely lithified nature of the rock and the small grain and particle sizes present, but there is importance in understanding their nature as the Bakken is being evaluated as a potential target for CO₂ enhanced oil recovery (EOR).

This study utilized a newly developed analytical tool coupled with standard methods to better understand the composition and distribution of clay minerals, organic matter, and porosity in samples from the Bakken Formation, an unconventional oil and gas play. Detailed morphologies and chemical compositions of the samples were obtained with field emission scanning electron microscopy (FESEM) coupled with energy-dispersive spectroscopy (EDS). Furthermore, a new software suite called Advanced Mineral Identification and Classification System (AMICS) was used to classify and quantify the mineralogy, organic matter content, and porosity from the FESEM images. Image analysis was performed on high-resolution FESEM images of the samples as an alternative corroborative approach to characterize key features of interest within shales and other tight rocks. In addition, x-ray diffraction (XRD) and x-ray fluorescence (XRF) methods were used to obtain bulk mineral, clay mineral, and bulk chemical compositions of the samples for validation purposes.

The characterization data highlight interesting lateral and vertical variations related to deposition and subsequent diagenetic alteration across multiple well sites of the Williston Basin. Differences in lithological fabric, mineral, and elemental content are distinguishable in comparable facies across well sites. Diagenetic alteration was noticeable in FESEM imagery as well as in clay mineral results obtained via XRD. Corroborative methods proved to define diagenetic-influenced characteristics with micro- and nanoscale fabrics that could impact various parameters such as maturity, recovery, clay content, micropore networks, and CO₂ interactions for either storage or EOR methods.

THE CLAY STORY OF ANCIENT MARS, AN UPDATE

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A decade of orbital and in-situ investigations of the hydrous clay mineralogy of Mars have revealed blanket-ing aqueous alteration involving a variety of formation and diagenetic mechanisms, and an evolution with time. A paradigm established 10 years ago has withstood intense scrutiny. Mars experienced a clay-forming era early in its history (circa 4 Ga, probably since earlier times), which transitioned to evaporitic salty deposits, as the geologic and hydrologic activity of Mars waned. Open, fiercely-debated questions remain: did the bulk of alteration involve meteoric waters in open-system environments, or was it restricted to the sub-surface under a mostly frozen-over surface, save for episodic climatic excursions. Also of critical importance, the organic matter retention and preservation potential of Martian clay-bearing environments have yet to be fully assessed.

Detailed orbital and rover analyses of the mineralogy and geomorphic context at Mars reveal that the dominant alteration mechanism, as preserved and observed today, formed Fe/Mg-rich clays, with higher temperature derivatives down to several kms within the crust. The mechanism responsible for their formation at a planetary scale is not well understood. This is a critical cross-disciplinary question in Mars, Earth and life sciences because those clays are found in terrains as old as Hadean Earth, of which only scant evidence remains. Efforts are ongoing to constrain what may have been a generic process on primitive water-rich terrestrial planets. Together with the proposed biogenic potential of clay-rich environments, clay deposits are prime targets for future rover exploration as well as for in-situ resource utilization of human missions.

Diverse salt, clay-ish, oxide rich environments are also found in few well preserved terrains < 4 Ga and provide insight as to the range of geochemical conditions experienced at Mars. Terrestrial insight has proven invaluable to interpret those terrains, and analog studies in the field and in the lab continue to provide refined interpretations.

Here we will review the remote investigation methods available at Mars currently and in the near future, discussing their strengths and limitations. We will then discuss both the planetary-wide trends in terms of clay environments, and the more localized regional diversity that has been found as a function of geologic setting and time. A methodological approach to the large and varied datasets of Mars aqueous alteration available should allow lifting some degeneracy as to the actual geochemical environments on ancient Mars. We will conclude by discussing the next generation of analytic tools that will be required to further their study at Mars and to rigorously assess the much heralded exo-biological potential of Mars.

SOLUTION NMR AT GEOCHEMICAL PRESSURES

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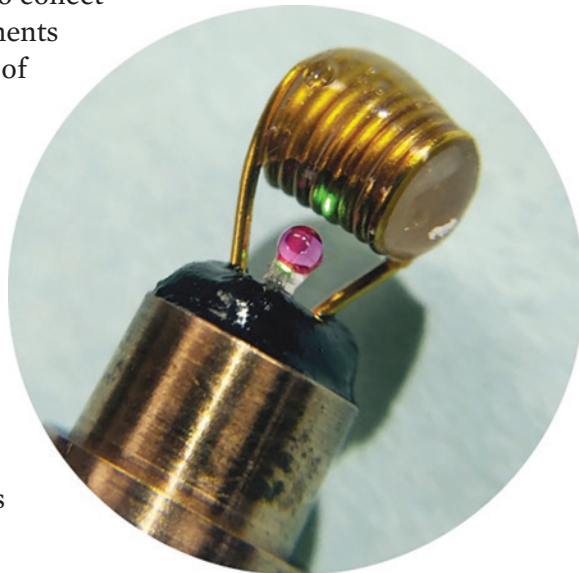
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Geochemists make predictions for solution chemistry to 6.0 GPa and 1200°C. These predictions are based, in part, on estimates of the static dielectric constant of water from molecular-dynamic simulations and extend well beyond the range where spectroscopies can easily test them. This gap in understanding led my group to invent a simple NMR probe that has been used to collect spectra on solutions to 2.9 GPa, and we think that measurements to 4.0 GPa are not difficult. Diamond-anvil technologies, of course, can reach to much higher pressures, but these are for volumes that are nanoliters or less, and these are much too small for solution NMR to detect solute speciation.

There is a new universe of chemistry to explore. In some of the first experiments, we discovered that the freezing pressure of water can be exceeded substantially, by as much as a factor of ~ 2 by colligative properties. For pure water, the dielectric constant exceeds 105 at even moderate pressures, making the dissociation constants of simple acids and water increase by orders of magnitude. The pK_a for dissociation of boric acid, for example, increases by 5 orders of magnitude up to 1.0 GPa.

We built the probe around a clamped-cell apparatus from solid-state physics and use a ruby sphere coupled to a fiberoptic cable to estimate pressures (Figure). We are now adding the capability to increase temperature as well as pressure.

The device is so simple that undergraduates can make meaningful measurements in a week using standard spectrometers, such as exist at every university.



REDUCTION OF PHYLLOMANGANATES BY ORGANIC ACIDS: EFFECTS ON MINERAL STRUCTURE AND TRACE METAL FATE

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It has long been recognized that small organic acids cause the reductive dissolution of birnessite-type layered manganese oxide minerals. However, the persistence of these phyllomanganates in soils and aquatic sediments demonstrates that in natural systems such reduction is often incomplete. Recent work has shown that dissolved Mn(II), a product of manganese oxide reduction, may react with these minerals, forming Mn(III) sites that alter the mineral structure. In addition, Mn(II) alters how trace metals bind to layered manganese oxides, affecting how these important mineral sinks controls contaminant fate and micronutrient availability. Our present work seeks to determine how partial reduction of phyllomanganates by small organic acids affects the structure of these minerals as well as the binding of the trace metals nickel and zinc. Oxalate, citrate, and 4-hydroxybenzoate were investigated to evaluate dicarboxylic, tricarboxylic, and aromatic acids. All acids first undergo a 2-electron transfer expected for carboxylic acids, consuming the initial organic acid. Citrate and 4-hydroxybenzoate cause more extensive mineral reduction, indicating that their oxidation products also react with phyllomanganates. These redox processes caused subtle structural changes in the remaining manganese oxide nanosheets, including lattice expansion, improved sheet stacking, and capping of vacancy sites, similar to the effects of dissolved Mn(II). Each organic acid also caused redistribution of trace metals among sites capping vacancies in the phyllomanganate sheets, on the sheet edges, and, for nickel, filling sheet vacancies. The specific behavior varied among the organic acids, pH conditions, and initial Mn(III) contents of the mineral, with the largest impacts observed for citrate and 4-hydroxybenzoate. These ligand-specific effects likely relate to difference in metal complexation strength and oxidation rate among the compounds. Organic acid-phyllomanganate reactions thus likely preserves the overall sheet structure while increasing Mn(III) content and altering the affinity of these minerals for contaminants and micronutrient.

FORMATION AND OXIDATION OF Fe(II)-MG TRIOCTAHEDRAL SMECTITES ON EARLY MARS

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Orbiter and rover operations have detected widespread occurrences of clays in the Noachian-aged crust of Mars, primarily trioctahedral Fe-Mg smectites. These clays formed through aqueous alteration of the basaltic Martian crust, possibly in the subsurface via diagenesis or by hydrothermal fluids. Many occurrences of Fe-Mg smectites on Mars are either ferric or mixed valent in nature. The formation of such phases requires oxidation of iron during basalt alteration, which is difficult to reconcile with the anoxic conditions expected for the Noachian and possibly the early Hesperian. This suggests ferric iron-bearing clays observed today may be oxidation products of ferrous clays that formed earlier in the planet's history. Terrestrial analogues for anoxic alteration of basalt to smectites are difficult to access, primarily occurring within deeper portions of altered oceanic crust, and past drill cores show evidence of post-sampling oxidation. We have thus conducted a series of experimental studies to assess the secondary minerals formed during basalt alteration under anoxic conditions and the resulting products of later oxidation. Experimental studies reveal that trioctahedral Fe(II)-bearing smectites (saponites) are the primary alteration product under such conditions. These clays are highly susceptible to oxidation by photochemically-generated species, such as hydrogen peroxide, but undergo limited oxidation upon exposure to oxygen, generating mixed-valent smectites with occasional iron oxides. Ferric iron-bearing smectites observed on Mars, including at Gale crater, are consistent with Fe(II)-Mg smectites that later experienced oxidation. This raises the possibility that oxidation of the surface of Mars postdates periods of widespread clay formation.

NONTRONITE AS NATURAL SOURCE AND GROWTH TEMPLATE FOR (NANO)MAGHEMITE [γ - Fe_2O_3] AND (NANO)WÜSTITE [Fe_{1-x}O]

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Nontronites are iron-rich dioctahedral smectites that serve as a natural source of nanomaghemite and nanowüstite, which are industrial minerals widely used to develop biomedicine and semiconductor applications. The integration of various bulk analytical techniques and computational calculations to study the structure of nontronites show that their contents of tetrahedral Fe^{3+} surpass theoretical values. Consequently, the microstructure of nontronite has only been partially understood.

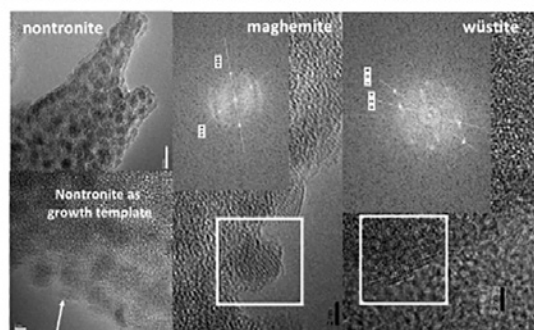
Three nontronites (NAu-1 and NAu-2 from South Australia) and NG-1 (Högen Hagen, Germany) were studied as received using high-resolution techniques, namely, High-Resolution Scanning and Transmission Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (HRSEM and HRTEM-EDS), and Electron Spin Resonance Spectroscopy (ESR).

Nontronite surfaces contained abundant nanodomains (predominantly ≤ 2 -nm in diameter), homogeneously distributed, mostly circular in shape, discrete, crystalline, and composed by a single phase. Nanodomains were found invariably associated to nontronite surfaces, mostly embedded although loosely bound at times. Noteworthy were nanodomains showing non-round contours, a signature of halted growth.

Nanodomain abundance related to the tetrahedral Fe (or unit cell formulae). If theoretical contents of tetrahedral Fe in nontronite were higher (NAu-2, NG-1) then the nanodomains were found to be less abundant and more heterogeneous in size and shape. Acquired Miller diffraction indexes for Fe nanodomains confirmed the presence of maghemite [γ - Fe_2O_3] and wüstite [Fe_{1-x}O]. Most remarkably, wüstite, a highly-reduced mineral remained stable under oxic conditions, so the small size of wüstite and its interactions with nontronite surfaces inhibited the oxidation of structural Fe by atmospheric oxygen.

Finally, we speculate that mineral microregions containing nanomaghemite and nanowüstite may form a Fe mixed valence system showing electronic and magnetic properties resembling those characteristic of Fe(II)-Fe(III) minerals. This paper shows that nontronite serves as source of industrial minerals, maghemite and wüstite, which results of utmost interest. Maghemite is considered a biocompatible material for it is non-toxic to humans, whereas wüstite is a well-known mineral historically used in the metallurgy industry and currently used for the development of semiconductor materials.

Nontronite as natural source and growth template for nanomaghemite and nanowüstite



APPLICATION OF SOLID STATE NMR AT MINERAL/WATER INTERFACE: A MOLECULAR LEVEL INVESTIGATION OF FLUORIDE REMOVAL BY NANO-SIZED HYDROXYAPATITE

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Elevated levels of fluoride (F^-) in groundwaters of granitic and basaltic terrains is a worldwide environmental problem, which affects millions of people. Hydroxyapatite (Hap) has been shown to be a strong sorbent for F^- ; however, the molecular level mechanisms have not been clearly addressed, owing to the lack of spectroscopic analysis. Here we provide a novel ^{19}F solid state NMR method to investigate the F uptake mechanisms by synthetic nano-sized HA. Our experiments showed that fluoride uptake mechanisms depends on pH concentration dependent. At pH 7 and fluoride concentration less than 50 mM, observation of a single ^{19}F solid state NMR peak at -103 ppm, which could be assigned to fluoapatite ($Ca_{10}(PO_4)_6F_2$), suggested that fluoride substituted the tunnel hydroxyl group in the Hap structure. At higher fluoride concentration (e.g. 100 mM), two ^{19}F NMR peaks were observed at -103 and -108 ppm. This suggests the formation CaF_2 precipitates ($\delta(^{19}F) = -108$ ppm). Analysis with TEM and XRD further confirmed this finding, and indicates it is crystalized. Interestingly, we found that a much lower fluoride concentration (e.g. 10 mM) would induce the formation at CaF_2 precipitates. In contrast, at pH 10, CaF_2 precipitates did not form even at fluoride concentration up to 500 mM. This is attributed to the pH-dependent stability of Hap. The substitution mechanism at certain pH and fluoride concentration clearly interpreted the regeneration mechanism of Hap for defluorination, and demonstrate that Hap is an ideal material for high-fluoride groundwater remediation.

AL/FE PILLARED FROM SYNTHETIC HIGH CHARGED NA-2-MICA

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Clay materials are used in different environmental processes due to their physicochemical properties of swelling and cation exchange^[1] Their capacity of being pillared with aluminum oligomers and other metals^[2], allow the increment of surface area, acidity and catalytic properties. In particular, the pillaring with iron improves the interaction with organic molecules and have been designed with the potential use in slow release formulations (SRFs) of herbicides,^[3] phenol degradation and catalytic oxidation of volatile organic compounds (VOCs).

In this work Al/Fe Pillared micas were obtained, for the first time, from synthetic mica, Na-2-Mica, with a nominal composition of $\text{Na}_2[\text{Si}_6\text{Al}_2]\text{Mg}_6\text{F}_4\text{O}_{20} \cdot \text{XH}_2\text{O}$, which has striking swelling and cation exchange properties. This Al/Fe PILCs were characterized by XRD, FTIR, XRF, Mossbauer Spectroscopy and N_2 Adsorption. The interlayer space was swelled by the exchanged of interlayer Na^+ by octylammonium. Intercalating solution were prepared mixing $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solutions with different molar relation Fe/Al+Fe from 0.05 to 1^[4]

Molar ratio of $\text{OH}^-/\text{Al}^{3+}+\text{Fe}^{3+} = 2.0$ was used during the hydrolysis with 0.4M solution of NaOH, keeping the pH below 1.8 and this intercalating solution was kept stirring at room temperature for 1 day. A second modification of this process was carrying out without pH control obtained a final pH of 4.4 with molar relation Fe/Al+Fe of 0.05. The intercalating solution was added to organomica by dripping at room temperature and stirring, next a hydrothermal treatment at 80 °C for 4 hours, the solid was washed on dialysis membrane, dried and calcined at 400°C.

The sample Al/Fe PILC with molar ratio $(\text{Fe}/(\text{Al}+\text{Fe})) = 0.05$ keeping a DRX signal in low angle, in the first method one when the pH close to 1.8 the basal spacing was 14Å, as well as dealuminization process was show by XRF analysis and DRX pattern in High-angles region showed the crystallinity structure was affected, and the pilarization process is carried out by iron nodules in the interlayer. In the second method when the pH range was from 2.5 to 4.4 the basal spacing was 18Å, a typical signal of Keggin pillared clays corresponding to Fe/Al Pillars.^[3]

The surface area of the solids obtained increases from 50 to 80 m^2/g and size pore increase from 47.2 Å to 50.1Å for the molar ratios of 0.05 and 0.5 respectively presents by isotherm type IV characteristic of mesoporous materials.

INVESTIGATING THE H-ISOTOPE COMPOSITION OF BOUND WATER IN VERY LOW PERMEABILITY CLAY-RICH SEDIMENTARY ROCKS

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The isotopic compositions of porewater associated with clay minerals in sedimentary rocks can reflect not only original depositional fluids but also rock-water interaction during post-depositional processes. Post-crystallization H-isotope exchange between clay minerals and porewater is now generally accepted to occur, even at low temperatures, given sufficient time and an appropriate rock-water ratio. It is also possible that differences in isotopic composition can arise between porewater bound to clay mineral surfaces and that which remains mobile. These putative differences, however, are poorly explored. For our study, we have chosen Ordovician shales from Ontario that provide excellent examples of clay-rich rocks with low permeability and low water content. Bound-mobile water isotopic fractionation may be observable in such systems. Our pXRD studies show that these shales consist mainly of quartz, calcite and clay minerals with minor amounts of dolomite, consistent with previous reports [1]. The main clay minerals are illite, kaolinite and chlorite, with minor to trace quantities of swelling clay minerals. To provide a baseline for this clay assemblage, we are also investigating CMS Source Clays for possible H-isotope fractionation between bound and mobile water: illite (IMt-1), kaolinite (KGa-1), and chlorite (CCa-1). For all samples, pXRD patterns have been completed for Na-, Ca- and K-saturated aliquots of the <2 µm size-fractions. In next steps, each sample will be evaluated for differences in H-isotope composition between bound and mobile water, following soaking in isotopically labelled waters at temperatures ranging from 25-90°C for periods of weeks to months. Isolation and H-isotope analysis of the clay-associated water will be achieved by *in vacuo* stepwise heating, and water contents and H-isotope compositions will be measured at each step. The temperature steps for collection of water are being guided by the weight loss patterns evident from *in vacuo* TGA analysis of each clay and shale sample. The stepwise heating will ultimately end with extraction of clay hydroxyl groups, and comparison of their H-isotope compositions to samples not treated with isotopically labeled water.

[1] Guillet, G. R. (1977). *Clay and shale deposits of Ontario* (Vol. 2358). Toronto, Ontario: Ontario Ministry of Natural Resources.

POLYANILINE/ATTAPULGITE-SUPPORTED NANOSCALE-VALENT IRON FOR THE RIVAL REMOVAL OF AZO DYES IN AQUEOUS SOLUTION

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Polyaniline/attapulgate-supported nanosized zero-valent iron composites were synthesized by liquid-phase chemical reduction method and used for the removal of two kinds of dyes. The removal property and degradation mechanism for azo and non-azo dyes in aqueous solution were investigated. The results showed that the removal efficiency of azo dyes is obviously better than that of non-azo dyes due to the reductive cleavage of the N=N by nanosized zero-valent iron rather than depending on the adsorption.

MEASUREMENT OF POROSITY SIZE AND DISTRIBUTION IN SHALES AND OTHER TIGHT-ROCK RESOURCES

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Horizontal drilling and hydraulic fracturing of non-conventional resources such shales, marls, and other tight rocks has revolutionized the energy industry. Understanding the properties of these resources is key to better and more efficient extraction of oil and gas. Two critical components of any reservoir are the storage capacity of the rock (porosity) and the connectivity of the pores to allow flow through the rock to the well bore (permeability).

The size and distribution of the pores and what fluids are filling the voids are necessary to understand and model the behavior of unconventional reservoirs. SANS and other experiments often show a bi- or tri-modal distribution of pore sizes consisting broadly of nanometer and micrometer pores. The μm -porosity is readily visible with standard thin section or SEM imaging and is often used to describe the rock. Although volumetrically, the μm -pores may be more abundant, numerically, the nanometer pores are many orders of magnitude more abundant due to the size differential. Consequently, nanometer pores have a significant effect on the rock properties and flow of fluids and gas through the rock. With careful SEM analyses, one can attain resolutions down to around 3nm but it is extremely difficult. Some of this nanometer porosity is related to exfoliation and stacking of clay platelets. However, a significant amount of nanometer porosity is due to the structure of the kerogen. In kerogen, μm porosity is readily apparent as large pores using standard imaging methods. Kerogen, however, has a second nanometer porosity due to its physical structure which can be envisioned as a colloidal material of small spheres or cross linked rods, depending on the thermal maturity (Alcantar-Lopez and Chipera, 2013). Stacking arrangements of these colloidal particles will always have some void space at the interstices of the particles. A semi quantitative assessment of nanometer vs. micrometer pore distribution in rocks can be readily determined by measuring the total porosity in a rock using standard TRA (Total Rock Analysis) methods and by using sorption methods (e.g., N₂ or water vapor) to determine the volume of the nanometer porosity.

Pores can be associated with various minerals and classified according to how they exist. For example, it is well known that organics form a strong pore network. Calcite in the form of fossils can provide porosity, but in the form of cement, will destroy porosity. Likewise, porosity will develop in clay minerals. Using Least-squares refinement methods, we can better associate porosity with the various mineral phases and quantify how much each phase contributes. This works well in shale where porosity is associated with organics and clay minerals but where the porosity is intergranular and not associated with any particular mineral or phase such as in sandstones, the lack of any mineral association becomes diagnostic.

Alcantar-Lopez, L. and Chipera, S. (2013). Improving our understanding of porosity in source rock reservoirs through advanced imaging techniques: URTEC 1619700, p. 1614-1623

TUMOR TARGETING DRUG-CLAY HYBRID DELIVERY SYSTEM IN THE ORTHOTOPIC CERVICAL CANCER MODEL

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Attempts have been made to explore new drug delivery systems (DDS) based on clay nano-vectors for chemotherapy.

In the present study, an injectable drug-clay hybrid DDS with high colloidal property is presented. In order to realize such a colloidal hybrid drug, methotrexate (MTX), an anticancer agent, was immobilized in the interlayer space of clay nano-vector, layered double hydroxide (LDH), by co-precipitation and hydrothermal treatment. Thus prepared hybrid drug, MTX-LDH, was chemically, structurally, and morphologically well-defined. The resulting two-dimensional drug-clay nanohybrid showed excellent colloidal stability not only in deionized water but also in an electrolyte solution of Dulbecco's Modified Eagle's Medium with 10% fetal bovine serum, in which the average particle size in colloid was determined to be around 100 nm with the polydispersity index of 0.250. The targeting property of the present nanohybrid drug was confirmed by evaluating the tumor-to-blood and the tumor-to-liver ratios of MTX with anionic clay carrier, and these ratios were compared to those of intact MTX in the C33A orthotopic cervical cancer model. The biodistribution studies indicated that the mice treated with MTX-LDH showed 3.5-fold higher tumor-to-liver ratio and 5-fold higher tumor-to-blood ratio of MTX than those treated with intact MTX.

Based on the present results such as homogeneous particle size, biocompatibility, and high therapeutic value of this drug-clay nanohybrid system, we could propose it as a promising platform DDS technology for the treatment of cancer.

BOROCAPTATE-CLAY HYBRID FOR BORON NEUTRON CAPTURE THERAPY

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An attempt was made to apply layered double hydroxide (LDH) as a boron delivery carrier for boron neutron capture therapy (BNCT), which needs a sufficient amount of boron in tumor cells for its successful administration. To meet this requirement, a nanohybrid (BSH-LDH), mercaptoundecahydro-closo-dodecaborate (BSH) anionic molecules in LDH, was developed as a boron delivery system. The cellular boron content upon permeation of BSH-LDH nanoparticles ($42.4 \mu\text{g}^{10}\text{B}/10^6 \text{ cells}$) in U87 glioblastoma cell line was found to be ~ 2000 times larger than the minimum boron requirement ($\sim 0.02 \mu\text{g}^{10}\text{B}/10^6 \text{ cells}$) for BNCT, and also orders of magnitude higher than the previous results ($0.2 \sim 1.5 \mu\text{g}^{10}\text{B}/10^6 \text{ cells}$) by those applied with other targeting strategies, and eventually resulted in excellent neutron capture efficiency even under such low dose ($30 \mu\text{g}^{10}\text{B}/\text{mL}$) and weak irradiation ($1 \times 10^{12} \text{ n/cm}^2$ corresponding to 20 min) condition. According to the biodistribution studies in xenograft mice model, the tumor-to-blood ratio of BSH in the BSH-LDH-treated-group was found to be 4.4-fold higher than that in the intact BSH treated one in 2 hours after drug treatment. The present BNCT combined with boron delivery system could provide a promising integrative therapeutic platform for cancer treatment.

A NEW ANTIDEPRESSANT CLAY HYBRID DRUG; ARIPIRAZOLE-MONTMORILLONITE

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Aripiprazole (APZ) is a psychotropic drug, which is available on the market as Abilify® tablet. However, APZ is very poor in aqueous solubility and unpleasant in taste, and therefore, shows low bioavailability upon oral medication, and as a consequence, low patients' compliance, respectively. In this study, we prepared an advanced nanohybrid system based on cationic clay, montmorillonite (MMT), as a drug delivery vehicle, not only for taste masking but also for solubility enhancement of APZ (i.e., APZ-MMT). To improve the efficacy of taste masking and solubility of APZ, the APZ intercalated MMT, APZ-MMT, was first prepared and then further coated with a cationic polymer, polyvinylacetal diethylamino acetate (AEA). *In-vitro* dissolution tests at neutral pH showed that the amount of drug released from the AEA coated APZ-MMT was greatly suppressed (< 1%) for the first 3 min, suggesting that AEA coated APZ-MMT could be a potential formulation for taste masking of APZ. Notably, in a simulated gastric juice at pH 1.2, the total percentage of APZ released in the first 2 h was increased up to 95% for the AEA coated APZ-MMT. Furthermore, *in-vitro* release profile was determined to be almost similar to that of Abilify®, a medication currently available on the market. *In-vivo* experiments using Sprague-Dawley rats were also performed to compare the pharmacokinetics of the AEA coated APZ-MMT and the commercially available Abilify® as a control. The AEA coated APZ-MMT exhibited about 20% higher systemic exposure of APZ and its metabolite, the dehydro-APZ, as compared to Abilify®. It is, therefore, concluded that a new MMT-based nanovehicle, coated with a cationic polymer, could be an advanced new drug assisted by clay delivery system not only for taste masking but also for enhanced bioavailability of APZ.

TOXICITY MECHANISM, TOXICOKINETICS, AND IN VIVO TOXICITY OF CLAY MINERALS

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Clay minerals have been widely applied for biological purpose due to its high reactivity, chemical versatility, ion exchange capacity, and low toxicity. Along with nanotechnology development, the size of clay minerals falls into nanoscale, which raises public concerns about their potential toxicity. In the present study, in vitro and in vivo toxicity of clay minerals, such as layered double hydroxide (LDH) and montmorillonite (MMT), were evaluated in terms of cell proliferation, oxidative stress, inflammation response, and oral toxicity. Toxicokinetic behaviors of LDH and MMT, including absorption, distribution, and excretion, were also evaluated after single-dose oral administration to mice.

The results demonstrate that the cytotoxicity of LDH and MMT was low compared to other inorganic nanoparticles, but size-dependent inflammation response was induced by LDH, which was strongly associated with induction of oxidative stress. Oral absorption of LDH and MMT was extremely low and did not accumulate any specific organ. Furthermore, both LDH and MMT induced no acute toxicological abnormality following oral administration, as observed by no changes in body weight gain, organosomatic index, and biochemical parameters. These findings will provide critical information about safety aspects of clay minerals and their biological application at safe levels.

^{10}B -CARBORATE-CLAY HYBRID SYSTEMS FOR BORON NEUTRON CAPTURE THERAPY

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Layered double hydroxide (LDH), an anionic clay, has been extensively studied in various aspects including gene or drug delivery systems (DDS), since they have been considered as an important research area not only in chemotherapy but also in gene therapy.

More recently, we applied the drug delivery strategy not only to chemo- and gene therapies, but also to boron neutron capture therapy (BNCT), since it has long been needed to develop a novel boron carrier to deliver boron-containing molecules, such as carboranes or carborates, into cells sufficiently. The present boron-LDH hybrids, ^{10}B -carborate-clay ones, is demonstrated in terms of their toxicities, cellular uptake behaviors and neutron capture efficiencies in *in-vitro*, and their bio-distribution studies in *in-vivo*.

In this presentation, the future direction with this 2D-DDS strategy will be suggested to build up a new platform technology for advanced BNCT assisted by DDS technology, which could provide a promising integrative theranostic action in chemo- and radiation therapies.

THE ENIGMA OF HALLOYSITE

G. Jock Churchman*

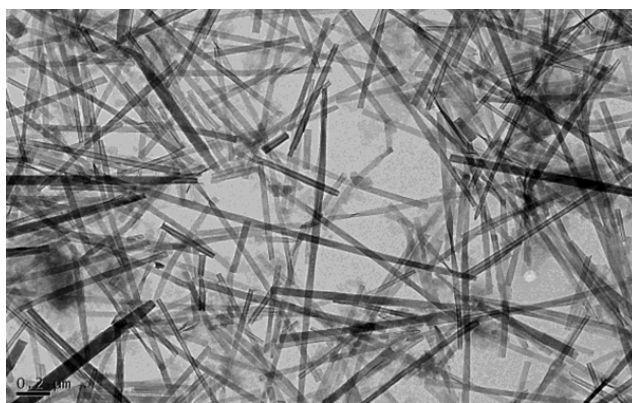
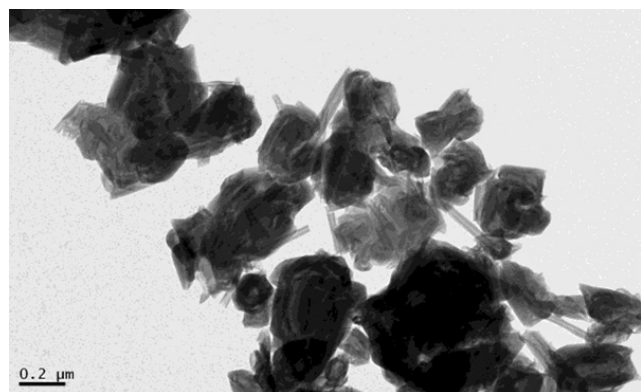
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Halloysite has long been a curious clay mineral. It is also widely varied in its expressions. More recently halloysite as HNTs, or halloysite nanotubes, has proven to be potentially very useful in a wide number of nano-applications, including as a filler, a carrier, a template for reactions, and a catalyst. It has even been proposed for the controlled release of drugs, e.g. for cancer.

Examples of halloysite from New Zealand, Australia, the USA and Hong Kong are presented. The paper will discuss the definition of halloysite, which is based on its interlayer water. It will also outline how shapes of halloysite can transform into other forms. Typically, spheroidal halloysites have been seen to give way to tubular forms and then sometimes to platy forms, and even book-like aggregates, although drying may lead to kaolinite in platy and book forms. Prismatic shapes may derive from tubular forms. Although it is generally likened to kaolinite, organic complexes of each show their essential structural differences, with those of halloysite apparently showing some similarities to those of dickite.

Halloysites form at acid pHs, but not at alkaline pHs. They have unexceptional tetrahedral Al contents and no interlayer cations. Indications of these come from Al-NMR and Quasi-Elastic Neutron Scattering. They also have low CECs. The formation of halloysite is aided by the continuous availability of water, hence deep in weathering profiles and with high rainfall, while kaolinite is formed in drier environments. The sizes of halloysite crystals reflect the contents of Fe and sometimes also Mn in their formation environment. Zeta potentials indicate that interlayer water is likely attracted and held as H-OH by contrasting charges on adjacent atomic sheets (tetrahedral Si and octahedral Al).



Examples of the range of shapes of halloysite: Te Puke (New Zealand), left, and Patch clay (Australia), right. Both scale bars are 0.2 μm in length.

STRUCTURE, DYNAMICS AND REACTIVITY OF C-O-H FLUIDS IN NANOPOROUS REGIMES

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Unconventional hydrocarbons occurring in economic abundance require greater than industry-standard levels of technology or investment to exploit. Geological formations that host unconventional oil and gas fields and coal bed methane are extraordinarily heterogeneous and exhibit a wide range of physical and chemical features that can vary over many orders of magnitude in length scale. Of particular importance is nature of the microstructure and evolution of pore space in rocks, which are critically important factors controlling multiphase flow. Many unconventional reservoir lithologies are comprised of pore regimes ranging from relatively uncommon large macropores at the millimeter scale to more numerous small micropores at the sub-micron and nanometer scale. The size, distribution and connectivity of these confined geometries, the chemistry of the solid, the chemistry of the fluids and their physical properties collectively dictate how fluids migrate into and through these micro- and nano-environments, wet and ultimately react with the solid surfaces. Our current understanding of the rates and mechanisms of fluid and mass transport and interaction within these multi-porosity systems at the molecular scale is far less robust than we would like.

This presentation will take a two-fold approach to this topic area. First, we will provide a brief overview on pore types and their relationship with mineralogy in key gas shale formations with special emphasis on the Utica, Marcellus and Eagle Ford. We will highlight results from conventional methods such as SEM along with more sophisticated approaches including small- and ultra-small angle neutron scattering that contribute to two key science question areas: (a) What are the size, distribution, connectedness, and contribution to total porosity of nano- to micropores in representative gas shales? (b) How do these pore features vary with the distributions of clay and carbonate matrix and organic matter? The second more in-depth part of the presentation will focus the application of state-of-the-art experimental, analytical and computational tools to assess key features of the fluid-matrix interaction relevant to shale settings. The multidisciplinary approaches highlighted will include neutron scattering and NMR experiments, thermodynamic measurements and molecular-level simulations to quantitatively assess molecular properties of pure water, aqueous electrolytes and simple immiscible water-hydrocarbon mixtures confined to well-characterized porous media, subjected to temperatures and pressures relevant to subsurface energy systems. These studies conducted in concert are beginning to provide a fundamental understanding at the molecular level of how intrinsically different C-O-H fluids behave in confined geometries compared to bulk systems., and shed light on key geochemical processes such as fluid wetting, competitive sorption and the onset of mineral dissolution and precipitation.

MOLECULAR MODELING OF KEROGEN AND NATURAL GAS SYSTEMS

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Molecular simulation research has focused on studying kerogen and its interactions with methane, carbon dioxide, and water to better understand methane release mechanisms. Using a molecular model for over-mature kerogen, we have investigated (1) methane adsorption and release from nanoporous kerogen, (2) the interaction of CO₂, CH₄, and H₂O with kerogen, and (3) kerogen swelling with methane or carbon dioxide adsorption. Using molecular simulations, we show that methane release from the nanoporous kerogen matrix is characterized by fast release of pressurized free gas (accounting for ~30–47% recovery) followed by slow release of adsorbed gas as the gas pressure decreases. The first stage of methane release is driven by the gas pressure gradient, while the second stage is controlled by gas desorption and diffusion.

We then show that kerogen preferentially retains CO₂ over CH₄ and that the majority of CO₂ either generated during kerogen maturation or injected in enhanced oil recovery (EOR) will remain trapped in the kerogen matrix. The trapped CO₂ may be released only if the reservoir pressure drops below the supercritical CO₂ pressure. When water is present in the kerogen matrix, it can block CH₄ release. However, the addition of CO₂ may enhance CH₄ release because CO₂ can diffuse through water and exchange for adsorbed methane in the kerogen nanopores.

Using a hybrid Monte Carlo/molecular dynamics simulation, we show that a strong chemo-mechanical coupling may exist between gas adsorption and mechanical strain of a kerogen matrix. The results indicate that the kerogen volume can expand by up to 5.4% and 11% upon CH₄ and CO₂ adsorption at 192 atm, respectively. Gas uptake is also greatly enhanced by kerogen swelling. Swelling increases the surface area, porosity, and pore size of kerogen. These results illustrate the dynamic nature of kerogen, and suggest that the use of a rigid kerogen molecular structure in estimates of gas-in-place for a shale gas reservoir or gas storage capacity for subsurface carbon sequestration may need to be reconsidered.

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SURPRISING FINDINGS FROM SOLID-STATE NMR OF ^{13}C IN CARBONATES: ON THE PATHWAY TO “NMR” CRYSTALLOGRAPHY

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We are studying multiple carbonate species in an effort to use modern solid-state NMR tools and DFT calculations to obtain precise structures. Here, we have studied multiple hydroxy- hydrated magnesium carbonates (including hydromagnesite, nesquehonite, and dypingite) to obtain precise data about lineshapes. The lineshapes themselves are indicators about the symmetry found at the carbon site—as a carbonate, we would normally expect a 3-fold symmetric species (termed “axially symmetric”). We rarely find such perfect axial symmetry, and close examination of the crystal structure can help reveal sources of broadening, when including species slightly more distant than the first coordination sphere. These include the effects of nearby protons (^1H) from water and bicarbonate that distort the ^{13}C resonances.

We are using DFT calculations of atomic coordinates using CASTEP-NMR and VASP to predict NMR properties, and we refine our models with experimental NMR data using the technique of rotational echo double resonance (REDOR). Here, the (relative) scarcity of protons in the lattice permit us to pursue $^{13}\text{C}\{^1\text{H}\}$ REDOR to obtain precise ^{13}C - ^1H distances, to 3 significant figures.

CHEMISTRY AND ISOTOPES OF PLEISTOCENE CLAYS, OLDUVAI GORGE, TANZANIA: ORBITAL CONTROL OF EAST AFRICAN PALEOCLIMATE

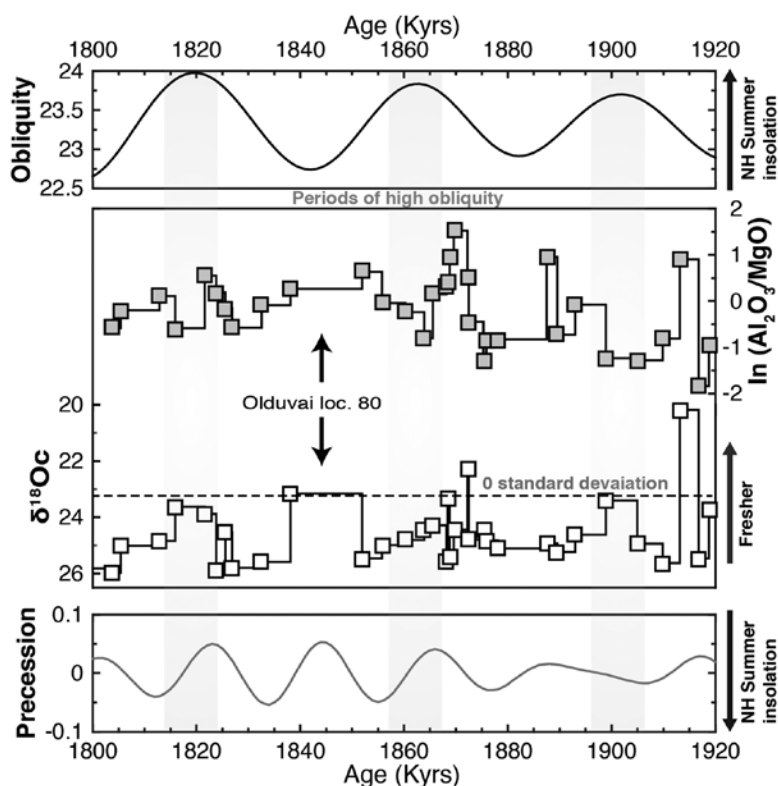
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Authigenic clay minerals can accumulate in lakes with saline, alkaline, and silica-rich waters, including Mg-rich smectite, illite-smectite, and illite, with dioctahedral, trioctahedral, and intermediate phases. Enhanced octahedral layer charge is commonly associated with more illite layers. In the Olduvai Basin, variation between Al-rich and Mg-rich clays reflects paleosalinity, which tracked paleo-monsoon intensity due to precession-controlled insolation (Deocampo et al., 2017). Here we show that the oxygen isotope composition of the authigenic clays similarly reflects paleolake water. The $\delta^{18}\text{O}$ of structural oxygen from clay fractions was analyzed using ClF_3 extraction and isotope ratio mass spectrometry. $\delta^{18}\text{O}$ varied between $\sim +20$ and $+26\text{‰}$ (VSMOW). Applying equilibrium fractionation factors assuming 15°C and mineralogy determined by XRD, we estimate the $\delta^{18}\text{O}$ of paleolake water varied between -2 and $+2\text{‰}$ (VSMOW), values that are in line with expected paleolake water compositions with varying degrees of evaporative concentration. There is a good match between oxygen isotope and geochemical results. Clay $\delta^{18}\text{O}$ tracks whole-rock $\text{Al}_2\text{O}_3/\text{MgO}$ through four of the five apparent geochemical cycles. Such cycles are interpreted as representing lacustrine salinity cycles driven by orbital precession, with perhaps some influence of eccentricity and obliquity.

The correspondence of the independent chemical and isotopic lines of evidence suggests that the impact of precession on moisture delivery to East Africa in the early Pleistocene. Given the cycle timings, it is also possible that orbital obliquity plays a role, implying that the East African monsoon system may be responsive to high latitude climate change following periods of obliquity minima and warming in the southern hemisphere. This has significant implications for ecosystem structure and environmental change through time, the evolution of early hominins, and the emergence of stone technologies and other behaviors among our ancestors.



RETENTION ON ILLITE CRYSTALLITE EDGES CONTRIBUTES TO CESIUM CYCLING IN THE UPPER CONTINENTAL CRUST

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Cesium (Cs) and rubidium (Rb) are large cations and strongly incompatible elements that follow a general geochemical pathway of potassium (K). In spite of similar geochemical behavior, Cs and Rb concentrate in the upper continental crust (UCC) preferentially to K, resulting in the Cs/K, Rb/K and Cs/Rb ratios in the UCC significantly higher than those in middle and lower continental crusts, MORB, and seawater. In soils—which typically yield Cs/K and Rb/K ratios several to tens of times greater than the UCC—Cs fixation in micaceous frayed edge sites (FES) is a suggested long-term, bio-unavailable retention mechanism. Illite and hydroxy-interlayered vermiculite are the common soil minerals known for high Cs and Rb selectivity and irreversible adsorption in crystallite wedges and FES [1].

After analysing 4000+ samples from 22 basins and sub-basins throughout the world, illite was identified as a potentially global sink for Cs. The Cs/K and Cs/Rb ratios in illite were found unique to a geologic section and location, therefore, they can be used as a tracer linked to particular sedimentary or diagenetic conditions. Combining these findings with the known mechanism of Cs and Rb fixation, it is now suggested that the mechanism of Cs-retention discovered in soils works in any geological environment, making illite strongly contributing to Cs cycling in UCC.

Using mass balance and realistic assumptions, illite was estimated to be responsible for up to 20% of Cs in UCC and it is the major sink for Cs in sedimentary basins. As found in this study, average Cs concentration in illite is 17.7 ppm. Assuming that this is the concentration that can be adsorbed only by illite FES, the entire Cs present in the Earth oceans can be irreversibly adsorbed by just several cm-thick illite-rich sediment covering the sea floor, or by < 15 mg of illite suspension in 1 m³ of seawater. Because the equilibration Cs⁺ with FES in illite or inner-sphere fixing in vermiculite occurs instantaneously, any Cs⁺ contact with illitic material may result in its immediate fixation.

The order of cations selectivity and irreversible adsorption on illite, Cs⁺ > Rb⁺ > K⁺ > Na⁺, corresponds to their hydration enthalpy [1, 2]. This order corresponds to the order of the cations' relative depletion in global seawater with respect to the UCC. Cs adsorption by illite crystallite edges is now postulated as the mechanism controlling Cs cycling in sedimentary basins and the segregation of Cs and Rb geochemical pathways in UCC.

[1] Wampler et al. (2012), *Environmental Science & Technology* 46, 3837–3843.

[2] Rotenberg et al. (2009), *Geochimica et Cosmochimica Acta* 73, 4034–4044

PHASE TRANSFORMATION AND CRYSTALLINITY CHANGE OF IRON OXIDE NANOPARTICLES AND THEIR RETENTION OF AS, CU, AND ZN IN SIMULATED ACID MINE DRAINAGE NEUTRALIZATION BY CALCITE AND DOLOMITE

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One common remediation measure for acid mine drainage (AMD) is using carbonate minerals to neutralize the acidity and to trigger the precipitation of dissolved iron and other metals as oxides or hydroxides. Heavy metals can be immobilized by the iron oxides through incorporation or adsorption. These processes occur naturally if the AMD occurs in a limestone environment. Particle size, crystallinity, and stability of iron oxides are affected by the chemistry of the water solution. It can be expected that they would have different capacities in adsorbing/incorporating heavy metals. The iron oxides would transform to thermodynamically more stable phases with time. One question arises about AMD management is how the iron oxide mineral phase transformation with time affect the mobility of the adsorbed or incorporated heavy metals in the environment. The objectives of this study were to monitor 1) the type, crystallinity, and transform of iron oxides formed after neutralizing the acidity of AMD in the presence of calcite and dolomite, two most common carbonate minerals used in AMD remediation, and 2) the retention and release of As, Cu, and Zn on the iron oxides during the mineral phase transform and crystallinity change.

Two iron sulfate-rich precipitates, one dominated by copiapite, and the other by rozenite, from an oxidized mine tailing in Zimapán in Hidalgo state, Mexico, were dissolved in DI water to mimic AMD. These sulfate precipitates contained a few thousands or hundreds mg/kg of Zn, As, Cu, and other heavy metals. The AMD simulants were mixed with calcite and dolomite at 24°C, 50°C, and 80°C for three months. The iron oxide mineral phase were quantified with XRD and characterized with electron microscopes. The supernatant chemistry were analyzed with pH meter, AA, and ICP.

The acidity of the AMD simulants could be neutralized quickly by calcite and dolomite, the pH of AMD supernatants increased from 2.5 to 7 and more than 95% of iron precipitated out within three days. Only morphous or poorly crystalline iron oxide nanoparticles formed at room temperature. With increasing time, temperature, or both, lepidocrocite, goethite, hematite, and magnetite formed depending on the composition of starting AMD. The hematite crystallite size increased from about 30 nm to about 60 nm at 80°C in two months. When the rozenite-AMD simulant interacted with calcite, amorphous phase and lepidocrocite crystallites with a particle size of a few nm formed at room T. When the temperature was increased to 80°C, magnetite nanoparticles with diameter of about 16 nm formed rapidly, but the crystallite size remained less than 30 nm after two months. As and Cu removal from the solutions was synchronized with the iron oxide precipitation, yet Zn removal from the solutions was dragged behind. Increasing the temperature speeded up the precipitation of iron oxide and the removal of heavy metals. None of the Fe or heavy metal showed an increasing concentration during the three month monitoring, suggesting that the heavy metals were not re-mobilized when the mineral phase transformation or crystallite size increment occurred.

FORMATION OF ZEOLITE MINERALS FROM VOLCANIC ASH: AN OVERVIEW.

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Zeolites are geologically important, constituting one of the largest groups of rock-forming minerals. These minerals form in a wide variety of low P, T environments. In the vast majority of these environments, volcanic ash serves as the highly reactive precursor material for zeolite formation in both closed and open hydrogeologic systems. Saline alkaline lakes are hydrologically closed systems that include both playa lakes and rift-type systems. The hydrolysis of volcanic glass controls solution chemistry in these strongly evaporative systems and produces strongly alkaline and saline waters. Zeolite formation in saline, alkaline lakes was studied by Hay (1966), Sheppard and Gude (1968, 1969, 1973), Hay and Sheppard (1977), Surdam (1977), and Surdam and Sheppard (1978). These studies demonstrated that solution composition is the primary control on the diagenetic reactions that transform volcanic ash and tephra across zones of increasing salinity and alkalinity into smectite, clinoptilolite and other K-Ca-zeolites, and finally K-feldspar. Although the diagenetic sequence of mineral formation is similar to that of playa lakes, anomalous Ca- and Mg-analcime compositions may be formed in rift-type systems where dolomitic tuffaceous marls are the precursor material.

Compared to saline-alkaline lakes, significantly different zeolite assemblages form in open hydrologic systems, even when the temperature and precursor material compositions of the systems are similar. Large volumes of volcanic tephra have been altered in sedimentary environments into zeolites by the action of percolating waters in open hydrologic systems. Vertical zonation of zeolites and other authigenic minerals, caused by chemical changes of downward percolating meteoric water, is typical of open hydrologic systems. Hydrolysis and/or dissolution of volcanic glass can produce strongly alkaline solutions with high cation to hydrogen ion ratios. In these systems, zeolite minerals form with or without clay minerals via complex reactions involving incongruent dissolution of volcanic precursor materials. In addition to clinoptilolite, mordenite, chabazite and phillipsite are common, early phases formed in the shallow portions of these open systems.

Although the exact mechanism of zeolite formation in these diagenetic sedimentary environments remains elusive, numerous field and laboratory studies have contributed to our increased understanding. Solution pH was shown by Donahoe et al. (1985) to control the distribution of aqueous aluminosilicate species and, as a result, the Si/Al ratios of zeolite minerals formed from highly alkaline solutions in laboratory experiments. While solution composition is the primary control on zeolite formation in closed systems, the composition and structure of the zeolites that form in open systems are controlled, at least in part, by the composition of the precursor volcanic material.

STRUCTURAL FEATURES OF HYDROTHERMAL ILLITE-SMECTITES IN METASOMATITES AT THE ANTEI-STRELTSOVSKOE URANIUM DEPOSIT (RUSSIA)

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The Antei-Streltsovskoe deposit (ASD) is located in Zabaykal'sky Krai in the eastern part of the biggest Russian uranium ore field, Streltsovskoe (SOF), which is confined to a caldera formed in the Late Mesozoic. Then the area of the ASD was subjected to a complex low-temperature metasomatic alteration which resulted in three stages of mineral formation: pre-ore stage (140-135 Ma), uranium ore stage (135±2 Ma) and the post-ore stage (135–117 Ma) (Ishukova, 2007). Mineralogical investigations of the SOF started since the 1960s. Numerous data have been accumulated that allowed different researchers to substantiate the schemes of stages and paragenetic sequences of mineral formation. However, in view of the multistage nature and duration of the hydrothermal processes at the SOF, a comparison of those schemes reveals differences for clay minerals, and especially illite-smectites. The purpose of this research is to study clay minerals from the wallrock metasomatites, to clarify some disputable aspects of genesis of this deposit. More than 50 core samples from wells 4 and 7 were selected for the study. These wells pass at 800-2200 m depths through the late Paleozoic granites of the Streltsovskaya caldera basement (Ishukova, 2007). Methods used were: XRD, quantitative analysis of bulk samples with the Rietveld method and simulation of XRD patterns of textured clay specimens for identification and quantification of mixed-layer minerals; FTIR spectroscopy (middle region); SEM; and EDS. The clay fraction was separated by sedimentation. Three associations of clay minerals were distinguished in the metasomatites of the ASD. The first consists of illite, mixed-layer illite-smectite with a low smectite interlayers content. The second association is distinguished by a much more higher content of the kaolinite-serpentine group (kaolinite, berthierine). The third association is distinguished by the presence of the chlorite group minerals. According to the previous researches and recently obtained results the main process of granite argillization at the ASD results in illite-smectite formation. XRD pattern simulation revealed the presence of mixed-layer illite-smectite together with the illite. However for the means of quantification of smectitic component in illite-smectites the XRD simulation method is quite time-consuming and could be inadequate when dealing with low contents of smectite interlayers. Thus, we used the combination of two modern methods proposed by (Sakharov and Drits, 2015, 2018). The first is based on the analysis of broadening of basal peak series. While the second method is based on the analysis of d-values of (003) and (007) peaks. This approach provided us with quite precise quantitative results on the smectitic content in smectite-poor illite-smectites. According to the obtained results we have found that illite-smectites with 8-11% smectite interlayers occur only above the depth of 1000 m, in the 1000-2400 m interval smectitic content is 2-6%, and finally below 2400 m it is less than 2%.

MORPHOLOGY STUDY ON MONTMORILLONITE GELS WITH DIFFERENT MICROSCOPY SCANNING METHODS

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Montmorillonite, also known as clay, is a member of the smectite, with one octahedral alumina sheet sandwiched by two tetrahedral silica sheets. It swells and forms gels at very low concentration, displaying diversity series of properties. It is believed that the morphology of clay particles in water determines the colloidal properties, such as yield stress, viscosity, viscoelasticity, and structural recovery behaviour.

Scanning electron microscopy (SEM) images provide with clear microstructure of air-temperature-dried montmorillonite gels. These images display flexible platelet-like layers with large surface area and thin thickness. The surface area can be as large as several square microns and the thickness is only several nanometers. These layers stack on each other in a parallel format, and contacting by face-to-face (FF) and edge-to-face (EF) interactions.

Low temperature field emission scanning electron microscopy (FFSEM) reveals the morphology of montmorillonite gels. The fractured surface exposes the inner microstructure of the gel after the sublimation of liquid nitrogen frozen water without destroy the particle arrangement. Regular-shaped honeycombs can be clearly seen in the FFSEM images. Water suffuses the honeycomb cells circled by clay particles. The widely open mouths of the honeycomb explain the low clay amount needed for a gel. The low temperature FFSEM images also display high-aspect-ratio platelet layers stacking by parallel format contacting with FF and EF interactions. Moreover, the walls of honeycomb cells contact with each other mainly by EF and FF interactions. The Y-shape contact results from EF attraction and FF repulsion. We should note that the FF repulsion works on the nearby layers within several nanometers, which is controlled by electrical double layers (EDL) of clay particles. Moreover, the structural balancing process of the honeycomb structure contributes to the long-time scale structural recovery behaviour of a montmorillonite gel. It takes long time to achieve the relative-balance state affected by the attractive and repulsive interactions between particles.

TRIPOLYPHOSPHATE EFFECT ON THE RHEOLOGY AND MICROSTRUCTURE OF MAGNESIUM CHLORIDE LOADED BENTONITE GELS

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Researchers have studied the bentonite gel behaviour while exposed to metal salt solution. But knowledge on dispersant impact on the gels is still lacking. As a regular dispersant, tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) has a pentavalent anion, while added into a bentonite gel, anion reacts with bentonite particles, which in turn changes the colloidal properties. What if the gel is prepared in MgCl_2 solution? More experiments need to be carried out to study the impact.

$\text{P}_3\text{O}_{10}^{5-}$ plays an important role in gel yield stress behaviour, including surface chemical equilibrium (SCE) yield stress and time-scale yield stress recovery behaviour. The addition of $\text{P}_3\text{O}_{10}^{5-}$ reduces SCE yield stress. Specifically, SCE yield stress reduces as the concentration of $\text{P}_3\text{O}_{10}^{5-}$, while it is lower than 1.0 dwb% (dry percent weight of bentonite). The SCE yield stress keeps stable afterwards. Time-scale yield stress recovery behaviour also relies on the anion concentration, the recovery time and recovered yield stress both decreases before $\text{P}_3\text{O}_{10}^{5-}$ reaching a certain concentration. The so called Leong Ageing Model and Nguyen-Boger Ageing Model both describe the structural recovery behaviour well. Rheology measurement results indicate that all gels are elastic fluids with shear-thinning property. However, as $\text{P}_3\text{O}_{10}^{5-}$ concentration increases, the elastic property reduces and viscous property increases. In other words, $\text{P}_3\text{O}_{10}^{5-}$ reduces the attraction and increases the repulsion among particles.

Honeycomb structure is revealed by cryo-SEM images. The wide-open mouth structure occupies the whole volume of the container, this explains the reality that only small amount of bentonite is needed for a gel. Moreover, repulsive interaction plays a key role in the formation of honeycomb structures, as well as attractive interaction. The attraction gathers all particles together and forms platelet layers, while repulsion helps bentonite platelets separate from each other and avoids agglomeration. Slightly movement of particles leads to imbalance of the microstructure. More particles should move in correspondence to reach the balance in a long time period. This explains the long-time scale recovery behaviour for these gels. The addition of anion reduces the strength of the microstructure, the balance of the microstructure is easier to achieve accordingly. This is the reason for recovery time decrease of high $\text{P}_3\text{O}_{10}^{5-}$ concentration gels.

CLAY GENESIS FROM VOLCANIC PARENT MATERIALS: DIFFRACTION TELLS ONLY PART OF THIS STORY

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Smectite group minerals are formed from the alteration of volcanic glass, other volcanic progenitor materials, and from soil mineral precursors. Smectites formed from the weathering of volcanic ash/glass or volcanoclastic rocks are found in clay dominant rocks such as bentonites. Pyroclastic minerals such as zircon, apatite, feldspar (labradorite) added further support to volcanic origin of these bentonites. A relatively few number of field/laboratory studies have actually showed smectite being formed from weathering ash/tuff (Zielinski, 1982). In many studies, smectites are interpreted as being formed from the reaction of glass-to-clay processes based primarily on X-ray diffraction results and in the absence of such fortuitous co-occurrence of glass, ash, and/or tuff and smectite clay. The study of glass to clay has also considerable pragmatic importance (e.g. high level nuclear waste) and in understanding the petrogenesis of clastic sedimentary rocks.

Several additional techniques have been used to characterize the formation of smectite in argillaceous rocks (elemental analyses, geochronological, stable isotope, scanning transmission electron microscopy-STEM). These data have been useful in describing the process of glass being converted to smectite. In one study of the K-T boundary marl at Stevns Klint, Denmark, smectite appeared to form as distinct 2:1 smectite layers by weathering/dissolution of impact-derived glass from STEM studies (Bauluz et al., 2000). Smectite was also found in marls above and below, and including the K-T boundary. This second smectite was thought to have been derived from the weathering of mafic volcanic progenitor based on the stratigraphic occurrences of that smectite near the K-T boundary and smectite Mg-rich composition. These data illustrated the need for more than one technique to understand the genesis of both types of smectite at the K-T boundary. The REE of smectite and illite smectite in bentonites and potassium bentonites might also fingerprint smectite formed from ash/glass and illite smectite diagenetically altered from smectite in some studies. These additional techniques, reviewed in part for this paper, provided further insight on the genesis of smectite.

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THE DERIVATION OF FORMULAS FOR SIMPLE PHYLLOSILICATE MINERALS

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Undergraduate and graduate students enrolled in mineralogy and petrology spend considerable time memorizing the formulas of common rock forming minerals. Most of these formulas are not retained for the long term by many students. The formulas for phyllosilicate minerals are lengthy. These formulas, even if they are committed to memory at some point in a student's career, are not retained long thereafter unless they are in regular use. This rote memorization can distract the student from the important jobs of learning about the structure, genesis, identification, their properties in soils and rocks (dispersion, cation exchange), and their uses of these minerals in our day-to-day lives. Phyllosilicates are well known for their uses in industry, advanced technologies, and even medicine (e.g. Moore and Reynolds, 1997; Williams et al., 2009). The students studying phyllosilicates need to keep these lengthy formulas in mind while learning more about the many and increasing properties, their genesis, and other interesting aspects of phyllosilicates. The students' interest and satisfaction in studying phyllosilicates will likely increase given a more convenient way to learn the formulas for the phyllosilicate minerals.

A method is described to derive the formulas of simple phyllosilicate minerals. This method is created to minimize the amount of rote memorization needed to state the formulas of phyllosilicate minerals. This method is focused on knowing both the types and compositions of sheets present in a given phyllosilicate mineral, their arrangement forming the layered phyllosilicate minerals, and the linkage of the two different type of sheets through the replacement of an OH atom in the octahedral sheet by an apical oxygen from the tetrahedral sheet. The number of OH in the final formula is equal to the number of OH in the octahedral sheet minus the number of OH replaced by the apical O (e.g. Hurlbut and Klein, 1977). The Si, Al and O are carried from the tetrahedral and octahedral sheets to the final formula. This method does not imply a mechanism of forming phyllosilicate minerals. With practice, students and experts will find the derivation to be convenient and easy to do. It is not necessary to memorize these phyllosilicate formula other than to know the compositions of the tetrahedra, octahedral sheets, and the amount and position of layer charge. The effort devoted to memorization can be used to understand further information about the phyllosilicate minerals.

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MICROBially MEDIATED ABIOTIC REDUCTION OF CLAY MINERAL IRON: UNDERSTANDING THE ROLE OF SECONDARY PRECIPITATES FOR CONTAMINANT REMEDIATION

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In subsurface environments, microbial activity leads to the abundant and sustained generation of aqueous Fe(II). We, and others, have demonstrated that aqueous Fe(II) can reduce structural Fe(III) in clay minerals, resulting in electron-doped minerals and the extent of structural Fe reduction depending on reaction pH, aqueous Fe(II) concentration, and clay mineralogy^{1,2}. The formed clay mineral Fe(II) could be a potent reductant for contaminant removal, in analogy to chemically reduced clay mineral Fe. However, electron transfer from aqueous Fe(II) also leads to the formation of solid Fe(II) oxidation product(s), with some controversy over the composition and identity of the secondary mineral phases. While earlier work showed the predominant formation of an Fe(III) phase similar to lepidocrocite³, recent work suggested that mixed valent Fe phases such as green rust could form⁴, which, in turn, could contribute to contaminant transformation.

Here we evaluated the reactivity of Fe(II)-reduced clay minerals and used two legacy contaminants, tetrachloroethene (PCE) and trichloroethene (TCE), as probe compounds. We compared the reactivity with dithionite-reduced clay minerals and for high and low Fe content clay minerals (nontronite, NAu-1; montmorillonite, SWy-2), to modulate the clay mineral Fe(II) concentration and the amount and identity of Fe(II) oxidation products formed. We complemented our reactivity study with techniques to identify the reactive Fe mineral(s) and used ⁵⁷Fe Mössbauer spectroscopy, XRD, and Raman spectroscopy.

Transformation of PCE and TCE was not observed for neither dithionite nor Fe(II)-reduced high Fe content clay mineral NAu-1. Transformation products were also absent in the presence of dithionite-reduced low Fe content clay mineral SWy-2 and were detected only in reactors containing SWy-2 amended with 20 mM aqueous Fe(II). Reference experiments with the same Fe(II) concentrations and in the absence of clay mineral showed similarly low PCE and TCE conversion extents of below 5% after 88 days. In the clay mineral-free reactors, we detected white rust (Fe(OH)₂) and the presence of Fe(II) in the aqueous phase, suggesting that clay mineral structural Fe(II) may not be a viable reductant for PCE and TCE. However, Mössbauer spectra of aqueous ⁵⁷Fe(II)-amended SWy-2, in which clay mineral Fe contributed less than 1% of the spectral area, revealed that white rust did not form at high Fe(II) concentrations when clay mineral was present. The data are consistent with the formation of a green rust-like phase and the simultaneous presence of sorbed Fe(II). We are currently collecting XRD and Raman data to confirm the presence of the green rust. We are also investigating whether the secondary mineral phase alone is the reactive Fe phase for PCE and TCE transformation or whether the presence of additional aqueous and/or sorbed Fe(II) is required.

^{64}Cu -DOPED ANIONIC NANOCCLAY FOR IN-VIVO PET IMAGING**Sairan Eom*, Goeun Choi, and Jin-Ho Choy***Center for Intelligent Nano-Bio Materials (CINBM), Department of Chemistry and Nano Science, Ewha Womans University, Seoul 03760, Korea*

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A biocompatible and stable ^{64}Cu -layered double hydroxide (^{64}Cu -LDH) as a PET imaging nanoclay for systemic delivery, was prepared by co-precipitation and hydrothermal method. According to the XRD and SEM studies, the ^{64}Cu -LDH maintained its lamella structure with plate-like morphology. And it showed its ^{64}Cu labeling efficiency of 99%. The doped ^{64}Cu was well incorporated into octahedral site of LDH lattice, and as a consequence, the ^{64}Cu -LDH was found to be chemically very stable not only in saline and PBS, but also in biological media such as mouse and human serums. Small animal PET images of the ^{64}Cu -LDH were obtained from 2 h to 48 h after i.v. injection in MDA-MB-231 xenograft mouse model, indicating that its tumor selectivity was increased by time. To enhance tumor uptake efficiency, the ^{64}Cu -LDH covered with bovine serum albumin (BSA) was attempted for PET imaging. And surprisingly, we found that the ^{64}Cu -LDH-BSA showed 2-fold higher tumor uptake efficiency compared to the intact ^{64}Cu -LDH. According to our previous studies on drug delivery systems (DDSs), it was already found that drug-LDHs could be permeated inside the cells very efficiently through the clathrin mediated endocytosis, resulting in enhanced therapeutic efficacy than free drug in various tumor-bearing mouse models. It is, therefore, concluded that the ^{64}Cu -LDH could be an advanced nanomedical device not only as the drug delivery carrier for cancer therapy, but also as the imaging and diagnostic agents.

INDUCED POLARIZATION AND PIEZOELECTRIC EFFECT BY NON-POLAR HYDROTALCITE-LIKE CLAY MINERAL

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Non-polar layered double hydroxide (LDH), hydrotalcite clay mineral, incorporated with yttrium in octahedral site $[\text{Mg}_2\text{Al}_{1-x}\text{Y}_x(\text{OH})_6 \cdot (\text{CO}_3) \cdot n\text{H}_2\text{O}]$, $x = 0-1$, Y-LDH] was successfully prepared by co-precipitation and subsequent hydrothermal reaction. Such a material with yttrium-90 isotope could also be applicable as a radiotherapeutic agent for nanomedicine. According to the X-ray diffraction (XRD) analysis for Y-LDHs, their lattice parameters were gradually increased from $a = 3.04 \text{ \AA}$ and $c = 22.71 \text{ \AA}$ to $a = 3.07 \text{ \AA}$ and $c = 24.04 \text{ \AA}$ with increasing the Y(III) content in LDH lattice from $x = 0$ to $x = 0.4$, indicating that the crystal lattice of LDH was further expanded along the crystallographic a and c -axes with an increasing Y(III) content. From the FT-IR spectra, it was found that a peak corresponding to the (O-C-O) symmetric vibration of CO_3^{2-} with D_{3h} symmetry was observed at 1357 cm^{-1} for the pristine LDH ($x = 0$). However, for Y-LDHs ($x = 0.1-0.4$), the peak at 1357 cm^{-1} was shifted to 1382 cm^{-1} with a new peak at 1520 cm^{-1} , which could be ascribed to the asymmetric and symmetric vibrations of CO_3^{2-} with C_{2v} symmetry, clearly due to the symmetry change of interlayer carbonate ions upon lattice distortion resulting from the partial substitution of larger Y(III) ions into the LDH lattice. According to the DFT calculation, it was understood that an isomorphous substitution of Y(III) in LDH lattice gave rise to the symmetry change of interlayer CO_3^{2-} ions, as confirmed by FT-IR study. It was, therefore, expected that such an induced polarization of interlayer CO_3^{2-} ions may result in piezoelectric property of non-piezoelectric LDH. In this presentation, the output voltage and current by piezoelectric effect of Y-LDH will be demonstrated for the first time. It is, therefore, concluded that Y-LDH can be applicable not only as a radiotherapeutic agent but also as a piezoelectric materials for nanomedicine.

CATALYTIC ROLE OF MINERALS FOR THE FORMATION OF RNA OLIGOMERS-BERNAL-I

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Dedicated to the Memory of George W. Brindley

As first suggested by J. D. Bernal, clay minerals play an important role as catalyst in chemical evolution by adsorbing the monomers of biologically important molecules on their surfaces, thereby bringing them into a favorable orientation for reactions to occur. We have demonstrated that montmorillonite catalyzed reaction of monomers produces short RNA chains under prebiotic conditions: More importantly, these *synthetic* RNA chains can replicate themselves to produce the complementary RNA chains.

In addition to their abundance on Earth, phyllosilicates have also been identified on Martian surface. Catalysis for the formation of RNA and protein chains, and protection of their monomers against radiation effects and shock impacts by clay minerals on Earth and on Mars and other planets may have played an important role in the events leading to the origin of life.

ROLE OF MINERALS IN THE EVENTS LEADING TO THE ORIGIN OF LIFE-BERNAL-II: PROTECTION OF BIO-ORGANIC MOLECULES BY MINERALS AGAINST RADIATION EFFECTS

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Mixtures of minerals and bioorganic compounds were irradiated by UV and gamma radiation. UV irradiation was performed in a Martian Simulation Chamber. The penetration depth of UV light into soil is about 1 mm depending on the particle size of the mineral. The same mixtures were irradiated by gamma radiation from a Co-60 source. Gamma irradiation was performed directly onto mixtures, and mixtures placed under 5 cm thick “Martian Garden”. Following the radiation, organics were extracted from irradiated mineral-organic mixtures and analyzed to see and compare the extent of mineral protection. Results demonstrated that minerals protect the organic molecules from the effects of UV and gamma radiation, as was first suggested by Bernal.

DEVELOPMENT OF MARTIAN REGOLITH SIMULANTS FOR EXPLORATION OF *IN SITU* RESOURCE AVAILABILITY AND POTENTIAL: PHYLLOSILICATES AND SULFATES ON MARS

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Data obtained from Mars Global Surveyor (MGS) and Mars Reconnaissance Orbiter (MRO) has vastly increased knowledge of Martian surface mineralogy [1-3]. The nature and extent of aqueous and other altered phases such as phyllosilicates, sulfates, and iron oxyhydroxides is better established. As such, the need for regolith simulants that reflect the heterogeneity of the Martian surface chemically and mineralogically has come into play [4-6]. The goal of this study was to create multiple simulants that better represent the variability of Martian regolith based on current understanding of the chemistry and mineralogy of certain deposit types found on Mars [1]. These simulants will be used to explore the potential fertility and toxicity of *in situ* Martian regolith.

To produce simulants, a combination of synthetic and field-collected samples have been obtained. These samples will be combined to form five different simulants assemblages. These include: 1. Basalt-type (unaltered), 2. Sulfate-type 3. Phyllosilicate I-type, 4. Phyllosilicate II-type, and 5. Carbonate-type. The five simulants broadly represent various geologic provinces on Mars [1]. These components will be combined in appropriate concentrations based on data from Mars Curiosity Rover, MRO and MGS missions [1-3], and Earth-based Martian analogs [7-9] (Table 1). The resulting simulant mineral assemblages will be treated to eliminate organic matter and sterilized. The simulants will be further examined using X-ray diffraction Rietveld analysis (XRD), X-ray Fluorescence (XRF), and imaging spectroscopy. This analysis will help to refine simulants and ensure that they adequately represent current understanding of Martian chemistry and mineralogy for the intended application.

The goal of this study is to create multiple simulants that will be used for future work in exploring the use of Martian regolith as an *in situ* material for planetary exploration. The most relevant and reproducible simulants will be used in plant growth experiments that seek to address some of the challenges faced in supporting a manned mission to Mars. The ultimate goal being to use simulants to address issues of toxicity and fertility of Martian regolith and understanding potential for past habitable environments on Mars.

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INTEGRATIVE RESERVOIR CHARACTERIZATION FOR CHEMICAL ENHANCED OIL RECOVERY, TAR SPRINGS FORMATION, ILLINOIS BASIN, UNITED STATES OF AMERICA

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Hydrocarbon reservoirs within the Illinois basin that have been extensively developed will soon reach the end of their production history without technological intervention. Although many of these mature fields have been waterflooded for decades and show a significant production decline, substantial amounts of residual oil remain in place making them ideal candidates for enhanced oil recovery (EOR) techniques. This research focuses on producing fields in southern Indiana that are being considered as a pilot study for surfactant-polymer chemical EOR. Using an integrated methodology that includes field geology, sedimentology/petrology, quantitative powder X-ray diffraction (XRD), infrared spectroscopy (FTIR), thermal analysis (TGA-EGA), and scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDX), we present an integrated approach to reservoir characterization of the Tar Springs Formation, one of several key upper Mississippian producing horizons within the basin. The characterization approach provided here explores reservoir architecture, connectivity, and petrophysical parameters as they relate to the mineralogy and chemistry of the reservoir.

Results show the pilot study reservoir is compartmentalized by five lithofacies each characterized by distinct physical and chemical properties: F1—very fine to fine grained horizontally stratified sandstone; F2—very fine to fine grained flaser bedded sandstone; F3—wavy bedded sandstone with very fine-grained sandstone and mudstone interlayers; F4—lenticular bedded silty mudstone; and F5—calcite cemented sandstone. Combined petrophysical and geochemical results suggest horizontally stratified and flaser bedded sandstone facies represent the best reservoir injection targets. Together, lithofacies F1 and F2 contain higher average porosity and permeability values, possess significantly higher quartz sand-clay ratios, and yield the highest amounts of residual oil. Wavy bedded, lenticular bedded, and calcite-cemented sandstone facies have the poorest reservoir quality that can be attributed to enhanced clay content that impairs porosity, permeability, and has led to diminished oil saturations. Major clay components of the Tar Springs Formation are distributed throughout the reservoir in varying proportions based on lithofacies and can influence not only flow parameters but interact with injected chemicals to alter fluid circulation and sweep efficiencies. This integrated approach to reservoir characterization has important implications for providing a framework for decision making concerning the future of other developed reservoirs that are considered close to abandonment in mature basins.

ANISOTROPIC FEATURES OF WATER DIFFUSION IN CLAY POROUS MEDIA: A COMBINATION OF COMPUTATIONAL AND EXPERIMENTAL METHODS

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Due to the strongly anisometric shape of clay particles, their mutual arrangement in compacted porous media is most often associated with the development of anisotropy in both particle orientation [1] and inter-particle pore network [2]. Such anisotropy in particle orientation is also enhanced during burial diagenesis and has significant impact on the directional dependence of preferential fluid diffusion [3].

In order to get additional insights into the role played by particle orientation on orientational dependence of water diffusion, several clay porous media were prepared using reference kaolinite KGa-2. These samples display similar porosity but contrasted anisotropy degree. Particle orientation was measured by wide-angle X-ray scattering after resin impregnation of the samples whereas experimental measurement of the water self-diffusion tensor was obtained by exploiting 1H Nuclear Magnetic Resonance Pulsed Gradient Spin Echo attenuation [4].

An algorithm, similar to the one proposed by Coelho et al. [5], was used to mimic the three-dimensional organization of clay porous media for particles having elliptic flat disk morphology [6]. Different porous media were generated at constant distribution in particle geometry but different anisotropy degrees, ranging from almost isotropic to very anisotropic orientation of particles. The obtained virtual porous media were used to perform Brownian Dynamics simulations, based on the consideration of water probes diffusion in interparticle porosity. The obtained results regarding water diffusion coefficients are found to be in fair agreement with experimental data. This allows getting additional insights onto the role played by particle organization on the overall macroscopic diffusion of water and on the associated self-diffusion tensor.

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EXPANDED USE OF CLAYS IN MEDICINE LINKED TO MODERN CHARACTERIZATION METHODS AND *IN VITRO* AND *IN VIVO* INVESTIGATIONS

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Clay minerals are used in three, broadly overlapping areas related to human health. There is a long history (more than 3000 years) of clay mineral intake for the relief of gastro/intestinal distress and related maladies. In “folk medicine” clays are ingested directly by humans and other animals (geophagy) with mostly untested consequences. Topical use in cosmetics and pelotherapy facilitate transfer of desirable or potentially harmful chemicals in the clay through the skin. Nanoclay minerals, especially organo-smectites and -kaolinite, are becoming widespread in the pharmaceutical industry as drug delivery systems. Some clay materials have the potential to kill pathogenic bacteria. Clays owe their reported efficacy to the high adsorption and absorption characteristics, cation exchange capacity, high surface area, low solubility, reactivity towards acids, low hardness and very small particle sizes of the clay-sized phyllosilicates in the materials.

Many recent investigations rely on sophisticated characteristics revealed by X-ray powder diffraction, scanning transmission X-ray microscopy, nano secondary ion mass spectrometry, scanning transmission electron microscopy-electron energy loss spectroscopy, near edge X-ray absorption fine structure, neutron activation analysis, alpha and gamma ray spectroscopy, size exclusion chromatography, high pressure liquid chromatography, infrared spectroscopy, confocal microscopy, and other analytical instruments and procedures to obtain information on clay composition, reaction products, and spatial distribution of components. Other investigators assessed potentially harmful health effects of clay minerals with modifications of standard *in vivo* and *in vitro* toxicological procedures. The *in vivo* results are difficult to extrapolate because the surrogates may not have the same behavior as humans. Test solutions and out of body differences in potentially toxic reactions further complicate *in vitro* interpretations. In general, experimental results suffer from a paucity of mineralogical data and lack of specificity of cell data. Many results are anecdotal and fail to establish causality. Operational procedures must be evaluated critically for each biosystem and clay type.

New toxicology protocols for and the availability of clay minerals with unique physical, chemical, and physical chemical properties support the contention that applications in the drug and other industries will continue to grow.

THE INFLUENCE OF CLAYS ON HUMAN HEALTH: A MEDICAL GEOLOGY PERSPECTIVE

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Clay is unique especially from the perspective of medical geology, that is, the impacts of geologic materials and geologic processes on animal and human health. Clay is the only natural material that can impact human health through all routes of exposure: ingestion, inhalation, and dermal contact. Moreover, these impacts can be harmful as well as beneficial. Ingestion of clay, a form of geophagy, has been practiced for millennia and is still widely practiced today. Humanoids have been ingesting clay for at least two million years to ease indigestion and counteract poisons. There may be some additional benefits of eating clays such as providing some nutrients but these benefits are far outweighed by the likely negative consequences such as tissue abrasion, intestinal blockage, anemia, exposure to pathogens and toxic trace elements, and potassium overdose. Inhalation of airborne minerals including clays has impacted the health of millions. In the 1930's thousands of people living in the Dust Bowl in the U.S. southwest inhaled copious amounts of clay contributing to deadly 'dust pneumonia.' Using clay as a poultice to stem bleeding and cure certain skin ailments is an age-old practice that still has many adherents. A classic recent example is the use of certain clays to cure Buruli ulcer. However, walking barefoot on clays in certain volcanic soils can result in non-filimental podiconiosis or elephantitis. The absence of clays in soils can have serious health consequences. In South Africa clay-poor soils yield crops lacking in essential nutrients and may be the principal cause of Misileni joint disease. Clearly, a detailed knowledge of the clays in the environment can have significant benefits to human health and wellbeing.

SPECTRAL AND OPTICAL PROPERTIES OF $\text{Fe}^{3+}/\text{Fe}^{2+}$, MG, AL SMECTITES TO IMPROVE PLANETARY REMOTE SENSING

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Secondary minerals produced by aqueous alteration of crustal rocks provide critical clues about the geochemistry, oxidation state, and extent of aqueous activity in the environment in which the secondary minerals formed. Therefore, alteration minerals can be key indicators of the geological history and habitability of objects throughout the solar system, provided that such minerals can be reliably detected and adequately characterized on other planetary bodies. Due to their ubiquity and geochemical sensitivity to their formation environment, Fe-, Mg-, and Al-bearing smectites are therefore key target materials in planetary exploration. Despite their importance in planetary science and many studies about Martian clays, and meteorites, smectite clays have not been comprehensively characterized as standards to allow for accurate and nuanced remote sensing based identification and quantification. Smectite composition can vary nearly continuously between Fe-, Mg-, and Al-rich end members by octahedral cation substitution, along with Al substitution for Si in the tetrahedral layer to balance charge (Grauby et al. 1994; Andrieux and Petit 2010). The composition and iron oxidation state can be indicative of the conditions in which the clay minerals formed (Catalano 2013).

The suite of smectite clays commonly used as standards for comparison with planetary data (IR, XRD, UV) only represent a handful of end-member type compositions. The ability to determine the conditions in which a smectite mineral formed, including the aqueous geochemistry and redox state, and by proxy the potential for habitability, is presently limited by the ability to accurately identify and measure smectite composition, mineral assemblages and abundance. Detailed characterization of the full compositional range of smectite minerals using techniques analogous to those employed in planetary exploration will help improve those limits. We are synthesizing a suite of mixed Fe/Mg smectites that represent intermediate cation compositions and both ferric and ferrous iron. Samples are characterized using X-ray diffraction to confirm mineral purity, and the spectral reflectance is measured using an ASD field spectrometer (0.4-2.5 μm) and a Nicolet FTIR spectrometer (1.5-45 μm). Reflectance spectral responses are being collated into spectral libraries for use by the planetary science community. Further, the real and imaginary indices of reflection, necessary to enable quantitative abundance modeling from surface reflectance measurements, are numerically derived from the laboratory spectral measurements. Finally, these samples are also being characterized with UV Raman (428 nm) and Green Raman (535 nm) to provide library Raman spectra for forthcoming datasets from the Mars2020 rover SHERLOC and SuperCam instruments.

HIGH-RESOLUTION PORE NETWORK AND MINERALOGICAL MODELING OF SEALING SHALES AT THE ILLINOIS BASIN–DECATUR PROJECT

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Shales and mudstones act as seals, baffles, and flow barriers for hydrocarbon reservoirs, natural gas storage sites, and carbon dioxide (CO₂) storage complexes. Their low permeability and high capillary entry pressure are critical to the retention and vertical migration of fluids in individual reservoirs and the hydrodynamics of entire sedimentary basins. One fluid of particular interest is supercritical CO₂ that can be injected into geologic reservoirs to mitigate atmospheric emissions from industrial activity. At the Illinois Basin–Decatur Project (IBDP), CO₂ is injected and stored in the Cambrian-age Mt. Simon Sandstone at a depth of approximately 2100 m. Three laterally continuous shale formations are considered major seals within the storage complex including the Cambrian-age Eau Claire directly overlying the reservoir, the Ordovician-age Maquoketa, and the Devonian-age New Albany. Furthermore, internal mudstones within the reservoir itself may act as baffles inhibiting the upward migration of CO₂. Using focused ion beam scanning electron microscopy (FIB-SEM), mercury intrusion porosimetry (MIP), x-ray diffraction (XRD) spectroscopy, and quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN), we investigated the nanoscopic pore networks and mineralogy of the major sealing shales at the IBDP, as well as one mudstone interlayered between two reservoir injection zones to evaluate seal quality.

Results show that porosity and pore size generally decrease with depth. The mudstone within the reservoir has the lowest porosity, smallest pore sizes, and highest entry pressures of all the samples investigated. This mudstone is predominantly composed of illite (mica) and has a high content of hematite. The dense layering and lack of mineral heterogeneity in this mudstone is reflected by the low porosity and high entry pressures relative to the other samples examined. The primary reservoir seal, the Eau Claire Shale, is an illite/smectite-rich black shale and has comparable pore sizes and entry pressures to the shallowest seal, the organic-rich New Albany Shale. The Maquoketa has the highest volume of pore space and a predominant dolomitic component compared with the other clay-rich samples.

Although FIB-SEM underestimates pore sizes below its resolution, it reveals the characteristics of pores that are ineffectively identified and evaluated by MIP. FIB-SEM shows that mudstone baffles in the Mt. Simon reservoir lack a nanopore network and offers the greatest immediate sealing capability. The three shales at IBDP, however, are regionally thick and laterally continuous and therefore serve as more secure, long-term seals for retaining CO₂. Although all three shales are considered impermeable with negligible permeability (<0.01 mD), data indicates that the pore size, distribution, and connectivity within the shales are highly variable and indicate that the Maquoketa (a secondary seal) has the poorest sealing quality. With low pore connectivity, the primary (Eau Claire) and other secondary (New Albany) reservoir seals are the highest quality.

HIGHLY TUNABLE LIQUID CRYSTALLINE ASSEMBLIES OF SUPERPARAMAGNETIC ATTAPULGITE@ Fe_3O_4 NANORODS

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We report here the first synthesis of the uniform dispersed nanorods, which contains nonmagnetic nanorods attapulgite attached with magnetic nanoparticles Fe_3O_4 . These composite nanorods assemble into magnetically responsive liquid crystal with yellow Bragg reflections under an external magnetic field. The optical properties of the obtained liquid crystal can be controlled by the strength and the direction of the magnetic field as well as the concentration of attapulgite@ Fe_3O_4 . We demonstrate the use of these composite nanorods to fabricate display and photonic devices.

GENERALIZED (VIBRATIONAL) DENSITY OF STATES OF WATER IN SODIUM MONTMORILLONITE

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Generalized density of states (GDOS) spectra, as determined by neutron scattering, can probe clay-water interactions involving motions of H atoms that are usually inaccessible to infrared and Raman spectroscopies. Here we discuss results obtained using the thermal neutron triple-axis spectrometer TAIPAN, at the OPAL reactor run by the Australian Nuclear Science and Technology Organisation to assess the collective translational and librational motions of surface-bound water in hydrated sodium (Na) montmorillonite. The instrument was used a resolution of 0.5 meV (4 cm^{-1}) by employing a Cu200 double-focused monochromator spanning an energy range of 14–160 meV ($64\text{--}564\text{ cm}^{-1}$). Samples were pre-hydrated (several weeks prior to analysis) to 25, 75 and 170 wt% water content and presented as oriented film cylinders (providing a powder spectrum) covering an Al stub. Measurements were conducted at -253°C (20°K). Oven dried (OD) Na-montmorillonite was used as a reference that was subtracted from hydrated spectra to produce water GDOS spectra.

Fig. 1 shows resulting GDOS spectra. Second derivatives indicated the presence three or more components within each of the four main water bands observed between 70 and 350 cm^{-1} in the 170-OD spectrum, probably related to symmetric and asymmetric vibrations. Density profiles and power spectra for water confined within Na-montmorillonite interlayers calculated using Molecular Dynamics support this interpretation. The 75-OD water spectrum retained most of the same bands as the 170-OD spectrum, but nearly all of these features were unobserved in the 25-OD water spectrum which showed only two broad bands (near 110 and 440 cm^{-1}) with weak features near 145 and 330 cm^{-1} . These latter features have in the past been assigned to, respectively, water torsion ($\tau(\text{HOH})$) and deformation ($\delta(\text{HOH})$) of surface adsorbed water whereas the 235 cm^{-1} band in the wetter samples has previously been assigned to water which is H-bonded to basal oxygen interlayer surface. Given the greater intensity of these features with wetter samples these assignments are questionable. The GDOS data presented here on hydrated Na-montmorillonite thus infer that previous assignments of interlayer water torsion, deformation and H-bonding surface waters may require revision.

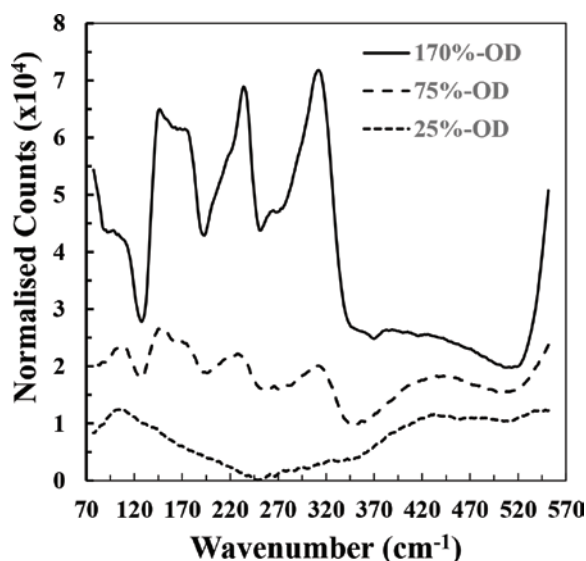


Figure 1. GDOS spectra (smoothed and subtracted) of adsorbed interlayer water in hydrated Na-montmorillonite.

FORMATION OF CLAY MINERALS ON MARS: INSIGHTS FROM LONG-TERM EXPERIMENTAL WEATHERING OF OLIVINE

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Laboratory experiments are useful to constrain the environmental parameters that have allowed the formation of the ancient hydrous mineralogical assemblages observed at the surface of Mars, which are dominated by ferric smectites. Weathering under a dense CO₂ atmosphere on early Mars is a process frequently invoked to explain their formation, but has proven difficult to test in the laboratory due to low reaction rates. Here, we present long-term weathering experiments under CO₂ and ambient air (470 days, at 45°C and 1 bar) of forsteritic olivine specially designed to increase as much as possible the amount of reaction products and thus allow their detailed mineralogical, petrological and chemical characterization by FTIR, SEM and TEM.

The formation of a Mg/Fe³⁺-rich smectite is clearly identified both under ambient air and under CO₂. Its presence is evidenced by IR data, with the appearance of a typical asymmetrical band at 2.31 μm with a shoulder at 2.29 μm attributed to Mg-OH vibrations in smectite, with a masked (Fe³⁺)₂-OH contribution at 2.29 μm for the CO₂ smectite. Interestingly, a similar spectral signature attributed to a smectite is reported from orbital IR data of Mars at Nili Fossae, a region where olivine is particularly abundant (e.g., Gaudin et al., Icarus, 2011).

However, important differences are observed between CO₂ and air conditions. The smectite formed under CO₂ has an average chemical formula per half unit-cell of Si_{3.92}Al_{0.16}Fe₃+0.78Mg_{1.66}Cr_{0.01}Ni_{0.06}K_{0.04}Ca_{0.04}.O₁₀(OH)₂. It is thus intermediate between a trioctahedral Mg-rich saponite and a dioctahedral ferric smectite. It is also clearly enriched in Fe compared its counterpart formed under ambient air, which has an average chemical formula per half unit-cell of Si_{3.68}Al_{0.12}Fe₃+0.37Mg_{2.61}Cr_{0.01}Ni_{0.02}K_{0.04}Ca_{0.25}.O₁₀(OH)₂. This result demonstrates that the enrichment in Fe observed for Martian smectites is to be expected if they were formed by low-temperature weathering under a dense CO₂ atmosphere. Another difference is the nature of the accompanying phases, which includes amorphous silica (in the form of opal spheres 10 to 100 nm in diameter) and Mg-carbonates under CO₂, but are limited to rare kaolinite under ambient air. The observation of kaolinite particles under air and the significant amount of Al measured in smectites under both atmospheres, despite the Al-poor nature of the initial material, shows that this element is easily concentrated by low-temperature weathering processes. At a larger scale, this concentration mechanism could be responsible for the formation of Al-rich upper horizons, as frequently observed on Mars (Mangold et al., this meeting).

CLAY-RICH FRACTURE-FILLING CEMENTS IN YELLOWKNIFE BAY, GALE CRATER, MARS: RECOGNIZING CLAY-RICH ROCKS WITH LASER-INDUCED BREAKDOWN SPECTROSCOPY

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During its traverse of Gale Crater's floor and ascent of Aeolis Mons, the Mars Science Laboratory (MSL) has documented numerous examples of clay minerals. A particularly interesting example of a clay-rich material was detected when the rover investigated a series of narrow (~2.7 mm width), curvilinear ridges that extend at least several centimeters in length. The ridges weathered in a raised relief and were distinctly characterized by the presence of internal banding that contoured the trend of the ridge. The raised ridges are interpreted as early diagenetic cracks that formed in the partly lithified Sheepbed mudstone; the cracks were subsequently infilled with one or more generations of cement that isopachously lined the margins. The various layers of cement likely provide a record of temporal changes in fluid composition and/or depositional conditions.

The ChemCam instrument revealed that the average major element composition of the raised ridges is close to that of a Mg- and Fe-rich trioctahedral smectite and is broadly similar to the alteration minerals previously identified in the Sheepbed mudstone by X-ray diffraction. These raised ridges are likely the most clay-rich features that have been analyzed on Mars by the ChemCam instrument thus far. As such, they represent a unique opportunity to better understand the spectral signatures of clay-rich targets as measured by laser-induced breakdown spectroscopy (LIBS). This is particularly pertinent as MSL is approaching the clay-bearing unit, which will be the first region explored by the rover that bears a spatially expansive orbital clay mineral signature.

Here, we provide a review of the elemental geochemistry of the raised ridges in Yellowknife Bay, provide an updated dataset based on the recent major-element recalibration of the ChemCam instrument, and discuss current efforts to establish robust strategies for recognizing and interpreting clay-rich targets in remotely-sensed LIBS data. We place particular emphasis on the observed co-occurrence of elevated Mg and Li within the raised ridges as Li adsorption on secondary smectites is a very efficient process during water-rock interactions and may serve as a reliable indicator of clay mineralogy. We are also actively working on the calibration of H in the ChemCam analyses to characterize the hydration state of these smectite clay minerals.

ISOTOPE OF THE SHEETS: TEMPERATURES, TIMING AND TRACING OF FLUIDS INVOLVED IN BENTONITE FORMATION

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Stable and radiogenic isotopes may yield useful and in part unique information on the formation temperature, timing and even types of fluids involved in clay formation in a variety of geological settings. This presentation will explore the use of stable hydrogen, oxygen, boron and radiogenic strontium isotopes in the genesis of bentonite deposits.

The equilibrium fractionation factors between smectites and water for oxygen and hydrogen isotopes are critically discussed and a new model for oxygen isotope fractionation for chemically complex 2:1 sheet silicates based on exchange vectors will be presented. The oxygen and hydrogen isotope compositions of smectites from several bentonite deposits suggest that meteoric waters play an important role in their formation or possibly during a later overprint. Only few deposits experience hydrothermal conditions with temperatures exceeding 40°C. The concentrations of tetrahedral coordinated boron in smectites are considered indicators for the salinity of fluids and show large variations. Most sodium bentonites formed from the interaction of brines with volcanic glass rather than of unmodified seawater. Boron isotope data of the smectites corroborate these conclusions. A study of the strontium isotope composition of exchangeable and fixed strontium in smectites and associated pedogenic and palustrine carbonates from the Bavarian bentonites indicates that interlayer strontium has at least partly exchanged after formation with more radiogenic fluids. Most illitic components in the 0.2 µm fractions of the bentonites are of detrital origin, however one sample is free of such detrital components and yields a formation age within 4 million years after volcanic ash deposition.

LIMITATIONS OF OBSERVED FIRST ORDER RATE CONSTANTS: A CASE STUDY ON AS(III) DEPLETION BY MN OXIDES

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Arsenic (As) contamination of drinking water is a threat to public health around the world. Manganese(III/IV) (Mn) oxides play a role in controlling As fate in groundwater by sorbing As and oxidizing more mobile and more toxic As(III) to less mobile and less toxic As(V). While this redox reaction has been the subject of extensive research, results across studies are inconclusive and often contradictory. The depletion of aqueous As(III) by Mn(III/IV) oxides is biphasic, with reported first order rate constants ranging seven orders of magnitude. To demonstrate potential causes of inconsistencies between studies, two datasets from batch reactions of As(III) with δ -MnO₂ were reanalyzed. The observed first order rate constants for As depletion are time dependent and do not fit pure kinetic rate models. A single dataset yields rate constants ranging from 3.0 to 25.0 hr⁻¹ ($R^2 > 0.80$), depending on when the initial rate is cut off. These rate constants were calculated using the linearized form of the first order rate law. Not forcing this equation through the origin ($\ln(C/C_0) = 0$ at $t = 0$) removes the assumption of a kinetic fit and results in rate constants approximately 50% lower than those forced through the origin. Observed first order rate constants are valuable in obtaining relative depletion rates within a study, but there are significant limitations when generalizing across studies on oxyanion depletion in the presence of Mn oxides. To better predict depletion rates, mechanistic modeling that accounts for differences in reactivity between Mn(III) and Mn(IV) as well as the sorption and desorption of As(III), As(V), and Mn(II) is needed.

SYNTHESIS OF QUATERNARY (ZNO/TIO₂/CDS/SiC) NANO-COMPOSITES USING ADVANCED PULSED LASER ABLATION TECHNIQUE

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A rapid, clean and one step pulsed laser ablation in liquids (PLAL) method has been employed at our laboratory for the synthesis of high-purity nanocrystals of quaternary (ZnO/TiO₂/CdS/SiC) nano-composite semiconductors [1-3]. In this context, second harmonic of Nd:YAG nanosecond pulsed laser was applied as an irradiation source for pulsed laser ablation of mixture of ZnO, TiO₂, CdS and SiC microstructures. Various analytical techniques were applied for the characterization of these synthesized nanocomposites. The morphology of these nanocomposites was investigated using High Resolution Transmission Electron Microscope (HRTEM), the crystalline structure was studied using XRD and optical properties were explored using UV-Vis Spectrophotometry, FTIR and Spectrofluorimetry. The XRD, HRTEM, optical absorption of the synthesized nanocomposites, reveal that the synthesized nanocomposites possesses much better characteristics as compared with the one prepared via complicated wet chemical methods.. The main aim of addition of ZnO in TiO₂ is to reduce the electron-hole recombination in the TiO₂ while CdS was used to increase the light harvesting efficiency of TiO₂ in the visible spectral region. The morphology of the hetero-structures acquired shows TiO₂/CdS/SiC was encased by ZnO catalyst tailoring it to have ZnO dominant optical and structural properties. The oxidation states of the elements in the nano-composite and presence of SiC and CdS was ascertained by an advanced technique like X-ray photoelectron spectroscopy.

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COMPARING ILLITIZATION IN LOWER PALEOZOIC SHALES AND SANDSTONES OF THE ILLINOIS BASIN: IMPLICATIONS FOR CARBON DIOXIDE STORAGE

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Diagenetic illite in shales and sandstones is often different based on morphology, illite polytypes, amount of smectitic interlayers, chemistry, and age. Despite these differences, the mechanism controlling the diverse crystal chemistry remains unclear. Permeability, mineralogy, chemistry, and fluid-rock ratio have been suggested to play a role. The influence on the storage properties of the different lithologies needs to be better constrained. In the course of the Illinois Basin Decatur Project (IBDP), 1 million metric tons of CO₂ were injected into the Cambrian Lower Mt. Simon Sandstone (LMSS). The reservoir is sealed by a number of shales (Devonian New Albany, Ordovician Maquoketa and Cambrian Eau Claire) and tight barriers such as the Middle Mt. Simon Sandstone. Illite is the most abundant clay mineral in the reservoir and sealing units. At times we find varying amounts of chlorite, kaolinite, and dickite.

Samples were taken from cored material of the wells CCS 1; VW 1 and GM 2, located at the IBDP sequestration site near Decatur, Illinois, USA, from depths ranging from 2157 ft (657 m) to 7028 ft (2146 m). XRD analysis was performed on bulk material and separated grain size fractions. The relative abundance of the illite polytypes *2M1*, *1M* and *1Md* were identified and quantified where possible. K-Ar age dating of three grain size fractions (2–0.6 µm; 0.2–0.6 µm; < 0.2 µm) was performed. The New Albany and Maquoketa shales contain the highest proportions of detrital *2M1* illite. Illite in the Lower Mt. Simon Sandstone was identified as solely diagenetic *1M* and *1Md* illite and contains the highest proportions of smectite in the illite/smectite mixed-layered minerals.

K-Ar ages, illite polytypes and SEM morphologies of diagenetic illite from these cores suggest multiple episodes of illitization from 360 to 220 Ma, spanning the same age range of ages within and surrounding the Illinois Basin, summarized in Grathoff et al. 2001 (GSA Bull. V113 no.8 1092-1104). Overall the ages are not what are expected in a typical burial diagenesis dominated system, where the ages should follow a depth trend, nor a pure fluid flow dominated system, where the youngest ages should be in the highly permeable sandstones. The youngest illites (220–250 Ma) are found in low permeable sandstones of the Middle Mt. Simon and of the Cambrian Argenta formation both surrounding the highly permeable Lower Mt. Simon sandstones (290 to 330 Ma).

MOLECULAR MODELING OF VIBRATIONAL AND ADSORPTION PROPERTIES AT CLAY EDGES

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Force field (FF) modeling of clay interfaces has been significantly enhanced by the extension of the ClayFF parameter set to include hydroxylated edge sites. Clay edges present several challenges for FF modeling compared to siloxane surfaces. First, the pH-dependent stoichiometry of edge hydroxyl groups requires FF parameterization for singly- or doubly-protonated hydroxyl groups as well as deprotonated sites. Second, the asymmetry of clay edges precludes the use of standard three-dimensional periodic boundary conditions (PBCs) commonly used to model clay interlayers. Modeling the interface of a fluid at a clay edge requires two-dimensional PBCs or the creation of an artificial nanopore between two edge surfaces so that three-dimensional PBCs can be used. Here we present results for two applications that address these challenges: (1) vibrational properties of edge hydroxyl groups in pyrophyllite; and (2) adsorption of organic molecules at kaolinite edges under different pH conditions.

Vibrational modes of edge hydroxyl groups are difficult or impossible to isolate from those in the interior or even adsorbed water. However, deuteration of edge hydroxyl groups by exposure of clay samples to D₂O vapor and subsequent dissociative D₂O adsorption could enable the measurement of vibrational modes of OD groups due to a mass shift from deuterium atoms. Using both quantum and FF methods, we have modeled the infrared spectra of edge OH and OD groups of pyrophyllite for comparison with infrared spectra. In another application, we used molecular dynamics simulations to investigate trends in the adsorption of a representative crude oil molecule at hydrated kaolinite edges with either charge-neutral or negatively-charged surfaces. Comparisons were also made by varying the aqueous cation composition from all monovalent to all divalent cations to test observed trends in low-salinity water flooding experiments.

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WHAT POLARIZED ATR-FTIR SPECTROSCOPY CAN TELL US ABOUT CLAY MINERALS?

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Molecular or particle orientations play a critical role in many aspects of material and environmental science. Fluids diffusion, liquid crystal display, polymeric fibers are just a few examples where the orientation determines the macroscopic properties of the materials. Vibrational spectroscopies are some of the few molecular level probes that are inherently orientation sensitive. This arises from the directional dependence of photon propagation that can be polarised in the plane normal to this direction.

Infrared spectra of minerals are the result of complex interplay between their intrinsic vibrational properties and the micro-structure and experimental geometry. While transmission measurements requires generally the complicated preparation of homogeneous KBr pellet, Attenuated Total Reflectance (ATR) technique gives similarly quasi-absorbance spectra with almost no preparation. When thin mineral film are deposited on the ATR crystal, optical theory is particularly relevant to discriminate optical effects (changes in refraction indexes) from material properties (orientational or textural effects). Combining with a polarizer allowing the selection of the orientation of the electric components of the electromagnetic radiation, numerous macroscopic and microscopic properties (oscillator strengths, anisotropic dielectric functions and refractive indexes, isotropic dichroism ...) can be obtained, providing a deep understanding on the origin of the recorded reflectance signal.

From the experimental reflectance spectra recorded on uniaxially oriented thin films (i.e. 10 nm) of selected clay minerals with two orthogonal polarization directions, the anisotropic macroscopic complex dielectric functions can be extracted allowing the determination of longitudinal and transversal optical modes that can be further interpreted based on oscillators dispersion theory. Subsequently, simple arithmetic equations are used to calculate the anisotropic complex refractive index to obtain the functional form of the dependence of the optical constants on wavenumbers. Next, the propagation of the radiation through the clay sample is developed offering a theoretical description of the optical properties of the materials. This step relates the optical constants to the spectroscopic observables, or, in other words, the molecular vibrations to the reflectance spectra. Since the system is optically described, the mean-squared electric field amplitudes in the laboratory frame are estimated to rationalize the orientation of clay platelets over the ATR crystal surface based on the experimental measurements of the linear dichroism.

After a short theoretical background, this presentation will show how anisotropic properties of vibrational modes can be extracted for a wide varieties of clay minerals, thus highlighting that ATR spectroscopy can provide valuable information generally hampered using other more conventional FTIR methods.

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THE OXYGEN ISOTOPE COMPOSITION OF SEAWATER THROUGH TIME: A PERSPECTIVE FROM IRON OXIDES AND CLAYS

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The isotopic composition of oxygen in seawater ($\delta^{18}\text{O}$) is a fundamental property of Earth's oceans, key to paleoclimate reconstructions and to our understanding of the origin of water on Earth, the water-rock reactions that govern seawater chemistry, and the conditions under which life emerged. Despite more than five decades of research, the coupled long-term geologic history of seawater temperature and $\delta^{18}\text{O}$ remains a topic of intense debate. The problem exists because the $\delta^{18}\text{O}$ values measured in marine precipitates (e.g., carbonates, cherts) reflect both their temperature of formation and the $\delta^{18}\text{O}$ of the seawater from which they formed. This duality has prevented a unique interpretation of a long-term secular increase in $\delta^{18}\text{O}$ values recorded in marine sedimentary rocks, which can be used to infer either much warmer ($>70^\circ\text{C}$) early oceans, much more ^{18}O -depleted seawater, or a combination of the two.

We addressed this problem with a new record of $\delta^{18}\text{O}$ in iron oxides formed in shallow marine environments through time. The advantages of iron oxides over the existing mineral repositories are that *i*) iron oxide $\delta^{18}\text{O}$ values are resistant to resetting under most conditions, and *ii*) oxide-water oxygen isotope fractionation is very weakly dependent on temperature. Consequently, any variation in well-preserved iron oxide $\delta^{18}\text{O}$ values should reflect mostly variation in the $\delta^{18}\text{O}$ values of the oxides' parent solution (seawater). The new record suggests that the long-term secular increase observed in the $\delta^{18}\text{O}$ values of various marine precipitates is due to an enrichment of seawater in ^{18}O rather than a cooling of the oceans over Earth history. The record suggests that Earth's climate has been mostly warm and stable over the past 2 billion years, implying the existence of efficient climate stabilization feedbacks. A possible driver of the long-term increase in seawater $\delta^{18}\text{O}$ values is a decrease in oceanic plate lifetime due to declining production of heat in the mantle over Earth history.

We are in the process of generating a comparable record in marine iron-bearing clays, such as glauconite and berthierine. Although the temperature dependence of clay-water oxygen isotope fractionation is stronger than that of iron oxides, ferrous iron-bearing clays serve as a built-in indicator for the absence of post-depositional interaction with oxidizing fluids. Together, the iron oxide and clay $\delta^{18}\text{O}$ records provide a robust history of seawater $\delta^{18}\text{O}$, thereby resolving a long-standing debate and providing new constraints on the long-term evolution of seawater chemistry and climate.

CONVERSION OF 1:1 CLAY MINERALS TO SMECTITE UNDER HYDROTHERMAL CONDITION: IMPLICATION FOR SOLID STATE TRANSFORMATION

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Understanding clay mineral transformation is of fundamental importance to unraveling geological and environmental processes, and to better understanding unique structure and property of phyllosilicates. To date, two pathways have been identified, i.e., the transformation among 2:1 type clay minerals (e.g., illitization of smectite) and from 2:1 type to 1:1 type (e.g., kaolinization of smectite). However, the transformation of 1:1 to 2:1 type has rarely been reported. In our recent study, hydrothermal experiments were conducted to investigate the possibility of the transformation of 1:1 type clay minerals into 2:1 ones, the effect of precursor minerals' structure on the transformation and the transformation mechanism involved.

The obtained products were characterized by XRD, TG, ²⁷Al and ²⁹Si MAS NMR, and HRTEM. XRD patterns of the hydrothermal products displayed characteristic basal spacing of smectite group minerals at 1.2–1.3 nm. This is consistent with HRTEM observations, in which clay layers with a thickness of 1.2–1.4 nm were found in all hydrothermal products and the chemical composition determined by EDS analysis is close to that of smectite. The consumption of surface OH in precursor minerals during the transformation led to a dramatic decrease of mass loss of dehydroxylation in TG curves. These results demonstrated that 1:1 type clay minerals can be converted to 2:1 smectite under hydrothermal condition. XRD patterns also indicated that the transformation of halloysite and kaolinite was easier than that of serpentine. The difficulty for the transformation of serpentine to smectite may be due to the lack of enough available Al in the reaction system, in which the substitution of Al³⁺ for Si⁴⁺ in the neo-formed tetrahedral sheet is critical to control the size matching between the neo-formed tetrahedral sheet and octahedral sheet in starting minerals. HRTEM images showed that the conversion of kaolinite and lizardite to smectite was accompanied by exfoliation. This led to a prominent decrease of the particle size in the hydrothermal products and the number of phyllosilicate layers contained therein. However, the transformation could only take place at the edges of an antigorite layer rather than the whole one, due to the strong Si-O covalent bonds connecting the neighboring layers in antigorite. The inheritance of such Si-O covalent bonds also resulted in non-swelling property of the neo-formed smectite transformed from antigorite. Two pathways were proposed for the transformation of 1:1 type clay minerals into smectite, i.e., conversion of one 1:1 type layer to one smectite layer (2:1 type) via attachment of Si-O tetrahedra onto the octahedral sheet surface of the starting minerals and two adjacent 1:1 type layers merging into one smectite layer. In the case of the latter, dissolution of octahedra and inversion of tetrahedral sheets took place during the transformation. Besides these two dominant pathways, precipitation and epitaxial growth of smectite were also observed in the cases of lizardite and antigorite, respectively. The present study suggests that solid state transformation is the main mechanism for conversion of 1:1 type clay minerals to smectite. Such transformation of 1:1 clay minerals to 2:1 ones could be the third pathway for the transformation of clay minerals in nature, and can well explain the formation of “polar layer” in mixed-layer phyllosilicates. These findings are of high importance for better understanding the transformation among clay minerals and unique structure of mixed-layer phyllosilicates.

NANOSCALE STRUCTURAL COMPLEXITY AND REACTIVITY OF SOIL MINERAL ASSEMBLAGES

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Soil solids comprise complex assemblages of multiple minerals, organic matter, non-crystalline solids, and biota in heterogeneous spatial arrangements. Knowledge about chemical speciation and reactivity of environmental contaminants and nutrients in soil matrices is largely derived from studies of well-defined model analogues of soil particles, such as synthesized or geological minerals. A lack of molecular-scale spatial resolution of many spectroscopic techniques limits the transferability of quantitative information about chemical speciation from model systems directly to soils. To gain insights on this knowledge gap between model systems and soils, our objective was to characterize nanoscale structural and compositional diversity of soil particles, and their reactivity with arsenate. Clay particles isolated from kaolinitic and smectitic Ultisols, Wyoming montmorillonite, and synthetic Al-substituted iron oxides were analyzed for particle morphology, crystallinity, elemental composition, and (in some cases) atomic structure using aberration-corrected scanning transmission electron microscopy (STEM) imaging (with 0.8-angstrom spatial resolution) and energy dispersive X-ray spectroscopy. The kaolinitic Ultisol was reacted with 300 mmol As(V)/kg at pH 5 to determine the spatial association of arsenic with various soil particles. Soil particles varied in crystallinity and compositional heterogeneity, as expected. Atomic structure could be imaged on highly ordered soil nanoparticles, which were probably iron oxides. Similarly, imaging of synthesized goethite (α -FeOOH) particles showed a well-defined atomic structure, whereas Al-substituted goethite (22% Al) had a poorly defined atomic structure with a non-uniform spatial distributions of Fe and Al. We also found poorly ordered soil nanoparticles that were largely composed of Fe-(hydr)oxide surrounding a Ti-(hydr)oxide core. However, many soil nanoparticles appeared as more complex assemblages of varying crystallinity dominated by Si, Fe, and Al; which showed varying degrees of As(V) accumulation. In some cases, only minor amounts of As were accumulated with minimal co-localization with Fe or Al-enriched regions, whereas other particles showed co-localization of As with Fe and Al that appeared to be in (hydr) oxides. The greatest As accumulation tended to be in compositionally diverse particles containing Fe, Al, Ca, and other elements. In essence, STEM analysis revealed diverse soil particles ranging from nanoparticles with well-defined atomic structure to poorly ordered, multi-element particle assemblages. Accumulation of As with the latter soil particles indicates the challenge of defining molecular bonding mechanisms of contaminants and nutrients on soil nanoparticles.

“DIGITAL SOIL MINERALOGY”: NEW APPROACHES TO OLD PROBLEMS

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Soils are complex materials and they perform many functions relating to biomass production, environmental interactions and biodiversity. In addition to various forms of organic matter, living organisms, gases, water and solutes, most soils consist largely of minerals derived from the soils geological ‘parent materials’, along with secondary minerals such as clay minerals and iron oxides, sometimes formed by weathering other times inherited or transformed. Additionally, the suite of minerals present in any given soil may be variously distributed amongst the sand, silt and clay particle size fractions, whilst also varying widely in chemical composition, crystal structure, surface area and solubility. Thus it has long been recognised that soil minerals are intimately related, both directly and indirectly, to many of the physical, chemical and biological properties of soils which in turn govern the functions soil may perform. Given the complexity of soil, however, it has been notoriously challenging to systematise soil property/mineralogy relationships.

Conventional approaches to the assessment of soil mineralogy by X-ray diffraction (XRD), the most widely used technique, typically involve a first stage of identification of the different minerals present and a subsequent stage that seeks to quantify their relative abundance. In recent years the availability of archived digital XRD patterns obtained from soil has increased, and attempts are now being made to generate datasets containing thousands of spatially referenced XRD measurements [e.g. those collected for the National Soil Inventory of Scotland (NSIS) and the Africa Soil Information Service (AfSIS)]. Since many soil properties are closely related to soil mineralogy, such datasets in combination with computational data analysis represent unique opportunities to advance the understanding of the role of soil minerals in governing many soil properties, processes and functions.

Use of data approaches such as cluster analysis and data mining allow XRD patterns to be treated simply as digital signatures which encode information on soil mineral (peaks) and amorphous (background) components. Viewed like this, conventional expert analysis and interpretation involving the steps of mineral identification and quantification become somewhat redundant, at least in the early stages of processing large data sets. Examples of these data based approaches that may be applied to unravelling and advancing understanding of soil property–mineralogy relationships will be illustrated using the NSIS and AfSIS data sets. Additionally, approaches to high throughput conventional quantitative mineralogical analyses by pattern fitting that can be applied to large and mineralogically diverse sets of soils to extract detailed mineralogical information will also be outlined.

Together these approaches begin to define a vision for an emerging data based field of ‘digital soil mineralogy’ aimed at providing a new way to evaluate and compare the influence of minerals on soil properties and to inform the sustainable soil use and management of the future.

THE EFFECTS OF CLIMATE, ENVIRONMENT, AND DIAGENESIS ON THE SPECTRAL PROPERTIES OF VOLCANIC SOILS ON EARTH AND MARS

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Visible/near-infrared (VNIR) spectral signatures consistent with smectite and kaolinite have been observed from orbit in many regions across Mars, and large stratigraphic horizons associated with a few of these clay-bearing deposits exhibit spectral signatures that have been interpreted as evidence for reduced Fe-bearing clays. Examples of these units occur together in Gale crater, and are future targets of exploration for the Curiosity rover. One hypothesis for the origin of these clays is that they represent ancient soils or leaching profiles formed in environments with different redox conditions. To better interpret these potentially pedogenic spectral signatures observed on Mars, here we evaluate the effects of climate, redox conditions, and diagenesis on the spectral properties and mineralogy of Mars-relevant volcanic soils on Earth.

We compare VNIR reflectance spectra, thermal-infrared emission spectra, and XRD of Hawaiian basaltic soils with various precipitation rates, soil ages, and drainage conditions, to basaltic andesite paleosols from the John Day Fossil Beds, OR, and periglacial basaltic andesite soils from the Three Sisters, OR. Spectral results show the progression of smectite and/or allophane to kaolinite and then gibbsite with age in rain-dominated soils. In snow dominated climates, soils are initially dominated by silica-rich poorly crystalline phases with non-allophane compositions, which eventually mature to smectites. High abundances of poorly crystalline phases are preserved in paleosols after burial. Poorly crystalline phases are a major component of all ancient sediment samples analyzed to date with XRD in Gale crater on Mars, which may suggest weathering in cold, snow-dominated climates during the early Hesperian (~3.7 billion years ago).

Redox state of the soils during formation is also discernable after diagenesis based on iron absorptions in VNIR spectra, and in fact, reduced soils exhibit much stronger iron absorptions after diagenesis than their modern counterparts. Modern reduced soils exhibit only weak broad VNIR absorptions that we attribute to green rust or other poorly crystalline Fe(II)-bearing phases, while paleosols exhibit complex strong absorptions that we attribute to iron in crystalline clays produced during diagenesis of the poorly crystalline phases. The intensity of these absorptions in the paleosols appears to increase with the degree of saturation of the original soil, where seasonally wet paleosols exhibit markedly weaker Fe(II) absorptions than perennially saturated paleosols. The spectral signature attributed to Fe(II) in clays on Mars may be consistent with these latter analogs, suggesting that these units may have been formed in a perennially saturated environment such as a lakeshore, wetlands, or near-surface aquifer.

MOLECULAR STUDY OF THE EDGE EFFECT ON AQUEOUS CATION ADSORPTION ON GIBBSITE NANOPARTICLES

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Edges play an important role in determining the adsorption and desorption properties of aqueous solutions at mineral interfaces. However, molecular simulation studies of ion adsorption at mineral interfaces have largely ignored such effects because of (i) poor understanding of the edge chemistry under different pH conditions and (ii) limitations of classical force fields (FFs) used in such simulations. Recent FF development, specifically parameters for simulating mineral edge surfaces that are compatible with ClayFF, enables us to simulate the interaction of aqueous solutions with different minerals surfaces and nanoparticles. We will present our molecular dynamics simulation results for aqueous solution interaction with gibbsite edge (1 0 0), basal (0 0 1), and nanoparticle surfaces. Our nanoparticle model has hexagonal shape and is comprised of (1 0 0) and (0 0 1) surfaces. Comparison of surface coverages for adsorbed ions calculated for (1 0 0) and (0 0 1) surfaces with those calculated for the nanoparticle indicates an enhanced ion adsorption on the nanoparticle. Our efforts at simulating solution interactions with clay-like nanoparticles allows us to develop mineral-fluid interface models beyond simple geometries such as a slit-pore. We will also present a methodology to prepare complex and realistic clay aggregate models with interlayer regions, interparticle pores, and interparticle boundaries at the atomistic scale for future investigation of the exchange of water and ions between interlayer and interparticle pores. This simulation methodology will advance our understanding of properties of aqueous solution near complex, realistic minerals interfaces.

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ADSORPTION OF FUMONISIN B₁ ON SMECTITE AND SYNTHETIC LAYERED DOUBLE HYDROXIDES

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Fumonisin causes leukoencephalomalacia (LEM) in horses, immunosuppression in poultry, pulmonary edema in pigs, hepatocarcinogenic and nephrotoxic in rats, atherogenic effects in vervet monkey, media hypertrophy of pulmonary arteries in swine, and brain hemorrhage in rabbits. Using clays or similar materials as adsorbing materials is a practical and economical measure to reduce or eliminate the bioavailability of mycotoxins such as aflatoxin to animals and humans. Unfortunately, such an effective adsorbent for fumonisins has not been identified even scattered clinic trials reported that bentonite clay might be able to reduce their toxicity. The determining mineralogical or chemical factors in controlling fumonisin adsorption are still unknown. The general objectives of this study were to investigate the adsorption and bonding mechanisms between fumonisin and two types of layer minerals: negatively charged smectite and positively charged layered double hydroxides (LDHs).

The speciation estimation suggested FB₁ existed as anionic form at pH above 4.4, and therefore, it could be expected that adsorption of FB₁ on smectite would decrease with pH, but the adsorption on LDH would increase with pH. However, experimental results indicated that both the adsorption of FB₁ on smectite and LDH decreased when pH is increased. The XRD and FTIR data suggested that smectite was able to adsorb FB₁ in its interlayer at low pH, and the interlayer adsorption was observable till pH 6. The results indicated that electrostatic attraction between the negative charge on smectite and the positively charged amino group of FB₁ was the main bonding force for the adsorption. The dissociation of the four carboxylate groups of FB₁ was responsible for its weak adsorption on smectite at higher pH.

The FB₁ adsorption on LDH was primarily driven by the electrostatic interactions between the anionic part of FB₁ and the positive charge sites on LDHs. The adsorption isotherms indicated that LDHs had similar adsorption capacity as smectite but much stronger affinity at weakly acidic pH about 5.2. The FB₁ can be adsorbed in the interlayer of LDHs with only partial anion exchange with NO₃⁻ or CO₃²⁻ in this experiment. The limited interlayer gallery space of about 0.3 nm in the FB₁-LDH complexes indicated that adsorbed FB₁ existed in a more extended configuration in the interlayer in LDH than in smectite. The amount of adsorption of FB₁ is positively correlated with the charge density of LDHs. However, competition between anionic FB₁ and OH⁻ for adsorbing site resulted in FB₁ adsorption reduced with increasing solution pH.

The observations suggested that both smectite and LDHs could be used as binding agents of FB₁ at low pH, but strategies should be developed to enhance the adsorption and stability of FB₁ on smectite and LDHs at neutral and alkaline pH.

APPLICATION OF ^{31}P NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY FOR UNDERSTANDING POLYPHOSPHATE DEGRADATION

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Polyphosphate is a group of polymeric phosphate molecules with at least three phosphate ions joined by phosphoanhydride (P–O–P) bonds, and are produced by a wide diversity of microorganisms and human activities. Despite the ubiquity and environmental significance of polyphosphate, little is known about their transformation and cycling in the environment. This presentation will summarize our recent findings on the degradation of linear polyphosphates mediated by biotic and abiotic processes, as well as the effects of a range of environmental factors, such as polyphosphate chain length and solution chemistry. Because polyphosphates contain characteristic structural moieties that can be distinguished by ^{31}P nuclear magnetic resonance (NMR) spectroscopy, their hydrolysis mechanism can be revealed through the temporal changes in NMR spectra. Our research revealed a terminal-only pathway for polyphosphate hydrolysis under varied conditions. The production of orthophosphate resulted in subsequent precipitation of calcium (Ca) phosphate mineral(s) in the presence of Ca^{2+} . Results from this work laid the foundation for better understanding the cycling of polyphosphates in aquatic environments.

CLAY MINERALOGY FROM TEMPERATE SOILS: NEW INSIGHTS FROM THE 42 PLOTS LONG-TERM EXPERIMENTAL SITE OF VERSAILLES (FRANCE)

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The complexity of the clay mineralogy from temperate soils is due to the different origins of the coexisting clay minerals, their wide range of particle sizes and the presence of several types of mixed layer minerals (MLMs). The X-ray diffraction (XRD) profile modelling approach applied on various sub-fractions (<0.05, 0.05-0.1, 0.1-0.2 and 0.2-2 μm) of the clay fraction (< 2 μm) was recently used to unravel the clay mineralogy from temperate soils [1, 2]. In line with these previous works and in order to get additional insights on the clay mineralogy from these soils, the methodology has been improved and applied on the historical “42 plots” long-term experimental site of Versailles (France), set up in 1928 to study the effect of various fertilizers on the properties of loamy soils (Haplic Luvisol).

The clay fraction of the surface soil sample collected at the beginning of the experiment in 1929 was separated into five sub-fractions (<0.02, 0.02-0.05, 0.05-0.1, 0.1-0.2 and 0.2-2 μm). The XRD profile modelling was performed on each sub-fractions in addition to the bulk clay fraction. The results show that the finest (<0.02 μm) and most reactive clay particles are not visible on the experimental XRD profile of the clay fraction whereas its relative proportion accounts for 31 wt.% of the total clay fraction. This finest fraction contains only two and three components MLMs constituted by 2:1 clay layers (illite, smectite and chlorite) without kaolinite. The finest sub-fractions (<0.02, 0.02-0.05 and 0.05-0.1 μm) are also mainly composed by MLMs with small coherent scattering domain sizes and these MLMs account for 82 wt.% of the clay minerals in the clay fraction.

The improvement of the approach will be discussed. The clay mineralogy of this soil will be compared to those previously obtained from other temperate soils involving different weathering processes in order to tentatively draw a general scheme of the clay mineralogy of temperate soils.

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TEACHING CLAY SCIENCE: FROM PAST TO PRESENT

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Methods of teaching science have always followed, and have been strongly influenced by, advances in the scientific fields themselves. This is particularly true in clay science. As new information becomes available instructors at all educational levels must learn to articulate and present that information in the classroom in a way that is logical and consistent with preferred methods of pedagogy. A classic example was the introduction of American Petroleum Institute Project 49, under the direction of Paul F. Kerr at Columbia University in the 1940s. The goal was to collect samples of representative clays, analyze them, and publish the results (Kerr, P.F. (1949) Reference Clay Minerals, A.P.I. Project 49, American Petroleum Institute). This suite of highly characterized clay minerals constituted a set of reference standards that were used throughout the world, and permitted both researchers and educators to pursue, for the first time, quantitative clay studies.

In recent years this trend toward the application of technology to study and teach about clays has emerged as an increasingly important feature of instructional delivery. Several examples will serve to illustrate some of these new technologies and their application to clay science instruction. We will examine both laboratory and lecture advances, and suggest that successful teaching of clay science depends upon students doing clay science as well as reading and engaging in presentations about clays. In addition to the broad range of X-ray, microscopic and spectroscopic technologies currently in use, teachers have benefited from an array of software developments such as programs for XRD peak deconvolution and quantification, and for calculating crystallite size (X-ray scattering-domain size) distributions. Much of this software is freeware and easily obtained from widely publicized websites. In the classroom, technology innovations include podcasting, distance learning methods such as WebPush and newly developed CD courses that offer a wide array of instructional options.

OPTIMIZATION OF ORGANO-MODIFIED SMECTITE OF HYDROTHERMAL SYNTHESIS SMECTITE BY TAGUCHI METHOD

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The organo-modified smectites are used in numerous industrial, material and environmental applications. In this work, trioctahedral smectite was synthesized by hydrothermal method based on the formula $\text{Na}_{Z+3X}(\text{Al}_{2(1-X)}(\text{Mg}_{3X*(1-Y)}, \text{Zn}_{3X*Y})\text{D})(\text{Si}_{4-Z}\text{Al}_Z)\text{O}_{10}(\text{OH}, \text{F})_2$. Taguchi method was applied in the experiments to optimize the interlayer swelling ability of the synthesized smectite.

In this Taguchi experiment, eight factors were chosen as significant parameters, including type of mineralizer, mineralizer amount, type of Zn & Al source, reaction time, Mg/Zn ratio in octahedral sheet, Al/(Mg+Zn) ratio in octahedral sheet, and Si/Al ratio in tetrahedral sheet. A series of the smectite was modified by using same concentration surfactant (CTAB) according to the cation exchange capacity (CEC) of synthesized smectite. The interlayer swelling ability and d-spacing of the organo-modified smectite were identified by X-ray diffraction (XRD). The results indicate that the Si/Al ratio in tetrahedral sheet, type of Al source and type of mineralizer are three of the most important factors affect the interlayer swelling ability of synthesized smectite. The d-spacing of the organo-modified smectite(1.3CEC) estimation can be exceed 2 nm on the synthesis condition that optimized by Taguchi method.

SYNTHESIS, CHARACTERIZATION, BIOAVAILABILITY, AND TOXICITY OF MONTMORILLONITE INTERCALATED WITH GLUTATHIONE

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Glutathione (GSH) is a powerful antioxidant protecting cells from reactive oxygen species (ROS), and plays an important role in detoxification and immune response. However, orally ingested GSH has low bioavailability because it is easily degraded to amino acid and has big molecular weight, resulting in low intestinal absorption. Therefore, the aim of this study was to enhance GSH bioavailability by developing GSH–montmorillonite (MMT) hybrid system. Moreover, GSH–MMT hybrids were further coated with polyvinylacetal diethylaminoacetate (AEA) for better stability after oral administration. The characterization of both GSH–MMT and AEA–GSH–MMT hybrids by powder X-ray diffraction (PXRD), fourier transformed infrared (FT-IR), and thermogravimetric analysis (TGA) confirmed successfully intercalated of GSH into MMT.

In vivo antioxidant activity assay revealed that AEA–GSH–MMT hybrid significantly increased antioxidant activity in the plasma after 1 h post-oral administration to mice. Pharmacokinetic study also indicated that AEA–GSH–MMT hybrid considerably increased the plasma concentration of GSH at 1 h post-oral administration. Both the hybrid systems remarkably enhanced GSH delivery efficiency to the main target organ, liver. The efficacy of the hybrid systems was more remarkable in GSH-deficient model mice. Moreover, the hybrid systems did not induce any acute oral toxicity. All the results suggest that GSH–MMT hybrid system has great potential to enhance bioavailability of GSH and provides new insight into their pharmaceutical application.

REACTIVITY OF IRON IN NATURAL AND SYNTHETIC FERRIC NONTRONITES

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Iron (Fe) can occupy mineral lattice sites in clay mineral structures. In the octahedral sheet of nontronite, iron can be in either +2 or +3 oxidation states, and this structural iron is redox active. Under oxic conditions, octahedral Fe(II) catalyzes the production of hydroxyl radicals from dissolved oxygen, promoting the oxidation of contaminants. Under anoxic conditions, octahedral Fe(II) was shown to reduce nitroaromatic compounds. In our work we found that when a portion of octahedral iron (~10 to 20%) in the octahedral sheet is converted to Fe(II), while leaving the majority of Fe in the +3-oxidation state, the surface of nontronite becomes reactive. Namely, activated nontronite surfaces are capable of oxidizing arsenic As(III) to As(V) under both oxic and anoxic conditions. This activation can also be achieved following the adsorption of Fe(II) onto the nontronite surface. This activation was observed for both natural and synthetic ferric nontronites. While reactive oxygen species forming in the presence of dissolved oxygen is the likely oxidant under oxic conditions, the oxidation pathway of As(III) under anoxic conditions is unknown.

To identify the reactive Fe(III) species in the nontronite structures we used a combination of experimental and computational methods, including X-ray absorption, Mössbauer, and diffuse reflectance spectroscopies, and density functional theory calculations. The proposed reactive species and mechanisms of electron transfer from As(III) to Fe(III) in ferric nontronites, corresponding changes in the solid-phase Fe speciation, and molecular-level insight from the computational results will be discussed.

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THE ATOMIC LEVEL STRUCTURE OF LAYERED DOUBLY HYDROXIDES AS SEEN BY SOLID STATE NMR SPECTROSCOPY AND OTHER TECHNIQUES

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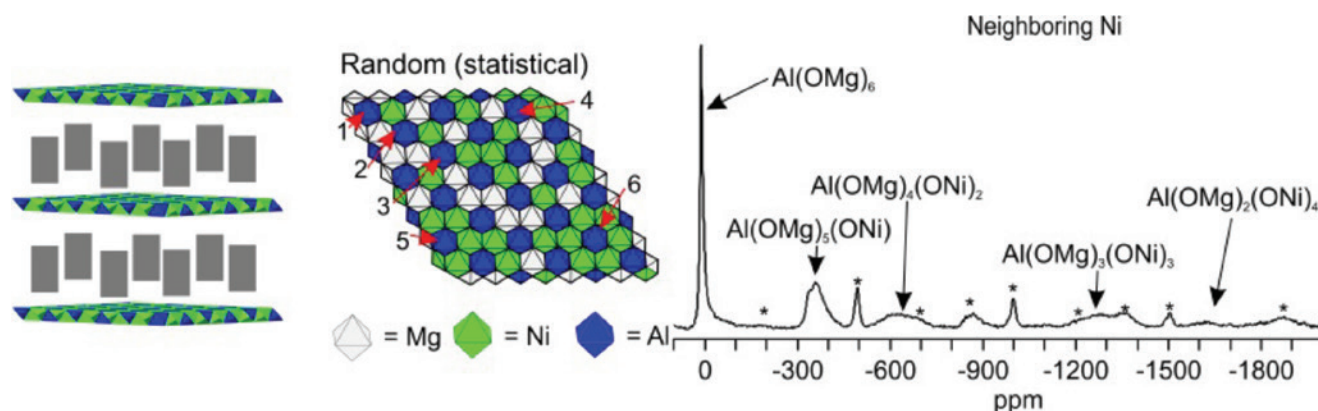
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Layered double hydroxides (LDH), anionic clay, find application within areas including environmental remediation, catalysis and as energy materials due to their flexible chemistry. However, LDH materials are notorious for their poor crystallinity and frequent stacking faults, which render structural characterization challenging. Solid state NMR (SSNMR) spectroscopy has proven a powerful characterization technique of the local environment in diamagnetic LDH materials, whereas studies of paramagnetic LDH-materials are scarce due to the strong paramagnetic interactions.

A nearly unexplored class of LDH is obtained by insertion of divalent metal ions into bayerite and gibbsite, the two common aluminum hydroxides. We will show how high field solid state NMR spectroscopy allowed for assessment of sample purity and detailed characterization of the samples. A detailed structural model was obtained combining the information from SSNMR, EXAFS, and PXRD.

Catalytic materials are obtained by doping paramagnetic Ni(II) into MgAl-LDH to form trimetallic MgNiAl-LDH. However, the distribution of Ni(II) in the LDH layer is nearly impossible to assess with diffraction based techniques, as NiAl-LDH are known for their frequent stacking faults and low crystallinity. Furthermore, the *a*-axis differ less than one percent for MgAl and NiAl-LDH due to the very similar ionic radii of Mg(II) and Ni(II). δ_{iso} (²⁷Al) allow for identification of the different Al environment and to probe the local magnetic interactions as the Ni(II) content and interlayer anion is changed.



CHARACTERIZING NANOPHASE MATERIALS ON MARS: SPECTROSCOPIC STUDIES OF ALLOPHANE AND IMOGOLITE

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The presence of allophane and other nanophase materials on Mars indicates a time when water was intermittent and short lived^{1,2}. These materials likely represent partially altered or leached basaltic ash³ and therefore, could represent a geologic marker for where water was present on the Martian surface. Further, they may indicate regions of climate change, where surface water was not present long enough to form clays¹.

We created a suite of nanophase materials of varying compositions. These synthetic samples were then spectrally characterized using Fourier transformed IR (FTIR) spectroscopy, visible/near-infrared (VNIR) reflectance spectroscopy, thermal infrared emission spectroscopy (TIR), magic angle spin nuclear magnetic resonance (MAS NMR), and Fe K-edge X-ray absorption spectroscopy (XAS). Compositions of the nanophase materials range from high-Si allophane (molar Al:Si = 1:2) to protoimogolite (molar Al:Si = 2:1), while spanning a range of Fe(III) isomorphically substituted for Al from 0-10 mol%. These compositions span the range observed in natural terrestrial allophanes⁴.

Differences in these spectra have been analyzed to show that changes in the chemical structure of allophane can be dictated by Al:Si ratio. VNIR reflectance spectra and FTIR transmittance spectra of Fe-bearing allophanes and imogolites indicate small changes in the OH features, consistent with Fe in the structure. Allophane bands occur at 1.38, 1.40, 1.92 and 2.19 μm . Imogolite bands are similar, occurring at 1.39, 1.92 and 2.20 μm . Shifts towards longer wavelengths were observed with the addition of Fe for OH bands near 1.4 and 2.2 μm in both samples. The OH band at 2.2 μm changes with the addition of Fe in the imogolite samples such that a shoulder forms at longer wavelengths (~2.22-2.23 μm) and the reflectance maximum does not return as high following this band. XAFS spectra indicate changes in octahedral sheet disorder due to the oxidation state of Fe. XAFS spectra also indicate changes in local atomic structure when changes in Al:Si occur. ²⁷Al MAS NMR data show an increase in Si correlating with more tetrahedral Al as well as a correlation with increasing Fe resulting in increased tetrahedral Al.

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³ Wada K. (1967) *Am. Miner.* 52, 690.

⁴ Farmer V.C. et. al. (1979) *Geochimica et Cosmochimica Acta* 43, 1417-1420.

THE SOLID-STATE TRANSFORMATION FROM BRUCITE TO CLAY MINERALS

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Brucite is one of the products during the serpentinization of ultramafic rocks, and has been recognized as a buffer in the processes. Our recent study showed that it could be transformed into clay minerals in the Al-containing hydrothermal systems (e.g., subduction zone). This may be of fundamental importance to grasping phyllosilicate crystal chemistry, unraveling geochemical processes, and to better understanding unique structure and property of phyllosilicates.

In this study, hydrothermal experiments were conducted to investigate the possibility of the transformation from brucite to clay minerals, and the mechanism involved. The obtained products were characterized by XRD, TG, FTIR, ²⁷Al MAS NMR, and HRTEM.

XRD patterns of the hydrothermal products display characteristic basal spacing of serpentine, saponite, and chlorite at 0.7, 1.2, and 1.4 nm with dramatic decrease of the reflections of brucite. This is consistent with HRTEM observations, in which clay layers with a thickness of 0.7, 1.2, and 1.4 nm are observed in the hydrothermal products except Sample Mg-7d. It is worth noted that all the brucite is transformed to clay minerals and no chlorite is found in Sample Mg-7d. The consumption of surface OH in precursor minerals during the transformation leads to a dramatic decrease of mass loss of dehydroxylation and the occurrence of new peaks at 550°C and 810°C, which is indicative of the formation of serpentine and 2:1 clay minerals, respectively. These results demonstrate that brucite can be converted to clay minerals under hydrothermal condition.

Two new signals occur at 11.4 and 67.4 ppm in ²⁷Al MAS NMR spectra of the hydrothermal products. With the extension of treatment time, the signal at 11.4 decreases and finally disappear in Sample Mg-7d. FTIR spectra show a structural hydroxyl stretching vibrations at 3683 cm⁻¹ and it disappears in Sample Mg-7d. This implies the migration of Al³⁺ from octahedral sheets to tetrahedral ones during the transformation under hydrothermal condition, which is consistent with our previous studies that the substitution of Al³⁺ for Si⁴⁺ in tetrahedral sheets is critical to control the size matching between the tetrahedral and octahedral in clay minerals. HRTEM images show the hexagonal morphology of brucite is inherited by all hydrothermal products with similar SAED patterns. Meanwhile, a layer consisting of the structures of serpentine and 2:1 clay minerals is observed in Sample Mg-6h.

Our results demonstrates that the brucite can be transformed to clay minerals under hydrothermal condition and the transformation mechanism is mainly a solid-state one. This study supplies a new insight for the reaction paths, geochemical cycle and mass transfer during the serpentinization processes in hydrothermal systems.

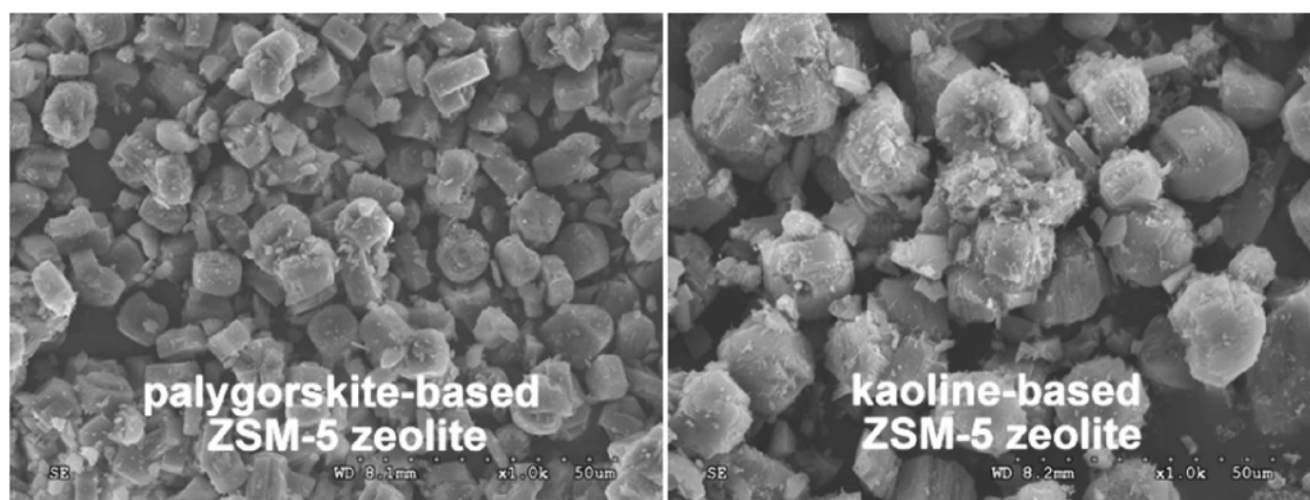
GREEN SYNTHESIS OF ZEOLITE FROM NATURAL CLAY UNDER MICRO-AMOUNT OF SOLVENT CONDITIONS

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A green and economical method has been developed to synthesis zeolite from natural clay. Palygorskite and kaoline were *in-situ* converted to ZSM-5 zeolite after adding halide, NaOH and micro-amount of water. Clay component were dissolved in the alkali liquor at the micro-interface of clay and alkali liquor and converted to ZSM-5 zeolite. The ZSM-5 zeolite exhibited high crystalline and hierarchical pore system. Clay could also converted to sodalite and zeolite A without mineralizer and template.



CHARACTERIZATION OF PARTICULATE PHOSPHORUS IN TILE WATERS FROM INTENSIVELY MANAGED AGRICULTURAL FIELDS IN THE MIDWESTERN U.S.

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In Midwestern U.S., the drainage of agricultural soils is managed by the tile drain system because of indigenous poorly drain clay rich soils, an accelerated subsurface flow of phosphorus (P) has been documented. Recent researches implied the important role of particulate P (PP) load in agricultural tile drainage and of high flow event in tile drainage P loss. It was hypothesized that P is transported in particulates/colloids to riverine system contributing to the negative environmental impacts in Midwestern U.S. In this study, assessment of physicochemical properties of PP in agricultural tile drainage samples after a heavy precipitation event was conducted using a combination of ^{31}P -nuclear magnetic resonance (^{31}P -NMR) spectroscopy, P K-edge XANES, X-ray diffraction, zetasizer, and transmission electron microscopy (TEM). Results show that significantly more colloidal (i.e. 1 nm- 2 μm) and silt-sized (i.e. > 2 μm) particles as well as higher dissolved total P (DTP) and dissolved reactive P (DRP) concentrations existed in river samples than tile samples. Tile samples showed similar zeta potential in each particle-size fraction and similar element distributions on colloidal fraction. However, colloidal P concentration and distribution are slightly different between tile and river samples: more colloidal total P and organic P existed in tile colloids than river colloids. Colloidal P contains orthophosphate with some mono- and di-ester and pyrophosphate, and is enriched in phyllosilicates and am. iron oxyhydroxides. These evidences suggested that tile particles may not be the predominant sources of river particles but will increase PP and organic PP concentrations if they are transported to riverine system.

PROBING THE HYDROPHOBIC / HYDROPHILIC NATURE OF CLAY MINERALS AT THE MESOSCALE SCALE

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Clay mineral-water interactions are critically linked to essentially all physical, chemical, and biological aspects of clay science. The interaction of water also regulates how organic molecules are stabilized on and, in some cases, transformed by clay minerals. Recently, clay minerals which were considered to be 'hydrophilic' (e.g., smectites) show surprisingly high affinities for strongly nonpolar organic solutes when weakly hydrated cations are present. In contrast, 'hydrophobic' clay minerals (e.g., talc and pyrophyllite) exhibit 'microscopic hydrophilicity' at low water activity. Finally, some clay minerals such as kaolinite are characterized by a dual nature having a polar surface on one side and hydrophobic surface on the other. The molecular mechanisms underlying this unexpected behavior will be examined at the mesoscale.

REDOX DEGRADITION OF PHOSPHONATE WITH FE-BEARING CLAY MINERALS UNDER SUBSURFACE RELEVANT CONDITIONS

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To ensure the efficient application of phosphonates, which are widely applied in oil fields to inhibit scale formation, it is important to understand their fate and transport under conditions relevant to subsurface sites. Clay minerals are ubiquitous in shales, the main reservoirs for unconventional oil/gas recovery, and they are important players in the redox processes of organic substances. However, the effects of clay minerals on the stability of phosphonates remain poorly understood. In the present study, diethylenetriamin epenta(methylene)phosphonate (DTPMP, a phosphonate-based scale inhibitor) was reacted with three model clay minerals—an Fe-poor muscovite, an Fe(II)-rich biotite, and an Fe(III)-rich nontronite—under subsurface relevant conditions (dark, low oxygen, 50-95 °C, and 102 atm CO₂). We found that in the presence of biotite, phosphonate degraded by up to 60%, and it released phosphate, formate, and new phosphonates. However, muscovite and nontronite had almost no effect on DTPMP degradation. In particular, the Fe(II) sites in biotite's structure play important roles the redox degradation of DTPMP. The reactive oxygen species generated through reduction of molecular oxygen by biotite Fe(II) sites were responsible for DTPMP degradation. Furthermore, at elevated temperatures, thermally promoted biotite dissolution induced more abundant and deeper surface cracks, exposing more reactive Fe(II) sites and enhancing DTPMP degradation. Due to biotite dissolution and DTPMP degradation, dissolved Fe and Al precipitated with phosphate or degraded DTPMP to form secondary minerals. The findings of this study can broaden our understanding of the roles of Fe-bearing clay minerals in the geochemical processes of redox-active substances and provide insights into the design and operation of engineered subsurface processes.

PHOTOCHEMICALLY-FORMED BIRNESSITE NANOSHEET LAYER STRUCTURES

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While abiotic processes are ubiquitous in nature, interestingly, a fast abiotic route for formation of Mn(IV) oxides in environmental systems has not been confirmed. In this presentation, I will present the photochemically-assisted fast oxidation of Mn^{2+} (aq) to Mn(IV) in a nitrate solution within hrs. Analyses of structures and oxidation states clearly indicated that a hitherto unconsidered inorganic abiotic process, nitrate photolysis, can enable the fast oxidation and the consequent formation of layered birnessite nanosheets, which are the most dominant phase of natural Mn(IV) oxide on the Earth's surface. Furthermore, in the presence of pyrophosphate (PP), we found that PP concentrations controlled the formation of disordered $\delta\text{-MnO}_2$ nanosheets and affected changes in their layer stacking and structures. With increasing PP concentrations from 0.3 to 2 mM, $\delta\text{-MnO}_2$ nanosheets showed better layer stacking and their structures were altered from hexagonal to orthogonal structure (more Mn(III) in layers). Our findings elucidate the considerable effect of abiotic processes that occur with sunlight exposure on the fate of Mn in natural systems. The findings also have important implications for sustainably synthesizing layered birnessite nanosheets with well-controlled structure properties.

INTERACTION OF NATURALLY OCCURRING RADIOACTIVE MATERIALS WITH CLAY MINERALS IN THE CONTEXT OF SHALE GAS EXPLORATION

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Nanoscale understanding and prediction of the structural, dynamic, and reactive properties of clay mineral interfaces and their interactions with dissolved inorganic and organic aqueous species is important for many natural and industrial processes related to energy, environmental, and geochemical applications, such as geological disposal of radioactive waste, shale gas exploration and exploitation, geological carbon sequestration, mineral weathering, etc. To study such systems on the fundamental molecular scale is not always feasible experimentally, and the results of such studies are often subject to considerable interpretation usually based on certain atomistic models. Rapid development of such atomistic computational modeling techniques in recent years [1] has already provided significant new quantitative details of the specific effects of the clay mineral structure and composition on the structure, dynamics and reactivity of interfacial and nano-confined fluids. However, in most computer simulations to date, clay particles are represented by their basal (001) surfaces only. Here we are using the recently developed modification [2] of the ClayFF force field [3] to realistically model the hydrated edges of finite size clay nano-particles in large-scale classical molecular dynamics (MD) simulations. The structure of aqueous solutions and ion adsorption at the (010) and (110) edge surfaces of kaolinite, montmorillonite, and muscovite are investigated in detail for a number of mono- and di-valent cations relevant for the problems of shale gas exploration, where they are suspected to negatively impact the environment as potentially mobile naturally occurring radioactive materials (NORMs). Specific surface adsorption sites are initially identified and then probed by the calculations of potentials of mean force [4] which provide detailed site-specific quantitative information on the free energies of adsorption and the thermodynamics of interfacial cation exchange.

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CLAYS IN OIL SANDS: AN UPDATE AND CALL FOR COLLABORATION

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Clays represent a major challenge for oil sands mining operations. While these particles are present in fairly small quantities in the richer ore bodies they can be present in increasing quantities in the more marginal deposits. In addition the hot water extraction process disperses these clays and causes them to segregate upon settling concentrating in the upper layers of the settling basins/tailings ponds. This has created a legacy of more than 1.1 billion cubic meters of clay enriched fluid known as fluid fine tailings. The high surface area of the clays combined with a dispersing water chemistry means that these fluid fine tailings settle and consolidate extremely slowly and in some cases only when left in perfectly quiescent conditions. This state is not compatible with the reclamation objectives of local stakeholders and regulators. Consequently, significant efforts are being made to treat these tailings using a variety of mechanical and chemical solid/liquid separation techniques.

In addition to the challenges of treating fluid fine tailings there are challenges with clays partitioning with the bitumen. One type of bitumen cleaning–naphthenic froth treatment–is particularly sensitive to the presence of ultrafine kaolinite and other clays.

One of the many challenges faced in tackling these challenges is a lack of measurement tools to successfully measure monitor the key aspects of the clay that cause the challenges.

This presentation will summarize the publically available information on the types of clay minerals found in the different oil sands deposits, the methods currently used to measure the presence of clays, and the known ways different types of clays impact the processes of concern. The objective of this presentation is to help educate clay experts on the challenges with clays in the oil sands industry with the hope of finding innovative new solutions to the challenges.

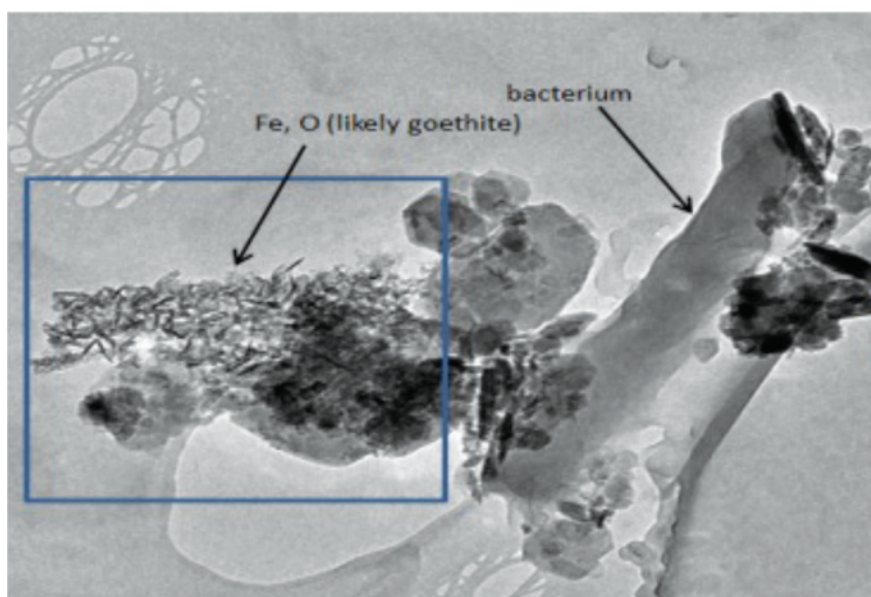
IMPACT OF THE UNIQUE MINERALOGY AND ORGANIC MATTER COMPOSITION OF THE RHIZOSPHERE ON URANIUM IMMOBILIZATION

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Subsurface contaminants move with groundwater flow and eventually resurface in wetlands. While many contaminants can move readily through aquifers, the movement of most contaminants is strongly attenuated in wetlands because of the presence of steep biogeochemical conditions that promote contaminant binding. A three-year field study in a uranium-contaminated wetland was conducted to study the role that the rhizosphere plays in uranium immobilization. Uranium concentrations were 15x greater in the rhizosphere than in the bulk wetland soil. The rhizosphere had elevated C, N, Mn, and Fe concentrations and total bacteria, *Geobacter*, and *Anaeromyxobacter* counts (as identified by qPCR). Based on Mössbauer spectroscopy, rhizosphere soil was greatly enriched with nanogoethite, ferrihydrite, and hematite, with negligible Fe(II) present. X-ray computer tomography and various microscopy techniques showed that root plaques were tens-of-microns thick and consisted of highly oriented Fe-nanoparticles, suggesting that the roots were involved in creating the biogeochemical conditions conducive to the nanoparticle formation. Furthermore, the rhizosphere contained several organic molecules that were not identified in the non-rhizosphere soil (54% of the >2200 ESI-FTICR-MS identified compounds). Rhizosphere OM molecules tended to have greater average molecular weights, less aromaticity, more carboxylate and N-containing COO⁻ functional groups, and a higher hydrophilicity than the non-rhizosphere OM. These OM properties tend to favor binding and immobilizing hard-acid metals, including uranium. XAS analyses showed that a majority of the U in the bulk wetlands soil recovered under unsaturated moisture conditions was in the +6 oxidation state and was not well correlated spatially to Fe concentrations. SEM/EDS confirmed that U was enriched on root plaques, where it was always found in association with P. Together, these findings show that plants can alter the mineralogical and organic matter conditions in a manner that are conducive to contaminant immobilization in wetlands. These findings have implications on the stewardship and long-term management of contaminated wetlands.



HOW WE USED IR-SPECTROSCOPY IN THE REYNOLDS CUP

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IR spectroscopy is a valuable and well established analytical tool in clay science because it provides information about mineral abundance and chemical composition of the individual minerals. In addition IR spectroscopy can be used to study surface complexes, short range ordered minerals and XRD-amorphous materials such as allophane, ferrihydrite, glass, and organic matter. However, IR spectroscopy is mostly used in a qualitative manner, quantitative methods are rare. Kaufhold et al. (2012) proposed an analytical protocol which allows for the quantitative assessment of IR spectra of clays based on manual fitting using a significant set of reference spectra. Since then BGR used this method as complementary tool for the investigation of the Reynolds Cup samples. The final results, however, were mostly based on Rietveld refinement. Nevertheless, some valuable information was gained from quantitative IR spectroscopy. The actual composition of the individual RC samples was compared with the composition derived from IR spectroscopy and the effects of the differences on the spectra (measured and fitted) were investigated. Generally, minerals differ with respect to their IR detection limit. Some of which cannot be detected at all (e.g. halite, pyrite,...), others having a low extinction coefficient and/or few characteristic bands (e.g. barite, amphibole), and some can be easily characterized by IR spectroscopy (e.g. quartz, kaolinite, carbonates). One important observation is that the sum of minerals of a class is often close to reality in contrast to the individual contents. This holds true e.g. for the class “illite-smectite interstratifications plus smectites plus muscovite” or for the class “carbonate minerals”. The same was observed for the feldspars and for kaolin group minerals. The individual contents can only be determined accurately if appropriate references are used. As an example, a certain amount of the kaolin group minerals can be fitted using a halloysite and a well crystallized kaolinite reference spectrum but the individual mineral contents only become accurate if the references used correspond to the actually present minerals and represent their specific degree of structural order. Therefore, the accuracy of quantitative IR values increases with the amount of additional information such as XRD data (e.g. estimation of the degree of structural order (crystallinity) of halloysite) or SEM (chemical composition of carbonates or feldspars as an example). The quantitative IR method proved to be particularly valuable when different clay minerals are present in a sample which cannot be described properly by XRD (e.g. because of absence of suitable structural XRD models). Several examples will be presented elucidating possibilities and limitations of the IR method for the quantification of Reynolds Cup samples.

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CELLULAR UPTAKE BEHAVIOR OF LAYERED DOUBLE HYDROXIDE BASED HYBRIDS WITH DIFFERENT SURFACE ROUGHNESS

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We intercalated both 1-butanedisulfonate (B) and anionic fluorescein dye (F) successively into layered double hydroxide (LDH) through ion-exchange (I) and reconstruction (R) in order to prepare LDH based hybrid with different surface roughness. According to the powder X-ray diffraction patterns and fourier-transform infra-red spectra of LDHs before (pristine) and after co-intercalation (BF-LDH hybrids), 1-butanedisulfonate were well organized between LDH layers and anionic fluorescein dye molecules were embedded among 1-butanedisulfonates. The scanning electron microscopy and dynamic light scattering analyses revealed that both BF-LDH hybrids had comparable size of ~180 nm. The zeta-potential of both BF-LDH hybrids was also similar showing 38.7 mV and 31.3 mV for BF-LDHI and BF-LDHR, respectively. Through atomic force microscopy and height profile analyses, we confirmed that the BF-LDHI has smooth surface with Ra value of 0.564 nm, while the BF-LDHR had relatively rough surface with Ra value 1.437 nm. The cytotoxicity of both BF-LDH hybrids was evaluated using trypan blue exclusion assay against human lung adenocarcinoma cell (A549) line. Both BF-LDH hybrids did not affect the cell viability reduction until the concentration of 200 µg/mL, which was selected for further cellular uptake study. The cellular uptake of both BF-LDH with different surface roughness was evaluated in A549 cell utilizing fluorescence-activated cell sorter. The BF-LDHI hybrid with smooth surface was determined 1.5 times more internalized into A549 cells compared with rough surface one (BF-LDHR).

MICROBE-MINERAL INTERACTION IN EXTREME ENVIRONMENTS

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Role of extremophiles in the biogeochemical Fe-cycling are of an important process resulting in the modification of mineral assemblages and hydrochemistry by the metal redox reaction. The unexpected biomineralization that bypass the thermodynamic barriers could be a consequence of bacterial survival and growth strategy in extreme conditions. Investigations on microbe-mineral interactions in such a harsh conditions, for example Antarctic region, hydrothermal vent, and active fault margin were performed by multi-disciplined microscopic and spectroscopic methods. Specifically, microbial structural Fe reductions in phyllosilicates and its implications will be discussed.

NOVEL ANTIMALARIAL DRUG-CLAY NANOHYBRID; ORAL AND INTRAVENOUS ADMINISTRATION ROUTES

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Artesunate (AS) is the most widely used artemisinin derivative as an effective anti-malaria drug. However, AS shows a low oral bioavailability due to the poor aqueous solubility and instability in acidic solution. Therefore, we incorporated AS molecules into hydrophilic zinc basic salt layers (ZBS), which was studied as a reservoir or carrier for fragile bioactive molecules, not only to increase aqueous solubility of AS but also to enhance its chemical stability under an acidic condition. According to the x-ray diffraction analysis, the basal spacing of ZBS-AS nanohybrid was determined to be 2.88nm, indicating that AS was successfully incorporated into ZBS layers, which was also confirmed by 1-D electron density profiles along the crystallographic c-axis and transmission electron microscopic analysis. The FT-infrared spectroscopic analysis revealed that AS molecules were deprotonated and electrostatically interacted with cationic zinc hydroxide sheets. From CHNS, TG and HPLC analyses, the content of AS encapsulated in ZBS vehicle could be estimated as ~46 wt%, and the chemical formula of thus prepared ZBS-AS nanohybrid was determined to be $Zn_5(OH)_8(C_{19}H_{28}O_8)_{1.1}(Cl)_{0.9} \cdot 3H_2O$. To enhance the dissolution property of AS in simulated intestinal condition, ZBS-AS nanohybrid was coated with enteric coating polymer, Eudragit® L100, (ZBS-AS-L100). Finally we have performed in-vivo pharmacokinetic study in rats via oral administration in order to compare absorption of AS of ZBS-AS-L100 nanohybrid with that of intact AS. And surprisingly, it was found that the former was ~6 times larger than the latter due to an enhanced solubility of AS thanks to the hybridization with hydrophilic ZBS. Therefore, ZBS-AS-L100 could be suggested as a promising drug delivery system for improving drug solubility and absorption. Additionally, we encapsulated AS molecules into layered double hydroxide (LDH) for intravenous injection, and then, systematically discussed on the AS release property in the simulated body fluid solution, which will be demonstrated in-detail in the presentation.

PARACELLULAR TRANSPORT OF ANIONIC CLAY VIA IN-VITRO FOLLICLE-ASSOCIATED EPITHELIAL MODEL

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Oral drug delivery is the most common route for drug administration due to its safety and convenience. Out of various oral drug delivery vehicles, anionic clay, such as layered metal hydroxides (LMH), has attracted a great attention due to its high biocompatibility, high anionic exchange capacity and controlled release behavior. In this study, *in-vitro* human Follicle-associated epithelium (FAE) model was used to observe transport pathways how 2D clay particles could be translocated across the cellular monolayer, with respect to its particle size from 100 nm to a few μm . The decrease in transepithelial electrical resistance (TEER) for the Caco-2 and Raji B co-culture monolayers incubated with clay nanoparticles suggested that the paracellular tight junctions became loosened. It was also found that the 100 nm sized clay particles showed better translocation than the other sized. And finally we were able to conclude that the present clay nanoparticles were translocated through paracellular transport pathway as well confirmed by the confocal images of co-culture cell monolayer.

CLAY MINERALS IN HYDROCARBON RESERVOIRS: COMPUTATIONAL AND EXPERIMENTAL STUDIES OF SMECTITE- H₂O-CO₂-CH₄ INTERACTIONS

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Clay minerals are ubiquitous in petroleum source, reservoir, and cap rocks, and their interaction with the aqueous, CO₂-rich, and hydrocarbon fluids present in these environments can play an important role in controlling the fluid behavior in, for instance, CO₂ floods or the use of CO₂-rich fracking fluids. The molecular scale hydration behavior of clay minerals has been studied for many years, but there has been increased recent interest in their interactions with CO₂ and CH₄. This presentation will discuss experimental XRD, IR, and NMR results for smectite-H₂O-CO₂ and smectite-H₂O-CH₄ systems obtained at *in situ* reservoir conditions (typically 90 bars fluid pressure and 50°C) along with the results of parallel computational molecular modeling using Grand Canonical Molecular Dynamics methods. Together, the results provide detailed structural, dynamical and energetic insight into the intercalation behavior. In all cases the solvation energy of the exchangeable cation and its size play critical roles in controlling this behavior. For smectite with dry CO₂, the results show that CO₂ spontaneously enters smectite interlayers containing large cations (e.g., NH₄⁺, Cs⁺, Ba²⁺) but not those with smaller cations (e.g., Na⁺, Mg²⁺, Ca²⁺). With the large cations, the thermodynamically stable state has a mono-layer of CO₂ under our conditions, and CO₂ solvates the exchangeable cations. For smectites in equilibrium with H₂O-saturated CO₂ (~0.4% H₂O under our experimental conditions) maximum CO₂ intercalation occurs at mono-layer basal spacings. At these basal spacings, interlayer H₂O can prop open the interlayer to allow CO₂ to enter with, for instance, Ca²⁺ as the exchangeable cation. The experimental ¹³C NMR spectra and the computational modeling show that the CO₂ molecules lie with their O-C-O axes parallel to the basal surface and undergo rapid rotation or librational hopping about an axis perpendicular to their O-C-O vector along with restricted wobbling perpendicular to the basal surfaces. Dry CH₄ enters smectite interlayers only when the exchangeable cation is large enough to prop the interlayer gallery open (e.g., Cs⁺). With H₂O present, CH₄ can enter the interlayer at basal spacings > ~11.5 Å and is displaced by H₂O as the relative humidity increases. In no case does CH₄ solvate the exchangeable cation. The thermodynamic driving force for CH₄ intercalation is small, resulting in a passive space-filling behavior.

BIOMINERALIZATION ASSOCIATED WITH MICROBIAL FE/AS REDOX REACTION IN EXTREME ENVIRONMENT: YELLOWSTONE NATIONAL PARK

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The biomineralization associated with microbially induced redox reaction is ubiquitous in natural environment, however the mechanism for the alteration and neoformation of mineral has not been fully understood. Natural samples (hot-spring water + sediments) were enriched with medium to maximize the bacterial activity and then compared with controls (no bacterial activity with addition of glutaraldehyde), and differentiate the biotic and abiotic process in mineral formation. The incubation experiments was performed up to 12 months, and the reactions were stopped at various time points.

New mineral formation of pharmacosiderite ($\text{KFe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot 6-7\text{H}_2\text{O}$), detected in XRD profiles only for the enrichment condition after 6-month of incubation, could be a consequence of microbial redox reaction. Oxyanion of arsenic (As) is likely to be reduced abiotically to arsenate via As-S complex at low pH condition (~4.0) similar to that in the present study area (3.5). Nonetheless, concentration of arsenite increased only for the enriched samples in first 6-month of incubation, suggesting that oxidative phase of As was originated by microbial As oxidation in the formation of pharmacosiderite. Indeed, the *aroA* gene (As-oxidase gene) of *Sulfurihydrogenibium* sp. detected in pyrosequencing analysis indicating the significant role of microbe in mineral alteration/formation process. This finding is important because unexpected biomineralization of pharmacosiderite was occurred in the natural setting. The mechanism and implications to the natural environments will be discussed.

MONITORING THE AZOBENZENE ISOMERIZATION IN LAYERED INTERCALATION COMPOUNDS USING THE INFRARED SPECTROSCOPY

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Azobenzenes are photoactive compounds which exhibit *trans-cis* isomerization upon UV light. When combined with a solid support they may serve as photosensitive materials. Several clay minerals were previously studied for this purpose. Their photoactivity was observed with UV-Vis spectroscopy and in some cases changes of the basal spacing were observed with X-ray diffraction. FTIR and Raman methods were employed in the studies of *trans* and *cis* isomers of pure azobenzene. The presented work concerns beidellite-azobenzene (BId) and kaolinite-azobenzene (M) hybrids and the investigation of their photoactive behavior. The minerals were pre-intercalated with alkylammonium cations and after that azobenzene (Az) was introduced. For the most part the XRD and FTIR methods were used for the materials characterization and to monitor the UV induced reactions. The UV power was set to 10 mW/cm².

The d_{001} values of the obtained materials increased to ~30–33 Å in case of BId and to 49–55 Å in case of M intercalates. This confirmed the successful Az intercalation into the interlayer spaces of the minerals. Absorption bands related to Az vibrations were visible in the FTIR spectra: the $\nu(\text{C-H})_{\text{ring}}$ modes in the 3100–3000 cm⁻¹ region, the $\delta(\text{C-H})_{\text{ring}}$ modes at 1299, 778, 691 cm⁻¹, and the $\nu(\text{C-C})_{\text{ring}}$ modes at 1583, 1484, and 1454 cm⁻¹. Bands in the 800–700 cm⁻¹ range were sensitive to the presence of *cis* or *trans* Az isomers, thus those bands were employed to monitor the Az behavior upon UV irradiation. Already after 15 minutes of UV irradiation a band appeared at 760 cm⁻¹ and its maximum intensity was achieved after 30 minutes of irradiation. This band is associated with the interaction between C-H groups from the opposite aromatic rings in Az molecule, which get closer to each other in the *cis* isomer. The reverse *cis* to *trans* reaction was attested by the decrease of the 760 cm⁻¹ band intensity, which was observed after 24 h from terminating the UV irradiation. The reversible *trans-cis* conversion was observed up to four cycles of alternating UV and Vis irradiation. Simultaneously the intensities of other bands related to the Az molecule decreased gradually due to its partial evaporation. The isomerization of Az resulted in changes of the d_{001} values observed in the XRD patterns. The shifts were particularly visible and regular in case of BId derivatives, where the d_{001} decreased by ~1–3 Å upon UV and was recovered upon Vis light.

The research revealed that the Az intercalated clay minerals are responsive to UV radiation. Although the basal spacing shifts were not always clear the Az isomerization was confirmed with the FTIR spectroscopy. This method proved to be a valuable tool for monitoring the photochemical reaction of intercalated azobenzene. It was possible to determine the rate of UV induced reaction and the behavior of Az was tracked upon the alternating UV-Vis irradiation.

QUANTUM CHEMICAL MODELING OF Fe(III) IN 2:1 DIOCTAHEDRAL SMECTITES

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For waste repositories, clays are used as technical barriers because of their versatile properties, such as low permeability, plasticity, and swelling. Additionally, clays minerals, due to their high specific surface, show a strong ability to sorb and exchange cations. These properties of clay minerals, and therefore of clays, depend on their structure and chemical composition.

The analysis of numerous experimental observations yields relationships between the structure of clay minerals and their composition [1,2]. An explanation for these correlations is often missing. We examined some of these relationships related to the Fe(III) content, by quantum chemical methods [3]. To this end, we applied density functional theory, specifically spin-polarized Kohn-Sham calculations, complemented by two types of corrections, (i) a self-interaction correction (DFT+U) to enable an adequate localization of the d electrons of iron as well as (ii) van der Waals corrections (D3 approach). The electronic structure calculations were carried out with the program VASP, which implements a periodic plane-wave based band structure approach together with the projector-augmented wave method to account for the core electrons. We considered up to two Fe(III) substitutions per unit cell in a series of smectite models. This corresponds to an iron content of up to 25 %. The layer charge was chosen to be either 0.25 or -0.5 e per formula unit.

Calculated exchange energies of octahedral and tetrahedral Al(III) with Fe(III) showed that octahedral Fe(III) is energetically more favorable than tetrahedral Fe(III), in agreement with experimental observations. The interaction of two octahedral Fe(III) substitutions was repulsive in all model smectites studied. Octahedral Fe(III) prefers sites distant from charged octahedral Mg(II) substitutions, but close to charged tetrahedral Al(III) defects. In consequence, octahedral Fe(III) substitutions were found to be more favorable for beidellitic mineral models with tetrahedral layer charges than for montmorillonitic models with octahedral charges. Depending on the type of charged substitution, octahedral or tetrahedral, we determined an energy preference for cis- or trans-vacant lattice structures, respectively. A larger iron content increases the preference for the trans-vacant structure. Thus, with growing iron content, our models predict that the ratio of trans- to cis-vacant structures as well as the fraction of tetrahedral charge increases, in agreement with known empirical correlations. These results demonstrate that empirical correlations can essentially be traced back to energy relations. Further insight is provided by analyzing structural parameters and the charge distribution in the model minerals.

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STRUCTURAL FEATURES OF MONTMORILLONITES FROM RUSSIAN DEPOSITS AND THEIR INFLUENCE ON SORPTION CHARACTERISTICS TOWARDS RADIONUCLIDES ^{90}Sr , ^{137}Cs , ^{233}U , ^{241}Am

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Bentonite clays and bentonite-based materials are well known for their adsorption properties and low permeability. They are widely used in the disposal of various industrial wastes, including radioactive. The main component of bentonite clays is a montmorillonite which belongs to the smectite group. Its characteristic feature are intercrystalline swelling, large specific surface area and high cation exchange capacity.

Samples for this research were taken from four deposits: Taganskoye (Kazakhstan), Dashkovskoe (Moscow region), Zyryanskoe (Kurgan) and 10th Khutor (Khakassia). The following methods were used to study the composition of bentonite samples and the structure of montmorillonites: PQXRD (Rietveld) for mineral composition, XRD analysis of oriented clay mounts for refinement of the structure of montmorillonites (Na, Ca, Li—exchanged samples were analyzed in air-dry and glycolated states), FTIR for raw material and <0.5 μm fractions and also DSC-DTG-TG coupled thermal analysis. For the analysis of surface and sorption properties several approaches were used: S_{BET} definition, volume and average pore diameter, CEC determination (MB and Cu [(Trien)]²⁺) the maximum adsorption values (A_{max}) towards Cs and Sr, total exchange capacity determination towards ^{90}Sr , ^{137}Cs and sorption capacity and distribution coefficient (Kd) towards ^{90}Sr , ^{137}Cs , ^{233}U , ^{241}Am . Selective desorption (sequential leaching) revealed the forms radionuclides' bonding to bentonite.

As a result of the study, structural features determining the sorption properties towards various pollutants including radionuclides were revealed.

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MICAS AS PROTECTIVE HABITATS OF CYANOBACTERIA AGAINST ULTRAVIOLET RADIATION

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Cyanobacteria are single celled prokaryotic organisms capable of autotrophic photosynthesis. Through this biologic process, oxygen was released into the atmosphere, and cyanobacteria are considered one of the major causes of the Paleoproterozoic Great Oxidation Event. Through photosynthesis, oxygen was released into the hydrosphere and atmosphere, changing the planet from a reducing environment to an oxidizing one. Prior to oxygenation, 3.5 Ga, the environment was reducing in nature and had high levels of UVR reaching the planet's surface unfiltered, as well as higher temperatures, and increased meteoric collisions. Aquatic cyanobacteria are limited in their environment as they must remain in water and in the photic zone, however there are samples which live terrestrially as well. These terrestrial organisms would have had to find means of survival and means of coping with those stresses. While cyanobacteria do possess certain biological adaptations to cope with the stress of radiation, there are also means to minimize exposure by developing small scale habitats within or below minerals and rocks. The phyllosilicates muscovite, biotite, and phlogopite are predicted to have been in existence dating back to the Hadean, >4.0 Ga, predating all known life forms indicating that they could have been used as a small-scale habitat. These minerals have all also been found in the soils of Martian samples and meteorites, indicating their presence throughout planetary systems.

These small-scale habitats provide a place for cellular growth which can protect them from harmful radiation while allowing them to undergo the photosynthetic process. In this study, laboratory incubation experiments demonstrated that filamentous cyanobacteria are able to colonize the phyllosilicates of interest. Colonies were exposed to ultraviolet radiation for up to 24 hours, and survival rates were determined using chlorophyll a, carotenoid, and phycocyanin-C assays. Samples were imaged using fluorescent and light microscopy, and population recovery time was investigated as well. Of the three micas investigated, muscovite provided the least attenuation of ultraviolet radiation, however it transmits the most visible light of the photosynthetically active wavelengths 680 and 700 nm, which are necessary for photoautotrophs to survive. When protected by biotite and phlogopite the cyanobacteria were able to tolerate longer exposure to ultraviolet radiation however, these minerals greatly decrease the quantity of transmitted visible light. Cyanobacteria biofilms were also exposed to UVR while under the protection of these mica minerals and the shifts in phospholipid fatty acids were also assayed. Significant shifts in several important fatty acids were detected such as linolenic acid and oleic acid, 18:3 Δ 3 and 18:1 Δ 9c, respectively. These changes depict the attempts of cyanobacterial cells to mitigate the damage from UVR. Phlogopite attenuates UV-B radiation, even when the sheets are less than one millimeter in thickness, can still transmit visible light, and were present on the early earth as well as on other planets, making it the most ideal small-scale habitat of the investigated micas.

POLARITY OF ILLITE-SMECTITE FUNDAMENTAL PARTICLES REVISITED: NEW EVIDENCE FROM VIBRATIONAL SPECTROSCOPY MEASUREMENTS

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The value of layer charge (Q) present on smectitic i.e. the wettable surfaces of mixed-layer illite-smectite (I-S) crystallites was demonstrated to be virtually constant and equal to $0.41 \pm 0.03 e^-$ per formula unit (p.f.u.) irrespectively of the percent of smectite interlayers (%S) in I-S [1]. This implies that layer charge in the external surfaces of illite fundamental particles is much lower than that of the non-expandable side i.e. that the illite fundamental particles are polar. Nevertheless, charge distribution between the two sides of the 2:1 layer of illite fundamental particles is still debated. The aim of the present work was to test this concept by measuring Q of the wettable I-S surfaces with the “O-D method”, a newly proposed spectroscopic layer charge measurement method [2].

The O-D method employs a precise position of the sharp, high frequency O-D stretching band of adsorbed D_2O at $2685\text{--}2700\text{ cm}^{-1}$, which was found to correlate linearly with Q in dioctahedral smectites [2]. I-S surface charge was measured for 41 well-documented I-S samples coming from bentonites and hydrothermal deposits and representing %S between 8 and 100%, and R ordering between 0 and 3 [1]. The measured layer charge averaged $0.47 \pm 0.04 e^-$ per formula unit and was narrowly distributed, irrespectively of %S and sample origin, the result close to earlier estimates based on chemical analyses. It is concluded that the O-D method measures only the surface layer charge present on the external I-S surfaces, without the influence of illitic charge. No difference in Q present on the wettable surfaces for samples with and without smectite monolayers was observed, which is in agreement with the polar model of illite fundamental particles and smectitic character of its external surfaces. On the other hand, a systematic increase of measured Q with decreasing grain size was noticed for ultrafine fractions. This trend suggests lower polarity of illite fundamental particles at the initial stages of nucleation.

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ENVIRONMENTAL FATE OF MANUFACTURED NANOPARTICLES IN SURFACE WATER DRIVEN BY HETEROAGGREGATION WITH CLAY COLLOIDS

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The fate of engineered nanoparticles (ENPs) in natural aqueous environments is influenced by dispersion and transport ever opposed to aggregation and deposition, all related to environmental factors as well as those intrinsic to the nanoparticles themselves. For example, at environmentally relevant concentrations ($\mu\text{g/L}$), TiO_2 ENPs likely have a higher probability of interacting with suspended particulate matter (SPM) such as clay colloids present at mg/L or greater concentrations in natural surface waters, rather than with themselves, favoring heteroaggregation scenario. With both high specific surface area and reactivity, the clay colloids may act as TiO_2 ENP carriers in the water column, strongly affecting their fate and transport via the heteroaggregation process.

Herein, mechanistic evaluation of TiO_2 ENP fate in surface waters was assessed by measuring their heteroaggregation with different types of mineral SPM. montmorillonite and illite were identified as the most abundant clay colloids present in the Rhone water SPM, cohabitating with a mixture of quartz, calcite, chlorite, feldspar and muscovite. These minerals were used to guide the selection of relevant SPM analogues. The TiO_2 ENPs ($\mu\text{g/L}$) were spiked into synthetic riverine waters containing one of the main SPM analogues, their mixture, or the natural Rhone water SPM. The TiO_2 ENPs demonstrated a significant affinity for clay colloids as well as for the natural SPM, which lead to rapid heteroaggregation measured by time-resolved laser diffraction, and removal from the water column due to sedimentation.

In addition to determining the ENP/clay heteroaggregation kinetics and attachment efficiencies, the influence of natural organic matter (NOM) on the TiO_2 ENP fate and behavior was also assessed. Four common families of NOM analogues (i.e., proteins, polyhydroxy aromatics, polysaccharides, and amino sugars) were added to the SPM-containing synthetic waters to evaluate the effect of NOM on the ENP/clay heteroaggregates.

These mechanistic data first suggest that clay constitute a relevant surrogate of natural SPM to study the fate of ENPs. Moreover, coupled to a river-scale fate model, they enable ranking the potential ENP fate scenarios and assessing their risk within natural aqueous environments. This work was funded by the French National Research Agency and the Swiss FOEN as NANOHETER under the frame of SIINN. <http://nanoheter.cerege.fr>

INFLUENCE OF VERNADITE CRYSTAL STRUCTURE ON ITS REACTIVITY: IMPLICATIONS FOR METAL SORPTION AND PHYLLO-TO-TECTOMANGANATE TRANSFORMATION

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Vernadite is a nanocrystalline and turbostratic phyllomanganate which is ubiquitous in the environment. Natural occurrences of vernadite essentially result from the biogenically mediated oxidation of Mn(II). Similar to birnessite, vernadite layers are built of $(\text{MnO}_6)^{8-}$ octahedra connected through their edges and frequently contain vacancies and (or) isomorphic substitutions by cations of lower valence. Both create a layer charge deficit that can exceed 1 valence unit per layer octahedron and thus induces a strong chemical reactivity. In addition, vernadite has a high affinity for many trace elements and possesses a redox potential that allows for the oxidation of redox-sensitive elements or molecules. As a result, vernadite acts as a sink for many trace metal elements.

The present talk will report on the crystal structure variability observed for biogenic vernadite and for synthetic analogues of vernadite using a variety of analytical techniques including wet chemical analyses, X-ray absorption fine structure spectroscopy, and modelling of powder X-ray diffraction patterns. In particular, the number of vacant layer sites, that of layer and interlayer Mn^{3+} , the resulting average Mn oxidation degree, the Na/Mn ratio, unit-cell parameters, and crystallite size will be determined as a function.

Reactivity of structurally contrasted samples with respect to metal sorption or to their conversion to tunnel structures (tectomanganates) will be discussed.

MINERALOGICAL EVOLUTION IN A TEMPERATE CULTIVATED SOIL ARISING FROM DIFFERENT AGRONOMIC PROCESSES AND K-UP TAKE BY PLANTS: INSIGHTS FROM THE MORROW PLOTS EXPERIMENTAL FIELDS

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Potassium is an essential plant nutrient, with roles in photosynthesis, water regulation and disease resistance. In soils, 95-99 % of potassium is commonly contained in the crystal structure of K-feldspars and micas such as muscovite and biotite. Under natural conditions, release of this structural K is strongly dependent on the nature of the soil parent material and the rate of climate-induced weathering. Nevertheless, the ability of plants to extract non-exchangeable K has been observed and rapid mineralogical changes have been noted in the rhizosphere of plant roots in laboratory experiments, such as the vermiculitization of micaceous minerals following plant growth on clay substrate.

Long-term field experiments such as the Morrow Plots, which were established on the Urbana-Champaign campus in 1876, offer a unique chance to look at the effect of continuous plant growth on the evolution of clay minerals in natural soils. The present talk will report on the use of full-pattern X-ray diffraction modelling to obtain a comprehensive compositional description the clay minerals of the Morrow Plots in different clay sub-fractions (2-0.2, 0.2-0.05, and <0.05 μm) and to compare and contrast, quantitatively, the effects of 110 years (1904-2014) of continuous plant-growth under different agronomic practices on the status and potassium content of clay minerals in the soil.

Present day mineralogical differences in the Morrow plots are limited to a statistically insignificant increase of illite and smectite layers in continuous corn plots compared to crop rotation ones. The increase of the relative proportion of <0.05 μm sub-fractions of all subplots regardless of agronomic treatment between 1957 and 2014 is accompanied by an increase of the cation exchange capacity, suggesting that the latter increase is due to the higher proportion of expandable mixed-layers in the <0.05 μm sub-fraction.

The absence of mineralogical contrast as a function of agronomical practices will be compared to previous reports on the clay mineralogy of the Morrow Plots and its origin discussed in the light of literature data on potassium extraction from micas. Implications for soil evolution under continuous cultivation will also be discussed.

EVOLUTION OF ADSORBED METAL CATION SPECIATION DURING ION EXCHANGE AT THE MUSCOVITE (001)–WATER INTERFACE

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Ion adsorption on mineral surfaces controls the mobility of elements in natural environments. Molecular-scale observations of the interfacial structure provide fundamental insight into the mechanisms. We monitored the evolution of adsorbed cation speciation during cation exchange at the muscovite (001)–water interface with *in situ* time-resolved resonant anomalous X-ray reflectivity. The observations revealed unique structural variations in Rb^+ adsorption and desorption processes during its exchange with monovalent Na^+ or divalent Sr^{2+} . Desorption of Rb^+ by Na^+ is slow (i.e., 90% desorption takes ~25 sec), and occurs as a stepwise process in which thermodynamically stable inner-sphere (IS) Rb^+ [1] transforms to less stable outer-sphere (OS) Rb^+ before desorption from the interface. Rb^+ adsorption is twice as fast as desorption, and proceeds directly to the IS species within the experimental time resolution (~1 sec) [2]. A different trend was observed when it exchanged with Sr^{2+} . The initial distribution of adsorbed Rb^+ has equal proportions of IS and OS complexes, which slowly transforms to the thermodynamically stable IS species over ~30 sec. This slow transformation appears to be related to a slower desorption of IS Sr^{2+} than OS Sr^{2+} . In contrast, Rb^+ mostly maintains its stable adsorption state during desorption by Sr^{2+} , which adsorbs and is quickly stabilized into its stable distribution. These results indicate that metal adsorption and desorption processes can be significantly affected by the charge of competing metal cations.

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THE STRUCTURE, CHEMISTRY, AND TRANSFORMATION OF VERNADITE IN A FERROMANGANESE CRUST FROM A NORTH-WEST PACIFIC SEAMOUNT

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Vernadite is a nanocrystalline Fe-bearing manganese oxide, which is widespread in soils, sediments, freshwater, and marine deposits. The vernadite plays a crucial role in many geochemical processes such as global manganese cycling and adsorbing of toxic metals (Pb, Cd, Zn, etc.). Despite their environmental and geochemical importance, their atomic-scale structures and transformation pathways remain controversial. The uncertainties are apparently due to the short-range ordering of the nano-minerals.

We collected vernadite nano-mineral in ferromanganese crust from a North-West Pacific seamount and performed hydrothermal annealing experiment. The crystal structure, chemistry, and transformation of vernadite have been investigated by X-ray powder diffraction (XRD), micro X-ray fluorescence (XRF) mapping, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray pair distribution function (PDF). The XRD patterns of vernadite show two broad diffraction peaks at ~ 2.44 Å and ~ 1.42 Å with very weak and diffuse (001) diffraction. Based on XRF mapping with SEM- and TEM-EDS analysis, the vernadite is associated with Mg, Si, P, K, Ca, Ti and trace amounts of Co and Ni. The TEM images show the sheet-like shape of ~ 7 Å- and ~ 10 Å- vernadite nanophases from the inner (older) to outer (younger) crust. The vernadite nano-minerals of outer crust are more poorly crystallized and contain higher concentrations of Fe than those of inner area. The PDF results of vernadite are similar to synthetic δ -MnO₂ and defective birnessite, indicating the phyllomanganate structure with ferric iron in the octahedral sites. In addition, we have discovered a new modulated structure of manganese oxide from its annealed products. The new manganese phase is 2-D plate morphology showing ~ 46 Å periodicity.

The results show that the combined method is a powerful solution to determine atomic structure and chemistry at the nanoscale. The method will have potential implications in environmental science for understanding poorly crystallized nano-minerals.

THE IMPACT OF DETRITAL CLAY MINERALS ON CONTAMINANT DYNAMICS IN AMD-IMPACTED SYSTEMS

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In AMD-impacted systems, the prevailing solid phases can function as excellent platforms for immobilizing metal contaminants by mediating reactions such as sorption, binding, electron transfer, and repartition of metals during mineral transformation. In environments where both neoformed nano- and micro-scale particles (nNP) and detrital nano- and micro-scale particles (dNP) are present, the fate of metal contaminants is controlled by complex geochemical and microbiological processes [1]. For example, changing environmental conditions, such as shifts in solution pH and/or redox conditions often leads to microbially-mediated reductive dissolution of Fe(III)_{nNP} accompanied by a concomitant release of adsorbed and/or incorporated metals, thus substantially increasing contaminant mobility.

In this study we investigated metal immobilization mechanisms by the combined use of microbial community analysis, chemical extractions and synchrotron-based X-ray fluorescence (XRF), diffraction (XRD), and absorption (EXAFS) [2]. The use of an X-ray spot size as small as five micrometers allowed us to examine noninvasively heterogeneous AMD sediments collected from an abandoned coal mine in Southern Illinois. Our results showed that the bacterial and archaeal diversity was tightly controlled by the local geochemical conditions and was dominated by members of the Gammaproteobacteria, Acidomicrobia, Alphaproteobacteria, and Thermoplasmata classes known to be implicated in both Fe oxidation and reduction processes in acidic environment. We also found that the clay_{dNP} originating from the partial weathering of coal mining waste substantially increased the immobilization of metal contaminants by (1) enhancing heterogeneous precipitation of Fe(III)_{nNP} under oxic conditions, which then adsorbed or incorporated metals; (2) facilitating the transfer of previously immobilized metals from Fe(III)_{nNP} to clay_{dNP} during microbially-mediated dissimilatory reduction of Fe(III)_{nNP} coatings under anoxic conditions. Designing remediation strategies that incorporate clay_{nNP} could become a promising low-cost strategy for contaminant remediation in mining-impacted areas.

[1] Lefticariu, L.; et al., **2017**. *Science of the Total Environment* 575(1), 941–955.

[2] Sutton, S.R., et al., **2017**. *Journal of Environmental Quality*; 46(6), 1158-1165.

THE CONTRIBUTION OF DEHYDROGENATION IN THERMAL DECOMPOSITION OF Fe(II)-CONTAINING CHLORITES

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Two reactions: dehydroxylation and dehydrogenation control the amount of “structural water” transported by chlorites to metamorphic environments. By decreasing H content available for dehydroxylation, thus H₂O release, dehydrogenation leads to Fe(II) oxidation in the chlorite structure¹. Thermal decomposition of seven, monomineralic, tri-, trioctahedral chlorites from a common Mg-Fe series was studied in relation to these two reactions. Dehydroxylation was tracked thermogravimetrically (TG) under ramp heating conditions in pure nitrogen flow, up to 1000°C with 20°C/min rate, whereas dehydrogenation reaction was investigated by isothermal heating experiments (350–475°C for 24 and 48 h) performed on a selected chamosite. The TG was coupled with a quadrupole mass spectrometer in order to quantify H₂O and H₂ in evolved gases. Ex-situ samples collected after the isothermal, and ramp-heating steps were analyzed with Mössbauer spectroscopy and X-ray powder diffraction.

During the ramp-heating the total H₂/H₂O ratio was found to increase with Fe(II) content in the chlorite structure. The observed H₂ loss decreased the total mass losses upon dehydroxylation among all tested Fe(II)-containing chlorites (Fig.1). An increase in isothermal heating time resulted in an increase of dehydrogenation over dehydroxylation, which led to oxidation of almost 70% of Fe(II), in respect to maximum ~20% of oxidized Fe(II) after dehydroxylation-dominated ramp heating. Dehydrogenation was most intense in a narrow range of isothermal temperatures (390–410°C) and produced a discrete population of ferric chlorite, observed in XRD pattern with d-space of 1.39 nm, in coexisting with 1.42 nm of the initial chamosite. Higher isothermal temperature turned out to be more favorable for dehydroxylation. The broadening of 00l XRD reflections seemed to have the mixed-layer character phases of original, dehydroxylated and dehydrogenated chlorites.

Thermal decomposition of all Fe(II)-bearing chlorites involves two distinct but overlapping reactions: dehydroxylation and oxidative dehydrogenation, proceeding simultaneously (in time), but independently (in mechanism), and both without the presence of oxygen. Therefore, TG method in principle fails in determination of “structural water” content H₂O(+) in Fe(II)-chlorite and hence all Fe(II)-bearing phyllosilicates.

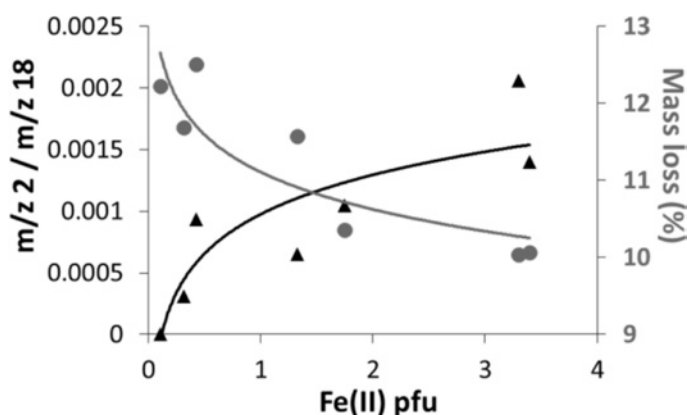


Fig. 1. The total H₂/H₂O ratio and the experimental total mass losses during the ramp-heating experiments, plotted as a function of Fe(II) content in seven studied Mg-Fe chlorites.

¹Borggaard, O.K. (1982) Oxidation and Reduction of Structural Iron in Chlorite at 480°C. *Clays and Clay Minerals*, **30**, 353–363.

INFLUENCE OF CRYSTAL ORIENTATION AND MOLECULAR DETAILS ON LONG-RANGE DISPERSION FORCES UNDERLYING AGGREGATION AND CO-ALIGNMENT BETWEEN CRYSTALS

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Oriented attachment of nanocrystalline subunits is recognized as a common crystallization pathway that is closely related to formation of nanoparticle superlattices, mesocrystals, and other kinetically stabilized structures. Approaching particles have been observed to rotate to achieve co-alignment while separated by nanometer-scale solvent layers. Little is known about the forces that drive co-alignment, particularly in this “solvent-separated” regime. To obtain a mechanistic understanding of this process, we used atomic force microscopy-based dynamic force spectroscopy with tips fabricated from oriented mica to measure the adhesion forces between mica (001) and TiO₂ (001) surfaces in electrolyte solutions as a function of orientation, temperature, electrolyte type, and electrolyte concentration. For mica system, The results reveal a ~60° periodicity as well as a complex dependence on electrolyte concentration and temperature. A continuum model that considers the competition between electrostatic repulsion and van der Waals attraction, augmented by microscopic details that include surface separation, water structure, ion hydration, and charge regulation at the interface, qualitatively reproduces the observed trends and implies that dispersion forces are responsible for establishing co-alignment in the solvent-separated state. For TiO₂ system, due to the under-saturated 4-coordinated Ti atoms on (001) surface, the surface is unstable and will be stabilized by chemisorption and physisorption of water. We investigated the effects of H-bond network on the surface. van der Waals and hydrogen bonding are the origin of adhesive forces. Molecular dynamics simulations that incorporate relevant molecular details provide a qualitative explanation for the observed orientation-dependence and suggest that hydrogen bonding is predicted to be the main source of the forces at a short range. Similarly as Mica system, we show that the forces exhibit 90° periodicity with respect to the lattice mismatch angle, which is generally consistent with the square-lattice arrangement of Ti⁴⁺ centers on the rutile TiO₂ (001) surface.

BIOAVAILABILITY OF TETRACYCLINE TO ANTIBIOTIC RESISTANT *ESCHERICHIA COLI* IN AQUEOUS CLAY SUSPENSIONS

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The objective of this study is to evaluate the bioavailability of clay-sorbed tetracycline to bacteria for expression of antibiotic resistance genes in water. Tetracyclines are a class of antimicrobials frequently found in the environment resulting from their extensive use in human and veterinary medicine and in animal agriculture. A fundamental unanswered question is whether the extensive binding of tetracycline to soil clay minerals reduces or eliminates its bioavailability to bacteria for invoking antibiotic resistance genes. In this study, a bioreporter *E. coli* MC4100/pTGM was used as a probe strain to measure the bioavailability of tetracycline sorbed by smectite clay. Liquid chromatography coupled to a tandem mass spectrometer was used to quantify tetracycline concentration in solution and in the *E. coli* strain. In dilute clay suspension, desorption of clay-sorbed tetracycline into bulk solution was the major but not the singular exposure pathway to bioreporter for activating bacterial antibiotic resistance genes. Direct contact of *E. coli* bioreporter with clay surfaces was another important pathway in which clay-sorbed tetracycline could be transferred into the bacteria, and activate the antibiotic resistance genes. For the smectite clays with sorbed tetracycline after two cycles of desorption, reducing solution volume resulted in more bacterial populations attached to mineral surfaces, leading to the increasing expression of tetracycline resistance genes. The strong fluorescence emission from the bioreporters cultured on clay surfaces clearly indicated that clay-sorbed tetracycline was still bioavailable to *E. coli*. In this instance, biofilm formation could possibly facilitate the bacterial access to clay-sorbed tetracycline. Bacterial attachment to geosorbent surfaces is most common in soils, which could apparently enhance bacterial access to soil-sorbed tetracycline. The increased selective pressure could be created and exert onto the surrounding microbial communities for the development and enrichment of antibiotic resistance genes.

HETEROGENEOUS POLY(IONIC LIQUIDS) CATALYST ON NANOFIBER-LIKE Palygorskite SUPPORTS FOR BIODIESEL PRODUCTION

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New heterogeneous poly(ionic liquids) catalysts (PAL-PILs) were successfully prepared by grafting polymerization of acid ionic liquids (ILs) (1-butylsulfonate-3-vinylimidazole hydrogen sulfate) onto nanofiber-like palygorskite (PAL) supports that had been, in advance, covalently modified by γ -methacryloxypropyl trimethoxy silane (OPAL). Using the ester yields and PILs grafting degrees as main indexes, the optimized immobilization conditions were that the mass ratio of OPAL to ILs monomer was 1:2, the immobilization temperature and time were 60 °C and 30 h, the initiator (2,2'-Azobis(2-methylpropionitrile) dosage was about 5 wt. %, respectively. Then, the esterification between methanol and oleic acid was carried out to investigate the catalytic properties of PAL-PILs. For the homogeneous ILs catalyst, the yield of methyl oleate was about 85%. For the PAL-PILs, on which only about 41% of ILs used in homogeneous catalysis was immobilized, the yield could reach over 69% after reacting only 5 h at 75 °C at atmospheric pressure, when the molar ratio of methanol to oleic acid is adjusted to 12:1. More importantly, the yield of methyl oleate still maintained at about 22% after 6 recycling experiments. Moreover, the PAL-PILs catalysts exhibited efficient catalytic properties and could be recycled easily. These results offer great potential for the PAL-PILs in the biodiesel production for further research.

STRICT ION-EXCHANGE MODELING FOR CATION SELECTIVE ADSORPTION ON NA-MONTMORILLONITE

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Various types of ion-exchange models have been developed to simulate cation adsorption in clay minerals. However, many complex assumptions and parameters are involved in most models. In this study, a strict ion-exchange model was developed to predict alkali cation (i.e. Cs^+ , K^+ , Na^+ , Li^+) adsorption in Na-montmorillonite.

Cation adsorption envelopes and isotherms were conducted. Then strict ion-exchange model was built, which involves three basic assumptions: (1) all reactions are ion-exchange reactions; (2) all reactions follow mass balance, and (3) charge balance. An IExfit software (<http://www.alfisol.com>) was specifically developed for the strict ion-exchange model.

The strict ion-exchange model simulated the cation adsorption on Na-montmorillonite (NaMt) very well. Two types of cation adsorption sites (site S1 and S2) were predicted from the model. The cation adsorption equilibrium constant K at site S1 was much higher than at S2 for all the cations. The cation adsorption equilibrium constant K increased in the sequence of $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ at both sites. The Na^+ adsorption equilibrium constant K increased in the presence of other co-adsorbing alkali cations at both sites, and the enhancement effect followed the sequence $\text{Li}^+ < \text{K}^+ < \text{Cs}^+$. This increase in Na^+ adsorption strength can be explained by the nano-pore inner-sphere enhancement effect^{1,2}.

X-ray diffraction analysis of the clay minerals showed that NaMt with Cs^+ adsorbed had the smallest interlayer d001 spacing compared to other cations, which was consistent with the strong adsorption strength of Cs^+ . The interlayer d001 spacing suggested that all the cations were partially dehydrated in the interlayer and were probably adsorbed via an inner-sphere mechanism.

This study showed that the strict ion-exchange model provides a feasible and efficient tool to simulate alkali cation adsorption on montmorillonite. Moreover, Na^+ is a significant competitor in ion-exchange reactions in montmorillonite instead of an inert background electrode. The adsorption strength of Na^+ is enhanced by the presence of other alkali cations as is qualified by the increase in its equilibrium constant K values.

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ZN ISOTOPE FRACTIONATION DURING SORPTION ONTO AL OXIDE: MOLECULAR LEVEL UNDERSTANDING FROM ZN EXAFS INVESTIGATION

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Zn stable isotope signatures have proved effective in tracking Zn sources in polluted environments, however, interactions between Zn in solution and in minerals in soils and sediments can lead to notable Zn isotope fractionation and affect Zn source identification. Therefore, it is important to understand Zn isotope fractionation during its sorption onto soil minerals and the underlying mechanism. In this study, we quantify zinc isotope fractionation during its sorption onto Al oxide, by performing experiments under various pH and total Zn concentrations and measuring Zn isotope signature using Multicollector-Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS). Results showed a systematic enrichment in heavy Zn isotopes on the surface of Al oxide, with $\Delta^{66}\text{Zn}$ adsorbed-solution ranging from $0.50 \pm 0.16\text{‰}$ at low pH (e.g., pH 6) and low concentration (e.g., 0.2 mM) to $0.10 \pm 0.02\text{‰}$ at high pH (e.g., pH7.5) and high concentration (e.g., 0.8 mM). These different magnitudes of Zn fractionation are related to structural differences between Zn sorption mechanism existing on the high pH (octahedrally coordinated Zn by oxygen atoms) and low pH (tetrahedrally coordinated Zn by oxygen atoms), as evidenced by Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. EXAFS analysis also suggest Zn-Al layered double hydroxide (LDH) formed at high pH and high concentration, the structure of which has a Zn-O bond distance of 2.06 Å. In contrast, at low pH or low concentration, results from EXAFS indicates Zn sorbed as an inner-sphere surface complex, with Zn-O interatomic distance being 1.99 Å. These two distinct mechanisms indicate that Zn isotope fractionation is dominantly controlled by the chemical composition of the solution (pH, concentration) and these factors should be considered when using Zn isotope to track pollution source.

HETEROGENEOUS REDUCTION OF 2-CHLORONITROBENZENE BY CO-SUBSTITUTED MAGNETITE COUPLED WITH AQUEOUS Fe^{2+}

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This study investigated the heterogeneous reduction of 2-chloronitrobenzene (2-Cl-NB) by Co-substituted magnetite ($\text{Fe}_{3-x}\text{Co}_x\text{O}_4$, $0.00 \leq x \leq 1.00$) coupled with aqueous Fe^{2+} . Magnetite (Fe_3O_4) has been applied extensively to environmental remediation because of its unique structural, electronic, magnetic, and redox properties. The interaction of magnetite with aqueous Fe^{2+} could efficiently reduce many environmental contaminants, e.g., organics, heavy metals, and radionuclides. In natural environments, iron ions in magnetite can be replaced isomorphously by other transition metal ions. Among the substituted magnetites, Co-substituted magnetite ($\text{Fe}_{3-x}\text{Co}_x\text{O}_4$) is an environmentally benign material because it can easily be separated from solution due to its ferromagnetic nature. The strong Fe-Co interaction also suppresses Co leaching. Moreover, Co substitution introduces the thermodynamically favorable redox pair Co(II)/Co(III) which may not only change the surface properties and microstructure of magnetite, but also may promote structural electron transfer during the reaction. All of these factors are also expected to affect the reducibility of magnetite coupled with absorbed Fe^{2+} from solution. All studied samples had a spinel structure with Co(II) preferentially occupying the octahedral sites. The effect of aqueous Co^{2+} concentration and the total Co level were compared to confirm the significant role of Co substitution on the reduction processes. Both the reaction kinetics and electron transfer amount illustrated that Co substitution generally promoted the reduction activity of magnetite/ Fe^{2+} systems, while an overdose of Co ($x \geq 0.85$) retarded the process. A good linear correlation ($R^2 \geq 0.94$) between the observed rate constant (k_{obs}) and the electrical conductivity of the $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ was established. The result may be ascribed to not only the occupancy and valence of Co but also to the structural Fe(II) content. The redox pairs Co(II)/Co(III) and Fe(II)/Fe(III) in the octahedral sites accelerated the electron transfer between absorbed Fe^{2+} and $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ -2-Cl-NB. However, as Co substitution increased up to 0.85, the structural Fe(II) occupying the octahedral sites of magnetite was too low to induce effective reductive reactivity. During the redox reaction, the surface Fe^{2+} of $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$ was gradually oxidized without the obvious phase transformation.

CO-ADSORPTION OF PHOSPHATE AND Cd(II) ON IRON (OXYHYDRO)OXIDES: A COMPARATIVE STUDY ON FERRIHYDRITE, GOETHITE, AND HEMATITE

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The adsorption and co-adsorption behaviors of phosphate and Cd(II) on three iron (oxyhydr)oxides, which are ubiquitously reactive constituents of soils, sediments, and aquifers, were comparatively studied by batch adsorption experiments and *in situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. Ferrihydrite (Fh) showed the strongest capacity in the uptake of phosphate and Cd(II) in single adsorption systems, followed by goethite (Gt) and hematite (Hm). The adsorption of phosphate on the three minerals showed significant differences in the bonding modes as well as the protonation states. On the surface of Gt and Hm, two complexes primarily formed with their proportions differed. The non-protonated bidentate complex was the dominant complex on Gt at pH 5–9, while the dominance of complexes on Hm changed with solution pH. Phosphate species on Fh were more diversified due to the diversity of surface sites. In the simultaneous adsorption systems, synergistic adsorption of phosphate and Cd(II) on the three minerals were observed. Besides, the relative affinities of the minerals to phosphate and Cd(II) showed a positive relationship with the surface charge and a negative correlation with surface coverage. In addition to the electrostatic interaction, phosphate-bridged ternary complexes could form on the three minerals, contributing to the synergistic adsorption of phosphate and Cd(II). Results in this study suggested that the transformation of the amorphous iron (oxyhydr)oxide (Fh) to the crystallized minerals (i.e., Gt and Hm), accompanied by the decrease of the specific surface area and the reactive surface sites, might lead to the increase of ions mobility.

SIZE-DEPENDENT AGGREGATION OF HEMATITE PARTICLES IN AQUATIC ENVIRONMENTS

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The aggregation state of nanoparticles significantly impacts their transport, reactivity, bioavailability, and fate in natural waters. Studying aggregation behavior of nanoparticles in aqueous dispersions under environmentally relevant conditions is important for understanding the role of nanoparticles in a variety of biogeochemical processes. In this study, aggregation kinetics and aggregate structures of 9, 36, and 112 nm hematite particles in aqueous solutions at near-neutral pH were investigated by using time-resolved dynamic light scattering (TR-DLS) and in situ liquid-cell transmission electron microscopy (LCTEM), respectively. The attachment efficiencies, representing the probability of an irreversible attachment resulting from the collision of two particles, increased with the increase of NaCl concentration until the salt concentration reached the critical coagulation concentration (CCC). When particle loading was same, the CCC value of 9, 36, and 112 nm hematite particles was 55, 45, and 14 mM, respectively. When OmcA, a bacterial extracellular protein, is present in the solution with a low ionic strength (10 mM NaCl), the attachment efficiencies of hematite particles in all sizes first increased, then decreased, and finally remained constant with the increase of OmcA concentration. Although the changing trend of attachment efficiencies were different as the function of NaCl and OmcA concentrations, due to the different inter-particle interactions induced by NaCl and OmcA, attachment efficiencies changed more quickly in the case of the relatively larger particles as the NaCl or OmcA concentration increased. Aggregate structure of 9, 36, and 112 nm hematite particles were studied based on the statistic results of projected area equivalent diameters (D_m) and fractal dimensions of the aggregates that were observed in the LCTEM images. The values of D_m from LCTEM agreed well with the hydrodynamic diameters measured using DLS. When particle loading was same, the aggregates of 9 nm nanoparticles were statistically more compact and slightly larger than those of 36 nm nanoparticles. The findings in this study present the different aggregation behavior of the hematite nanoparticles with different primary particle sizes, which can provide new insights into the size-dependent reactivity and mobility of nanoparticles in aqueous environments.

HYDROTHERMAL SYNTHESIS OF CHLORITE FROM SAPONITE: KINETICS AND MECHANISMS OF SMECTITE-CHLORITE CONVERSION

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Smectite-chlorite conversion in response to increasing temperature is by far the most common series of trioctahedral clay minerals associated with chloritization under a range of geological settings. However, the kinetics and mechanisms of this process are still poorly understood. We conducted hydrothermal experiments to study the smectite-chlorite conversion by reacting saponite with varied amount of Mg^{2+} and Al^{3+} in NaCl solution at 340 °C and 14.5 bar. Reacted solution and solid phases were characterized by inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray diffraction (XRD), and scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX). Hydrothermal experiments reached steady state after 24 h with the formation of chlorite, while the formation of mixed-layered chlorite/smectite was not observed. Such a fast smectite-chlorite conversion appeared to take place solid state transformation as characterized by the formation of hydroxide layers in the saponite interlayers, coupled with the substitution of Al^{3+} for Si^{4+} in the 2:1 layers. Our results contribute to the fundamental understanding of smectite-chlorite conversion, and provide important information for assessing the influence of smectite-chlorite conversion on petroleum formation and qualities of chlorite-bearing reservoirs.

EFFECTS OF ORGANIC LIGANDS ON HEXAVALENT CHROMIUM REDUCTION BY STRUCTURAL IRON IN NONTRONITE

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Previous studies have shown that the presence of citrate decreased the Cr(VI) reduction rate by structural Fe(II) in chemically reduced nontronite (rNAu-2), but increased the amount of Cr(VI) reduction. In order to further explore the underlying Cr(VI) reduction mechanism by rNAu-2 in organic ligand-containing systems, the influences of different organic ligands (tartrate, malate, succinate, lactate, pyruvate, and propionate) on the Cr(VI) reduction by chemically reduced rNAu-2 were investigated under dark, near neutral pH condition (pH=6). Our results showed that the reduction rate and removal amount of Cr(VI) in ligand-containing system by structural Fe(II) in rNAu-2 was in the order: tartrate (with 2 -COOH and 2 - α -OH groups) > malate (with 2 -COOH and 1 - α -OH groups) > lactate (with 1 -COOH and 1 - α -OH groups) > pyruvate (with 1 -COOH and 1 - α =O groups) > no-ligand system > propionate (with 1 -COOH) > succinate (with 2 -COOH), which suggest that functional groups of these ligands such as - α -OH and - α =O, but not -COOH played critical roles in this process. In addition to the increased Cr(VI) reduction rate, the presence of tartrate, malate, and lactate resulted in higher concentration of aqueous Cr at the end of reaction, indicating the formation of soluble Cr(III)-organic ligand complexes. In contrast, systems containing pyruvate, succinate and propionate or in no-ligand system demonstrated similar aqueous Cr(VI) and total Cr concentration, suggesting the reduction product of Cr(VI) is solid, likely in association with nontronite. The increased amount of Cr(VI) reduction in the presence of organic ligands (tartrate, malate, lactate, and pyruvate) was likely due to a ligand-metal electron transfer mechanism when Fe^{2+/3+} was released from dissolution of rNAu-2. Our study highlights the importance of organic ligands on Cr(VI) reduction and immobilization when iron-bearing clay minerals are applied to treat Cr(VI) contaminant in organic rich environments.

MINERALOGICAL PROPERTIES AND ENVIRONMENTAL IMPLICATION OF MN-SUBSTITUTED GOETHITE

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Iron oxides are the most common natural adsorbents that remove various heavy metals from solution and retain it in the solid phase. Among various iron oxides, goethite (α -FeOOH) is uniquely important because of its widespread abundance, high adsorption capacity, and strong affinity for heavy metals. It has been disclosed that natural goethite generally accommodates various metals by Fe-substitution, which commonly remarkably alters its surface properties and environmental performance. In this study we characterized the structural and surface properties of synthesized Mn-goethite by using synchrotron-based X-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy, and specific surface area measurement. Mn substitution causes a slight decrease in the a and c of the unit cell parameters and an increase in the b direction. With the Mn content increasing, the particle size decreases gradually and the surface becomes roughened, both of which clearly increases the specific surface area. Therefore, the Mn-goethite shows much higher Pb^{2+} adsorption capacity than pure goethite due to increased specific surface area and modified surface complexes. Extended X-ray absorption fine structure analysis indicates that the binding structures of Pb^{2+} on Mn-goethite presents as edge-sharing complexes with a regular $R_{\text{Pb-Fe}} = 3.31 \text{ \AA}$ and a larger $R_{\text{Pb-Mn}} = 3.47 \text{ \AA}$. The enhancing Pb^{2+} adsorption can be attributed to the preferred Pb^{2+} binding on the Mn sites. The environmental behaviors of Mn-goethite are also different from the pure goethite in the fixation of arsenic. In solutions with pH 7, 1 mM Fe(II) and 0.3 mM As(V), As(V) could be rapidly adsorbed by goethite, while Mn-goethite shows much lower As adsorption capacity. In contrast, in an acid solution of pH 4, Mn-goethite can promote the removal of arsenic from solution. Extended X-ray absorption fine structure spectroscopic analysis shows that As(V) forms inner-sphere surface complex and no evidence indicates redox reactions between Fe(II) and As(V). In a summary, this study shows Mn-goethite may have great application potential for environmental remediation of heavy metal contamination.

DISORDER IN MG-Fe CHLORITES WITH SEMI-RANDOM STACKING AND POLYTYPES' INTERSTRATIFICATION STUDIED WITH POWDER X-RAY DIFFRACTION

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Chlorites are built of two main building blocks: the 2:1 layer and the interlayer octahedral sheet arranged alternately one to another. Depending on relative shifts in the **a** crystallographic direction, six different polytypes can be distinguished: Iaa, Iab, Ibb, IIaa, IIab, IIbb. Additionally, in the **b** direction adjacent layers can be shifted by 0 or $\pm 1/3b$. Semi-random stacking sequences represent mixed layering of structures containing all three types of shifts in **b** direction. In chlorites, the stacking pattern can be distinguished using major *hkl* reflections with $k \neq 3n$ ($20-28^\circ$ 2θ for $\text{CoK}\alpha$).

The main goal of this study was to use powder XRD data to determine chlorite structure, including stacking sequences and interstratification of different polytypes.

Seven Mg-Fe chlorites were chosen for the study as representative for a common chlorite series. The samples contained quartz and rutile impurities below 3% whereas the interstratification of 7 Å minerals above 20% was excluded. All samples were determined as IIbb polytype with monoclinic cell shape; the cell parameters were found using LaBail fitting. Further analysis was based on simulations performed in Sybilla3D program, which was modified by adding the parameter describing stacking disorder, understood as a probability of finding layer type *x* in mixed layered stacking, assuming R0 ordering and shifts along **b** direction about $+1/3b, -1/3b$ ($W_{\text{IIb},y=\pm 1/3b}$), the distribution of Fe between 2:1 and interlayer (R_{int}), the percent of layers shifted only in one direction (R_{shift}), and the fraction of different polytypes with a random interstratification model.

Comparing the experimental powder XRD patterns with models showed that the XRD features in the range $20-28^\circ$ 2θ ($\text{CoK}\alpha$) were strongly dependent not only on the percent of layers shifted by $\pm 1/3b$ ($W_{\text{IIb},y=\pm 1/3b}$), but mostly on R_{shift} parameter. In three analysed samples, where the *hkl* reflections with $k \neq 3n$ were slightly distinguishable, 70 to 90% of layers were found shifted in one $1/3b$ direction.

Regardless the chlorite chemical composition, the polytypes interstratification model returned the presence of 5 to 19% of Iaa, IIab, or IIaa polytype. Except the presence of IIaa polytype, similar conclusions, were given by Kogure and Banfield (1998) and Inoue and Kogure (2016), based on HRTEM study.

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COUPLED REDOX CYCLING OF MANGANESE AND CARBON ON IRON OXIDE SURFACES

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Mineral surfaces catalyze oxidation of divalent manganese (Mn(II)) by O₂ to form Mn(III,IV) oxides. Mineral surfaces are often coated with natural organic matters (NOM), which may affect Mn(II) oxidation. On the other hand, the presence of Mn(II) may affect NOM behavior on mineral surfaces. In this study, we examined Mn(II) oxidation on goethite surfaces in the presence of humic acid (HA) at pH 5–8 and various HA and Mn(II) concentrations. Results showed that the presence of Mn(II) remarkably increased HA adsorption whereas HA greatly impaired the extent and rate of Mn(II) oxidation on goethite surfaces. Mn(II) oxidation produced multiple MnOOH phases which in turn oxidized HA. These impacts were more pronounced at higher pH. Our results provide insights into coupled cycling of carbon, Fe and Mn that are often closely associated with each other in soils and sediments.

DYNAMICS OF MINERAL-ORGANIC MATTER COMPLEXES DURING MINCROBIAL FE REDUCTION

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The dynamics of mineral-organic matter (OM) complexes during dissimilatory microbial Fe(III) reduction have major implications for the biogeochemical cycles of Fe and the stability of associated OM. In this study, we synthesized three different mineral-organic matter (OM) complexes by co-precipitation of ferrihydrite and water-extractable OM in the presence of different clay minerals (kaolinite and montmorillonite). These complexes were bio-reduced by *Geobacter sulfurreducens* with H₂ or mineral-associated OM as electron donor. The rate and extent of Fe(III) bioreduction, as well as the release and transformation of organic matter (OM) in mineral complexes were investigated. Over a 10-day reduction period, 11.2%-22.4% of structural Fe(III) in ferrihydrite was reduced with H₂ as external electron donor, and ~ 50% mineral-associated OM was released from mineral complexes. Without H₂, about 2% of Fe(III) in ferrihydrite was reduced, suggesting that natural organic matter associated with minerals could provide electrons for microbial respiration. A faster reduction rate of Fe(III) in ferrihydrite was observed in the presence of clay minerals, possibly because biogenic Fe²⁺ was likely sorbed to the clay minerals, and thus the passivation effect was alleviated. The amount of OM release from the mineral complexes was basically the same with H₂ or mineral-associated OM as electron donor, even though the reduction extent was much higher with H₂ (11.2-22.4% vs. 2%), possibly because when OM served as electron donor, more extensive OM release and transformation may be required. In addition, when no external electron donor was present, microbes may have secreted more metabolites like organic acids to dissolve the mineral-OM complexes in order to help them better utilize the mineral-associated OM. Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) data revealed OM transformations as a result of microbial activity. Our results indicate that the dissimilatory iron reduction is an important mechanism for Fe dissolution and OM transformation, and the presence of clay minerals and exogenous electron donors significantly affect this process.

ADSORPTION OF PHENOL, PHOSPHATE AND Cd(II) BY INORGANIC-ORGANIC MONTMORILLONITES: A COMPARATIVE STUDY OF SINGLE AND MULTIPLE SOLUTE

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Organo-montmorillonite (OMt), modified by surfactant, is proved to be an efficient adsorbent for organic contaminants. Hydroxyl-metal pillared montmorillonites, on the other hand, exhibits a strong affinity for heavy metals and phosphate. Inorganic-organic montmorillonite (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 contaminant, 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. The findings may provide novel information for developing new effective IOMt adsorbents toward multi-contaminant, which are often encountered in practical scenarios.

Inorganic-organic montmorillonites (IOMts) obtained by modifying polyhydroxy-aluminum (Al_{13})-pillared montmorillonite (AlPMt) with the cationic surfactant (C16) and 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 Al_{13} contents of C16 modified AlPMts (C-AlPMts) decreased with increasing C16 loading while that of Z16 modified AlPMt (Z-AlPMts) 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 adsorptions of phenol on IOMts were not affected by the other two inorganic components and vice versa. Whereas the adsorptions of phosphate and Cd(II) were 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 Al_{13} content were much larger than that on IOMts with lower Al_{13} content. The adsorption mechanism for phosphate and Cd(II) uptake in the multi-contaminant system possible involve the formation of phosphate-bridged ternary complexes.

CONFORMATION OF ALKYLAMMONIUM CATIONS IN MONTMORILLONITE INTERLAYERS AS REVEALED BY NEAR-IR SPECTROSCOPY

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The properties of organoclays, employed in a variety of industrial and environmental applications, depend largely on the structure and arrangement of organic cations (surfactants), within clay mineral interlayers. Detailed information on the conformation of surfactants, most often alkylammonium cations, provides infrared (IR) spectroscopy. While mid-IR region has been frequently used to follow the conformational changes of the chains by monitoring the wavenumber shifts of the CH₂ stretching bands, the utilization of the near-IR (NIR) region is seldom though the first overtone and combination bands of the CH₂ groups appeared in this region. The main objective of the present work was to evaluate the effect of the chain length, head-group structure, and temperature on the ordering of surfactants in montmorillonite interlayers by NIR spectroscopy. The samples were prepared from Na-montmorillonite Jelšovský Potok (JP, Slovakia) and trimethylalkylammonium (C_N-N(CH₃)₃) and alkylammonium (C_N-NH₃) cations with increasing number of carbons (*N* = 6, 8, 10, 12, 14, 16, and 18) in alkyl chain. The NIR spectra of organo-montmorillonites showed the complex band in the 6100-5600 cm⁻¹ region related to the first overtone (2νCH) of the CH₃ and CH₂ groups. The position of the 2ν_{as}CH₂ component, observed in the 5820-5780 cm⁻¹ interval, reflected an abundance of disordered *gauche* and ordered *trans* conformers. With increasing alkyl chain length the band was shifted to lower wavenumbers indicating decreasing amount of disordered in favour of ordered conformers. The mutual comparison of the spectra of the samples with the same alkyl chain length but different head-groups showed that the position of the 2ν_{as}CH₂ band was always higher for C_N-NH₃-JP than for C_N-N(CH₃)₃-JP sample. Due to the different mode of head-group binding, namely N-H...O-Si hydrogen bonds for -NH₃ versus more flexible bonding of -N(CH₃)₃ to basal oxygens, the C_N-NH₃ surfactants adopted less ordered conformation than their C_N-N(CH₃)₃ counterparts. To probe the effect of temperature on the alkyl chains ordering the C₁₈-NH₃-JP and C₁₈-N(CH₃)₃-JP samples were examined. As a result of heating the occurrence of *gauche* conformers increased as indicated the upward shift of the CH₂ overtone band position by 5 and 3 cm⁻¹ for C₁₈-N(CH₃)₃-JP and C₁₈-NH₃-JP, respectively. The reverse changes were found for samples cooled to the temperature of liquid nitrogen. The combination CH₂ bands were shifted by ~5 and 3 cm⁻¹ to lower wavenumbers for C₁₈-N(CH₃)₃-JP and C₁₈-NH₃-JP, respectively indicating an increase of the amount of ordered conformers. Though the shift of the CH₂ bands in dependence on temperature was rather small, it is evident, confirming thus the potential of NIR spectroscopy to provide insight into the interlayer structure of organoclays.

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MONTMORILLONITIC CLAY APPLICATIONS IN WASTE WATER TREATMENT

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During several years and a fruitful collaboration, bentonite samples collected from various deposits in Romania, namely Orasul Nou—ON (Satu Mare County), Petresti—P (Cluj County), Valea Chioarului—VCh (Maramures County) and Gurasada—GS (Hunedoara County), were characterized in raw and treated forms, and tested in various waste water treatment processes.

A thorough characterization using bulk chemical analysis, X-ray diffraction, scanning electron microscopy—energy dispersive X-ray spectroscopy, N₂ adsorption and Fourier transformed infrared spectroscopy was realized. UV-VIS analysis was also used to investigate the interaction between the adsorbed dyes and the adsorbent surface.

Clay mineral samples were tested for the removal of heavy metal (e.g. Zn²⁺, Pb²⁺, Cd²⁺) and ammonium ions or for the adsorption of organic compounds such as phenol, pesticides and dyes. Metal modified clay samples were also tested as catalysts for wet air oxidation of phenol.

A number of operational parameters such as clay quantity, solid:liquid ratio, pollutant concentration, temperature, pH, air flow or type of batch conditions (immobile phases, magnetic stirring, shaker) were considered, in order to establish their influence over the process efficiency and adsorption capacity.

As superior valorization of this type of natural materials would bring added value to some environmental applications, future studies will focus on the synthesis of various metal based catalysts for advanced oxidation processes.

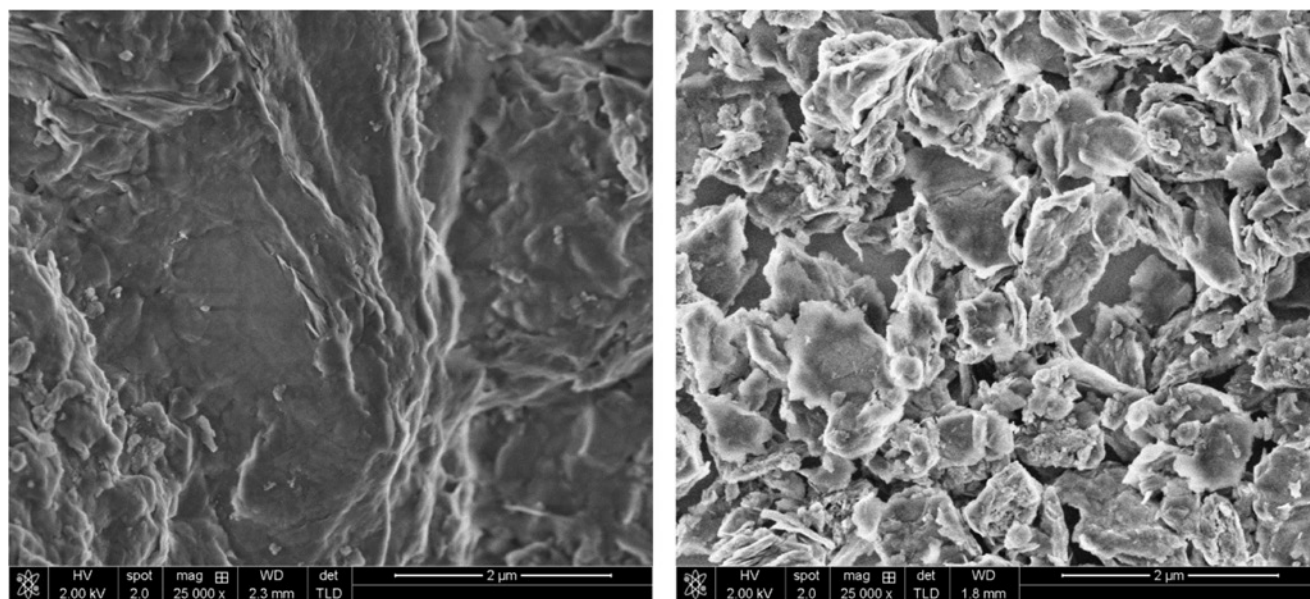


Figure 1. SEM images of P sample in raw (left) and Al-pillared (right) forms.

IMPORTANCE AND DIVERSITY OF GEOLOGICAL SETTINGS OF ALUMINUM-RICH CLAY MINERALS ON MARS

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Clay minerals on Mars have first been found by near-infrared (NIR) spectrometers onboard orbital missions (see Carter et al., this conf.). A huge diversity of hydrous silicates has been identified, from low-T species such as smectites to relatively high-T minerals such as prehnite or pumpellyite. The diversity of context in which they are found, from sedimentary layers to central peaks of impact craters, demonstrates that a single process cannot explain all their occurrences. Among clay minerals, aluminum phyllosilicates such as the kaolinite group are of strong importance because of their possible link to pedogenetic processes. For instance, kaolinite is clearly identified in NIR spectra from the presence of a 2.16-2.20 mm doublet, but the spectral signature does not provide a direct access to its temperature of formation or other parameter linked to its process of formation (see Baron et al., this conference). For instance, low-T kaolinite formed by pedogenesis has not a spectral signature much distinct from hydrothermal kaolinite. In addition, identification of shallow absorption bands can be difficult because spectra acquired from orbit through the atmosphere of a planet are relatively noisy. Thus, a detailed understanding of the context of formation of these minerals is required to enable a better understanding of their origin.

On one hand, Al-rich clays (such as kaolinite) are frequently observed as a thin layer (<20 m) overlying a thicker (>50 m) section of Fe-Mg smectites (such as nontronite). Because the same mineralogical stratigraphy extends over a region 300 by 300 km in size in the Mawrth Vallis region, this sequence has been interpreted as a potential pedogenetic profile. The same sequence has been observed in several regions of Mars of similar age (3.7-3.8 Gy), suggesting that a global episode of weathering occurred at this period. The presence of kaolinite-topped sequence of pedogenetic alteration on early Mars questions the actual climate of that period. While an Earth-like tropical weather is difficult to justify in Mars context, a temperate climate with potentially more acidic conditions may have triggered the observed sequence quicker than it would on Earth. On the other hand, a large number of Al-clays outcrops are not associated with underlying Fe-Mg smectites. Indeed, Al-clays have also been detected in the context of low-T acidic fluid circulation in sedimentary layers where minerals such as jarosite have been detected, as well as in crustal outcrops where hydrothermal alteration is favored.

COMPETITIVE SORPTION OF SULFAMETHOXAZOLE-TRIMETHOPRIM AND SULFAMETHOXAZOLE-CADMIUM (II) ON AN ORGANOCLAY

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Adsorption has been considered an effective separation method for removing emerging pollutants such as antibiotics and toxic pollutants such as heavy metals. The competitive sorption of the antibiotics sulfamethoxazole (SMX) and trimethoprim (TMP) and SMX-Cd(II) on an organoclay was studied in this work. The organoclay was prepared by sorbing the surfactant hexadecyltrimethylammonium bromide on bentonite. The effects of temperature and solution pH upon the sorption capacity of BHDTMA towards single SMX were analyzed, and the sorption of SMX on the BHDTMA was confirmed by FTIR analysis. The predominant sorption mechanism of SMX on the organoclay was partition due to hydrophobic interactions. Besides, the single adsorption of Cd(II) and TMP onto the organoclay was due to electrostatic interactions and hydrophobic partition, respectively. The competitive sorption of SMX-TMP was antagonistic because the sorption of one antibiotic on BHDTMA was reduced by the presence of the other antibiotic. This behavior is depicted in Figure 1. The competitive sorption of SMX-Cd(II) on organoclay showed that the sorption of SMX was non-interactive because it was not influenced by the presence of Cd(II), as shown in Figure 2. On the other hand, the sorption of Cd(II) was cooperative since the uptake of Cd(II) sorbed was considerably enhanced by the uptake of SMX sorbed on the organoclay. This increase in the adsorption capacity was because Cd^{2+} were sorbed on two types of sites: a) cationic sites of the organoclay and b) π -cation interactions between the aromatic ring of the SMX sorbed on organoclay and Cd^{2+} in solution.

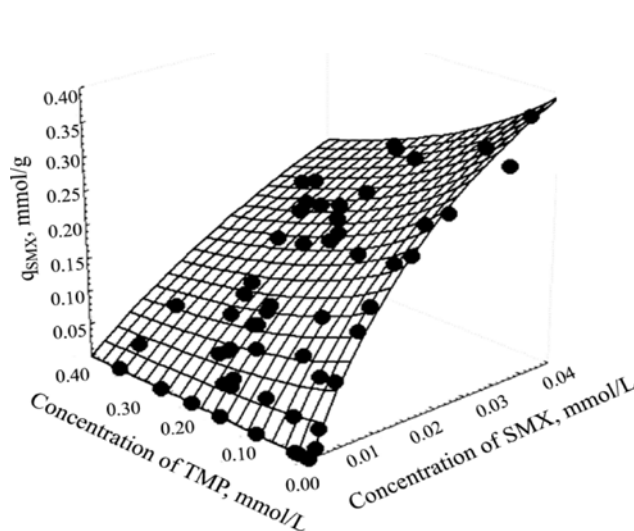


Figure 1. Uptake of SMX in the competitive sorption of SMX-TMP on organoclay. pH = 7 and T = 25 °C.

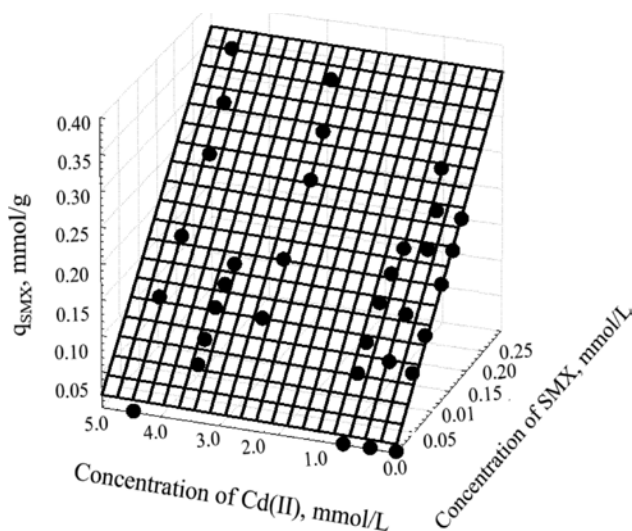


Figure 2. Uptake of SMX in the competitive sorption of SMX-Cd(II) on organoclay. pH = 7 and T = 25 °C.

PROBING THE MINERAL SURFACE REACTIONS OF RADIONUCLIDES WITH ADVANCED SOLID-STATE NMR TECHNIQUES

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Understanding the interactions between radionuclides and mineral surfaces is critical to modeling their flow and transport in the subsurface. Solid-state NMR spectroscopy provides a crucial tool in studying mineral surface reactions, but the study of radionuclide interactions and particularly those of actinides is challenging. Most transuranic actinides exist in natural waters in oxidation states that make their surface species paramagnetic (eg. Pu(IV), Pu(V), Np(VI)). Further, the radioactive nature of these samples requires small sample sizes which further constrain an already insensitive technique. In our work, we have been exploring the indirect effects of paramagnetism on the solid-state NMR of natural and engineered surfaces. We have also been developing statistical data processing methods which dramatically enhance the signal from mineral surfaces.

In the first portion of the talk, we will discuss the investigation of paramagnetic metal sorption to the amorphous silica surface. In these studies, we used the effects of the paramagnet on the variable contact time (VCT) $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR to determine the specific surface chemical environments that bind these metal species. Further, we show that these effects on the CP/MAS data sets can be observed at metal surface loadings in the range of nmol/m² surface coverages.

In the final portion, we will discuss new data processing methods for $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR data sets collected using CPMG-type acquisition. This new method presents a technique that provides dramatic time savings compared to standard processing methods for CPMG data sets and can be implemented using standard solid-state NMR pulse sequences and equipment commonly employed in most NMR laboratories. Further the method also produces useful spectral dynamics information such as T₂ relaxation and CP kinetics for surface environments. The combination of these methods now unlocks the capability to analyze the reactions that occur between radionuclides and the mineral surface at a detail level not provided by other analytical techniques.

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EPR DATING OF INDIAN REGOLITHS (KARNATAKA PLATEAU): RECORD OF THE ASIATIC MONSOON EVOLUTION

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The understanding of the evolution of continental surfaces under climatic and tectonic forcing (Retallack 2010) largely depends on our ability to date secondary minerals from the regolith, a challenging task owing their small size and the coexistence of several generations. Laterites, that are representing 80% of the global soil volume, are developed in the intertropical zone. Their secondary minerals, such as Fe oxyhydroxides, Mn oxides or kaolinite, can potentially be preserved over geological time periods. They were shown to record the influence of paleoclimates in tropical soils, as suggested by the geochronometers or isotopic tracers they may contain (Allard et al., 2018; Girard et al., 2000, Yapp, 2000).

In the research of paleoclimatic signatures, Indian laterites deserve a special attention. During its continental drifting, the Indian plate passed through several climatic zones that could affect the regional laterites development since its beginning (middle of the Cretaceous). This study focuses on two laterites profile of the South of the Karnataka plateau, a region intensively studied due to its strong west-east climatic gradient. Kaolinites are known to cumulate stable radiation-induced defects in their structure (Clozel et al., 1994) that can be used as geochronometers in tropical soils (Balan et al., 2005). The objectives are, for the first time in India, to date the co-existing kaolinites generations expected in the profiles and to correlate the corresponding ages to local or global climatic events that have affected the Indian plate during its history.

The resulting ages are varying between $0.229_{\pm 0.24}$ Ma to $40.73_{\pm 15.37}$ Ma. Samples can be divided between four families with ages clustered around 1.0, 3.5, 9.0 and 39 Ma. These kaolinites families, the 39 Ma one excepted, can coincide with local weathering pulses driven by the evolution of the Indian monsoon, as described in independent studies, confirming that local regional climatic events are prevailing on global forcing. This study also shows that the EPR dating can contribute to unraveling the complex history of tropical continental surfaces over geological periods.

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HALLOYSITE-BASED HYBRID COMPOSITES WITH SYNTHETIC LDH AND THEIR AFFINITY TO REMOVE ANIONS

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Halloysite is a 1:1 layered kaolin group mineral which often forms characteristic tubular particles. The complicated morphology is responsible for its relatively high specific surface area. In turn, the exposed surface hydroxyls are centers at which ions adsorption can take place. Raw clay minerals possess cation exchange capacity. Therefore their use for anions removal, which are commonly found in wastewaters generated by industrial activity, is not possible. Layered double hydroxides (LDH) are synthetic phases which in contrast to clay minerals show high affinity to anions. However, their high cost of production and structural instability in acidic solutions are their main disadvantages. Therefore, the research goal was to investigate the removal efficiency of selected anions by synthetic halloysite-LDH composites.

For the composites preparation a halloysite sample (H) was used from Intermark Company (Gliwice, Poland). In turn, Mg-Fe LDH was synthesized by co-precipitation method using Mg(II) and Fe(III) as chlorides. The LDH precipitation was carried out directly in H suspension with pH maintained at ~10.0. The amount of chemicals and H sample were calculated in order to obtain composites having 25% of freshly formed LDH. For the tests uncalcined and calcined (450°C, 3 h) materials were chosen.

The XRD and FTIR results confirmed the LDH formation in absence and presence of the halloysite as peaks and absorption bands of both mineral components were visible. The efficiency of Cr(VI) and S(VI) removal was tested in model aqueous solutions having initial concentrations (C_{in}) much higher than values found in industrial wastewaters. These covered the range of 0.2-5.0 mmol Cr(VI)/L and 1.0-10.0 mmol S(VI)/L with constant ionic strength set to 10.0 mmol NaCl/L. Among all tested materials, the pure Mg-Fe LDHs showed highest removal capacity in uncalcined and calcined forms. The removal was higher than 94% for Cr(VI) $C_{in} \leq 1.0$ mmol/L, and higher than 76% for S(VI) C_{in} equal to 1.0 mmol/L. At higher C_{in} the efficiency was lowered to 86% for Cr(VI) $C_{in} = 5.0$ mmol/L. In the case of S(VI) the removal decrease was significantly lowered to 65% (5.0 mmol/L C_{in}) and 30-40% (10.0 mmol/L C_{in}). In general a less efficient removal was noticed for the halloysite-LDH composites, in particular for the calcined versions. However for Cr(VI) C_{in} equal to 0.2 mmol/L the efficiency still maintained at 80%. In turn, for the S(VI) C_{in} equal to 5.0 mmol/L the removal was relatively high and reached 65%. The future research will concentrate of the efficiency and selectivity of Cr(VI) and S(VI) removal from industrial wastewaters and stability of the used halloysite-based composites.

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MAGHEMITE PARTICLES SUPPORTED ON HALLOYSITE AS MAGNETICAL-LY RESPONSIVE COMPOSITES FOR EFFICIENT AS(V) REMOVAL

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Magnetic separation is found as one of the most easy and convenient technique of solid separation from liquid medium. Therefore, recent research interest is focused on the application of magnetically responsive materials, formed by coating traditional adsorbents with metal oxide particles. The great attention is paid to Fe oxide particles, not only due to their magnetic properties but also their positive effect on adsorption efficiency. In this study, the adsorption mechanisms involved in As(V) removal were investigated. This was done by combining Mössbauer and X-ray photoelectron spectroscopy with tests of ionic strength and pH effect on adsorption. The desorption and adsorbents stability, defined as percentage release of Si, Al, Fe and As were also studied.

In present study, as the host for Fe oxide particles, halloysite (H) from Polish deposit Dunino (SW Poland) was chosen. The magnetic composites used in the study were prepared by co-precipitation method described previously [1]. The mass ratio of FeOx to H was set to 10% and 25% (HFe10, HFe25). As the additional modification the calcination was performed (HK, HFe10K, HFe25K). The adsorption experiments were carried out for As(V) concentration of 5 mmol/L and solid/liquid ratio of 20 g/L. The pH_{in} was in the 2-10 range. The ionic strength effect was studied for NaCl background electrolyte concentration of 0.005-0.1 mol/L and $\text{pH}_{\text{in}}=5.0\pm0.2$. As a desorbing solution 1 mol/L KH_2PO_4 was used.

The XRD patterns of studied composites showed basal peak of halloysite at 7.20 Å. The appearance of FeOx was confirmed by peaks positioned at 2.95 Å, 2.52 Å, 2.08 Å, 1.70 Å, 1.61 Å and 1.48 Å. Moreover, the Mössbauer spectroscopy revealed that FeOx particles can be identified as nanocrystalline $\delta\text{-Fe}_2\text{O}_3$. The adsorption experiment revealed the highest removal efficiency for the HFe10 and HFe25 at $\text{pH}_{\text{in}}=2$, equal to 89% and 83%, respectively. The changes in removal efficiency were connected to protonation/deprotonation of adsorbents surface, resulting in attraction/repulsion between As(V) and adsorbents surface. The ionic strength experiment showed changes in adsorption capacity of the studied adsorbents. Generally, it was observed, that increase of ionic strength results in an increase of adsorption capacity. This indicated the formation of inner-sphere complexes between As(V) and adsorbents surface. It was noticed that the changes in adsorption capacity were slightly higher in the case of calcined samples, what suggests that in this case physical adsorption mechanism took part to larger extent than in the case of uncalcined composites. This was also confirmed by desorption studies. For the HFe10K and HFe25K the percentage of desorption was higher and equal to 41 and 43%, respectively. The analysis of As3d spectra revealed the presence of As(V) and As(III). This revealed that besides inner-sphere complexes formation, the As(V) reduction with simultaneous Fe(II) oxidation also took place. The composites revealed high stability in the studied pH_{in} range. However, the slight increase in As release was observed for the calcined composites, which was also in agreement with desorption studies. The Al, Si and Fe release was low for all composites, what enables them to be used in wastewater treatment.

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THE ANATOMY OF AN ANTIBACTERIAL CLAY DEPOSIT

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The rapid rise of antibiotic resistant bacteria is seriously threatening our ability to treat life-threatening infections. As a result, our approach to medicine and agriculture will require significant changes if we are to successfully maintain current levels of healthcare and food security. A resurgence of inquiry into alternative antibacterial mechanisms has emerged as human pathogens have evolved antibiotic resistance. Certain naturally occurring clays have been shown to harbor antimicrobial properties and kill antibiotic resistant bacteria. These clays have been proposed as a new paradigm for fighting the potentially devastating effects of the post antibiotic era. Our research on the first antibacterial clay deposit in the U.S. (near Crater Lake, Oregon) provided a basic understanding of the role minerals can play in killing antibiotic resistant pathogens. One of the key components in the natural antibacterial clays is their ability to release soluble metals. These natural antibacterial minerals (Fe-sulfides and smectite) work by buffering solution pH (3-5) and redox potential ($> 600\text{mV}$) and maintaining hydration, while providing extended release of μM concentrations of Fe^{2+} , Fe^{3+} , Al^{3+} and reactive oxygen species (ROS). Metal solutions (Fe^{2+} , Fe^{3+} and Al^{3+}) which are not buffered by clays require higher (mM) metal concentrations to reach bactericidal levels. Understanding the geochemical and mineralogical processes that regulate the antibacterial activity of natural clays will help to usher in the medical application of new mineral-based antimicrobials.

EXTRACELLULAR ELECTRON TRANSFER AS A MECHANISM OF BIOGEOCHEMICAL WEATHERING OF Fe(II) SILICATES BY LITHOTROPIC IRON OXIDIZING BACTERIA

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Earth's Critical Zone is defined as the thin layer of terrestrial surface material ranging from the top of the vegetative canopy to the unaltered bedrock. At the base of the Critical Zone, bedrock is subjected to a variety biogeochemical process that work to alter both its physical structure and chemical composition, converting rock to regolith during the weathering process. The role of microorganisms in mineral weathering has long been recognized and is most often investigated through the lens of acid-base promoted dissolution or nutrient scavenging by heterotrophic microorganisms. It is important to note, however, that the rate limiting step in the weathering of Fe-bearing minerals is often the oxidation of Fe(II), and Fe(II)-bearing minerals potentially represent a vast reservoir of metabolic energy for lithotrophic microorganisms. Microbially mediated Fe-redox processes necessitate the involvement of dedicated outer membrane proteins to transfer electrons to (in the case of Fe(III) reduction) or from (in the case of Fe(II) oxidation) insoluble mineral phases outside the cell. Collectively these phenomena are known as extracellular electron transfer (EET). Reductive EET is well documented, typified by dissimilatory iron reducing heterotrophs including those of the genus *Geobacter*. Much less is known about oxidative EET by lithotrophic microorganisms, and in particular their role in mineral weathering at circumneutral pH.

This study investigated the role of lithotrophic Fe(II)-oxidizing bacteria (FeOB) in the weathering of Fe-bearing silicate minerals at Luquillo Critical Zone Observatory, PR, USA. Samples were obtained from the bedrock-saprolite interface within the Rio Icacos Watershed of the Luquillo Mountains in Puerto Rico in the summers of 2016 and 2017. Rio Icacos is underlain by the rapidly weathering Rio Blanco Quartz Diorite containing the biotite and hornblende. Prior geochemical evidence suggests the flux of Fe(II) from bedrock weathering supports a robust lithotrophic microbial community at depth. Current work confirms the activity of microorganism *in situ*, with a marked increase in ATP near the bedrock-saprolite interface. Saprolite recovered from the interface was used as inoculum to establish enrichment cultures with powdered Fe(II)-bearing minerals serving as the sole energy source. Monitoring of the Fe(II)/Fe(total) ratio and ATP generation suggested growth of microorganisms coupled to the oxidation of mineral bound Fe(II). Analysis of 16S rRNA gene and shotgun metagenomic libraries from *in situ* and from enrichment culture samples lends further support to FeOB involvement in the weathering process. Multiple metagenomic bins related to known FeOB, including *Betaproteobacteria* genera, contain homologs to model EET systems, including Cyc2 and MtoAB. Our approach combining geochemistry and metagenomics with ongoing microbiological and genomic characterization of novel isolates obtained from enrichment cultures provides insight into the role of FeOB in Fe(II)-mineral alteration as well as furthering our understanding of the biotic reactions contributing the globally important biogeochemical phenomenon of weathering.

IRON-SULFUR REDOX CYCLING AND CONTAMINANT MOBILITY IN THE UPPER COLORADO RIVER BASIN

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Biogeochemical iron and sulfur redox cycling profoundly affect metal and radionuclide mobility by driving local Eh conditions to either stabilize or destabilize redox-active species, and through the formation or dissolution of minerals that host contaminants through sorption and incorporation processes. Redox activity is particularly intense in sediments that are exposed to wet-dry cycling because the movement of water through sediments strongly influences nutrient availability and microbial activity. Infiltration and dry-down events, for example, can create biogeochemical hot moments that change microbial activity, initiate changes in sediment gas and water transport, and stimulate release of organic carbon, iron, and sulfur. Consequently, predicting iron and sulfur speciation and contaminant behaviour in sediments requires knowledge of spatial variation in sediment permeability and seasonal or episodic variability in moisture content.

In a series of studies, we have tracked solid-phase and dissolved Fe and S speciation within sediments of five uranium-contaminated floodplains across the upper Colorado River Basin in order to develop regionally relevant conceptual models of sediment redox and contaminant mobility. This region hosts a large number of contaminated U.S. Department of Energy legacy uranium ore processing sites. Moreover, recent studies suggest that sediment redox activity plays a major role in prolonging the longevity of uranium groundwater plumes. Our findings suggest that capillary fringe sediments are particularly important to contaminant behavior regionally because they are subject to large and rapid variations in moisture and redox conditions. Iron appears to play an important role due to its cycling between sulphide and oxide forms. The relative abundance of mackinawite and pyrite is particularly useful for evaluating the accessibility of sediments to episodic oxygen in-diffusion and for rationalizing molecular mechanisms of uranium accumulation. Insights from this research are helping to shape new molecular-hydrological models for uranium plume persistence across this important region and to link biogeochemical iron and sulfur redox cycling, hydrology, and contaminant behaviour at the system scale.

SIZE AND MORPHOLOGY CONTROLLED LAYERED DOUBLE HYDROXIDES FOR ANTICANCER DRUG DELIVERY AND TUMOR TRACER

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We investigated size and morphology effect of layered double hydroxide (LDH) nanomaterials in cellular uptake for their potential application as anticancer drug delivery carrier and tumor tracer. Cellular uptake test showed that LDHs having 100-250 nm was effectively internalized into cancer cells through clathrin-mediated endocytosis with good retention, while smaller or larger LDHs exhibited lower efficiency. In terms of particle morphology, LDHs with smooth surface was more taken up by cells than rough surfaced ones. Based on these findings, we intercalated anticancer drug methotrexate (MTX) into 150 nm sized and flat surfaced LDHs for drug delivery applications. According to the *in vitro* cell line test on human osteosarcoma MNNG/HOS cells, MTX-LDH hybrid showed dramatically enhanced anticancer efficacy as well as high cellular uptake of drug compared with MTX alone. *In vivo* study on tumor xenografted nude mice model also proved that the MTX-LDH had significant tumor suppression effect upon intravenous injection. In order to utilize LDH nanomaterials as tumor tracer, radioisotope Co-57 was incorporated into size and morphology controlled LDH through isomorphous substitution under hydrothermal condition. It was revealed that incorporated Co-57 was stable under human serum, showing less than ~20% of Co-57 release during 24 h. The Co-57/LDH showed fast and effect cellular uptake to CT26 and HepG2 cancer cells, showing injection dose 50% in 2 h. *In vivo* biodistribution experiments tested on CT26 xenografted Balb/c mouse model showed time-dependent tumor accumulation of Co-57 by LDH showing high tumor-to-organ ratios such as tumor-to-spleen of 4.5 and tumor-to-liver of 1.6.

A STUDY OF GEOLOGICAL DISPOSAL FACILITIES ALTERATION PHENOMENA IN BENTONITE

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Geological disposal of Higher Activity Wastes (HAW) involves the conjunctive use of engineered and natural barriers to prevent the release of radionuclides to the biosphere in amounts and timescales that could be detrimental to life and the environment. These barriers comprise: (i) the HAW package itself, (ii) a buffer or backfill material surrounding the waste, (iii) various repository sealing systems, and (iv) the surrounding geology.

Bentonite has been selected as one of the primary candidates to be used as a buffer and backfill material for HAW disposal, due to its high content of the clay mineral montmorillonite, which results in the material's: (i) high swelling capacity and therefore sealing capacity (ii) low hydraulic conductivity, and (iii) high cation exchange capacity (CEC) for intercepting contaminant ions. However, to evidence that bentonite is effective as an engineered barrier, the constituent montmorillonite must be investigated to demonstrate its ability to maintain its structural and chemical stability without significant alteration over hundreds to thousands of years when in contact with a highly radioactive and heat generating waste form.

In a Geological Disposal Facility (GDF), several materials, such as; carbon steel, copper, stainless steel and titanium have been considered as potential materials for HAW encasements. During the expected repository lifespan, metallic encasements will undergo alterations due to the temperatures arising from the wastes embedded inside, as well as, groundwater flow and microbiological activity. Under expected post-closure repository conditions, metallic iron is not considered to be thermodynamically stable, and hence arising corrosion products could interact with the surrounding buffer. The extent of these interactions will depend of a variety of factors such as the redox potential, temperature, pH, solute concentration and buffer material features.

Under post-closure conditions the geochemical environment at the bentonite-container interface is assumed to be reductive. The chemical and structural durability of the metallic container components will be informed by their behaviour in the presence of corroding species, which provides the main mechanism for degradation. After repository closure, anoxic corrosion will be the dominant process, and it will begin when the surrounding bentonite becomes water saturated, and water physically comes into contact with the structural metallic components.

Against this backdrop, the interaction between the corroded iron from the overpack containers and the montmorillonite buffer component, at temperatures up to $\sim 150^{\circ}\text{C}$, is an important issue that must be addressed in view of the long-term performance of the engineered barrier. To achieve a deeper understanding of the altered clay at the metallic components/clay interface, samples from the FEBEX-DP and ABM underground rock laboratory experiments have been analysed using a variety of laboratory techniques to examine interactions that have occurred over more than a decade of exposure.

VERSATILITY OF INFRARED SPECTROSCOPY IN THE INVESTIGATION OF CLAY MINERALS EXPOSED TO VARIOUS MODIFICATIONS

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Infrared spectroscopy in both, middle (MIR) and near (NIR) regions was used to investigate organically and mechanically modified smectites. Smectites exposed to various treatments change their properties and IR spectroscopy is able to provide direct evidence of such modifications. Present work was focused on a/ the study of the influence of central atoms carrying a positive charge on the mechanical and thermal stability of the used smectite, b/ adsorption process and possible interactions between organoclays and rhodamine 6G (R6G).

The organoclays were prepared from natural and synthetic smectites and four organic cations: tetraoctyl- and tetrabutylammonium (TBA, TOA) and their alkylphosphonium analogs (TBP, TOP). Quaternary phosphonium and ammonium samples showed distinctive spectral profiles of the C-H bands due to the different central atoms (N and P) of surfactant head-groups that affected the neighboring bonds of the methylene groups, thus also the frequencies and intensities of the related IR bands. Upon loading of organic cations into clay minerals, the bands attributed to the C-H vibrations appeared in the spectra: stretching ν C-H between 3000–2800 cm^{-1} and bending δ C-H in the range 1600–1300 cm^{-1} . Analogously, besides the first overtones 2ν and combination ($\nu+\delta$) bands of the structural OH groups and water molecules, the 2ν C-H (\sim 6000–5500 cm^{-1}) and ($\nu+\delta$)C-H (below 4500 cm^{-1}) bands of the surfactants were detected in the NIR spectral region. Organoclays subjected to a mechanical treatment exhibited the higher stability of the structure compared to the related unmodified smectite samples. While the IR spectra of unmodified smectites have undergone a significant change in the bands' positions and intensities reflecting extensive structural changes, the presence of organic cations preserved the structure of smectites as indicated by decelerated changes in their spectra. The larger organic cations used for modifications, the higher resistance to mechanical treatment was observed.

The adsorption of R6G on clay mineral and related organoclays was confirmed by the appearance of sharp peaks attributed to the δ C-H and vibrations of aromatic rings (1700–1300 cm^{-1}) which do not overlap with the δ C-H bands of the surfactants. Their intensities increased with the concentration of the dye. NIR spectroscopy displayed only negligible changes in the spectra after modification with R6G, although the dye was clearly detectable in the MIR spectra of all the measured samples. The appearance of an unidentified band at 6748 cm^{-1} , not visible in the pure R6G spectrum, could be attributed to the interactions of dye cations with smectite and its organic derivatives.

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THE ROLE OF MAGNESIUM IN METASTABILITY OF CALCIUM PHOSPHATE MINERALS

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Calcium phosphate minerals are typically the solubility-limiting phase for phosphate in calcareous soils. Despite the prevalence of magnesium (Mg) in calcareous soils, its role in the formation and stability of these minerals has been largely ignored. A series of two common calcium phosphate minerals, hydroxyapatite and brushite were synthesized in the presence of Mg and analyzed with a range of spectroscopic techniques to examine the effect Mg substitution has upon the local bonding environment and overall structure. Phosphorus K-edge X-Ray Absorption Near Edge Structure (XANES) and Attenuated Total Reflectance Fourier Transformed Infrared (ATR-FTIR) provide insight into the local structure while SP-XRD (Synchrotron Powder X-Ray Diffraction), and Transmission Electron Microscopy (TEM) were used for macrostructure. In acidic to neutral pH systems, Mg-bearing brushite phases were the dominant mineral forming over a wide range of Ca:Mg ratios. In neutral to high pH systems, a short-range order amorphous calcium phosphate (ACP) with a local structure analogous with hydroxyapatite precipitated for a wide range of Ca to Mg ratios. It can be inferred that the presence of Mg in soils leads to stabilization of the metastable brushite phase via cation substitution at neutral pH. At higher pH, Mg inhibits hydroxyapatite formation via poisoning of crystal growth propagation and leads to ACP metastability.

ROLE OF CLAY STRUCTURE, COMPOSITION AND REDOX CHEMISTRY IN IMMOBILIZATION OF CATIONIC AND ANIONIC RADIONUCLIDES

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Due to their characteristic swelling properties and high sorption capacity for radionuclides, clays are at the frontline of the battle to safely contain radioactive contaminants, both for monitored natural attenuation in the environment and in an engineered geological disposal facility (GDF) for radioactive waste. Clay minerals must have the necessary physical and chemical properties to limit the transport of cationic and anionic radionuclides, despite challenges presented by groundwater chemistry in the environment, and the evolving radioactive waste in a GDF. Understanding effects of clay structure, composition and redox chemistry on the performance of both engineered and natural barriers is a major requirement for safety performance assessments.

Here, we will present on clay sorption capacity and redox reactivity with respect to Tc(VII) (as the TcO_4^- pertechnetate anion), U(VI) (as the UO_2^{2+} uranyl cation) and I(V) (as the IO_3^- iodate anion), as a function of clay chemical composition, and in the presence of radiation effects experienced in a GDF. Batch testing, based on EPA 1314, will be used to determine sorption isotherms for clay at groundwater pH (~8.6) and at different solution to solid ratios. A range of different clay minerals will be evaluated with consideration of capacity for Tc/U/I sorption/reduction and long-term mobility performance (i.e., solubility of the precipitated phase). In particular, organoclays with and without sulfur amendment will be tested to investigate the role of clay-associated Tc sulfide products in the solubility and re-oxidation potential of Tc(IV). The physical effects of alpha-radiation, and the electrostatic effects of gamma-radiation, on clay-radionuclide interactions will be described for both model phyllosilicates and natural dioctahedral smectites, representing conditions experienced in close proximity to the radioactive waste containers in a GDF. Association of the contaminants with the different materials will be spatially resolved using X-ray microprobe (XMP), and the potential for redox reactions will be assessed using X-ray absorption near edge structure (XANES) spectroscopy.

TRANSFORMATION OF ORGANIC CONTAMINANTS ON MONTMORILLONITE CLAY MINERAL SURFACES

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Montmorillonite, as the most common clay mineral, is widely distributed in the environment. It is a 2:1 layered aluminosilicate clay with the specific surface area up to $800 \text{ m}^2 \text{ g}^{-1}$. Studies have shown that organic contaminants could be strongly adsorbed on montmorillonite, however, there is only limited information for the transformation of organic pollutants on montmorillonite surface.

Our previous research demonstrated that when montmorillonite is saturated with transition metals (e.g., Fe^{3+}), the clay mineral could induce the formation of organic radical cation through a single electron transfer, and subsequently forming dioxin and dioxin-like compounds. Since clay mineral is also the major component of mineral dust in the atmosphere, further studies are needed to investigate the similar reactions occurring in the atmosphere and the health effect.

In this study, the interactions of gaseous 2-chlorophenol with Fe^{3+} -saturated montmorillonite particles in a gas-solid system was investigated to simulate the reactions of mineral dusts with volatile organic pollutants in atmosphere. Results suggested that Fe^{3+} -saturated montmorillonite mediated the dimerization of gaseous 2-chlorophenol to form hydroxylated polychlorinated biphenyls, hydroxylated polychlorinated diphenyl ethers, and hydroxylated polychlorinated dibenzofurans. 2-chlorophenol was examined to explore their adverse impact on human health. Based on cell morphological analysis, cytotoxicity tests and Fourier-transform infrared imaging spectra, surface-catalyzed reactions of Fe^{3+} -montmorillonite with 2-chlorophenol significantly increased the toxicity of montmorillonite particle on A549 cells. Furthermore, the structural iron in montmorillonite also exhibited similar reaction with chlorophenol, and the reactivity was strongly dependent on the humidity of the system. Our results help to understand the interactions of volatile organic pollutants with particulate matter in atmosphere, and their adverse impacts on human health.

QUANTITATIVE TEXTURE ANALYSIS OF WET CLAYS DURING THIXOTROPIC HARDENING USING SYNCHROTRON X-RAY DIFFRACTION

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Thixotropy describes an interesting phenomenon that the strength and stiffness of soft clay increases with time after significant disturbance even if the boundary conditions remain unchanged. This study performed two-dimensional synchrotron X-ray diffraction to reveal how the microstructure of clays, including clay texture or fabric, varies with time (e.g., rearrangement and reorientation of clay particles), and the corresponding influence on the thixotropic hardening behavior was also studied to characterize the thixotropy-governed microscale soil fabric evolution.

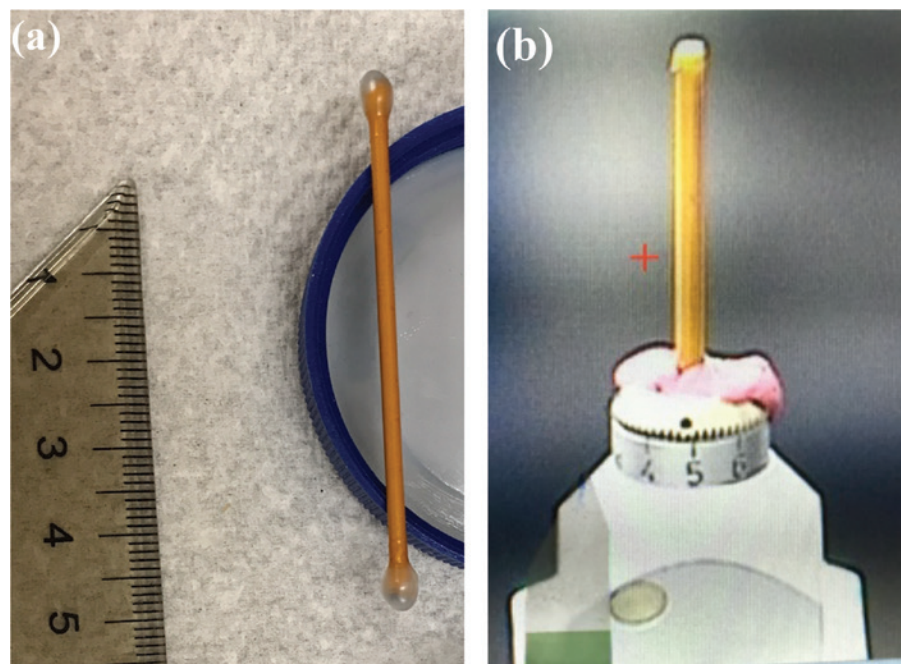


Fig. 1 (a) Sample preparation; (b) Experimental setup.

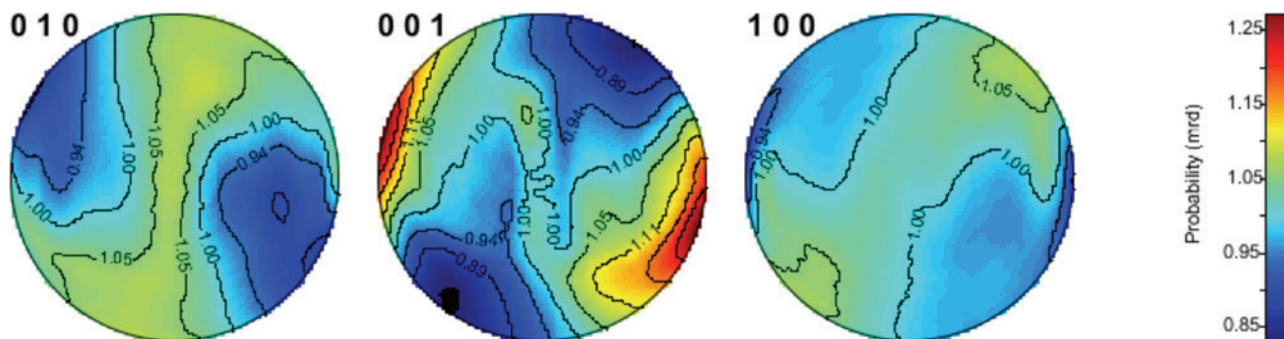


Fig. 2 Pole figures for KGa-2 at 6 days after sample prepared.

INVESTIGATION OF CLAY MINERALS AT THE ILLINOIS STATE GEOLOGICAL SURVEY

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The Illinois State Geological Survey (ISGS) is part of the Prairie Research Institute at the University of Illinois at Urbana-Champaign. The ISGS is a premier State Geological Survey, and for decades has served the needs of State of Illinois and the Nation with earth science information relevant to environmental quality, economic vitality, and public safety issues.

ISGS has a rich history in clay mineral research, which has played a critical role in the investigation of energy resources and deposits of industrial minerals. Due to their structure, chemical composition, reactivity, and exceptional properties, clay minerals are an extremely valuable resource in a wide variety of applications.

At the present time, clay mineral research at ISGS is vibrant and active, with a focus on characterization and quantification of clay minerals in sediments, sandstone petroleum reservoirs, clay deposits, and other geological specimens.

The goal of this presentation is to introduce the mineralogical and chemical characterization of clay minerals performed in the ISGS X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) Laboratories.

THE INFLUENCE OF TETRAHEDRAL AND OCTAHEDRAL IRON IN SMECTITES ON THEIR REDOX ACTIVITY IN NITRATE REMOVAL

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Nitrate contamination of natural waters and soils is a long-standing problem affecting the health of humans, animals, and other living organisms. Remediation technologies have been developing, but an economically and environmentally useful remediation method is yet undiscovered.

Recent studies revealed that reversed-charge, redox-active ferruginous smectite SWa-1 significantly degrade nitrate. The negative layer charge was reversed by the exchange of a polymeric cation (polydiallyldimethylammonium or poly-(D) glucosamine (chitosan)), which overcompensated the cation exchange capacity of the clay mineral. The positive charge on the clay mineral surface was determined by the zeta (ζ) potential of the resuspended polycation-clay composites. The structural iron was reduced from Fe(III) to Fe(II) in the mineral structure. The positively charged surfaces attracted the redox-active anions (nitrate), which were transformed to lower oxidation states by reoxidation of Fe(II) back to Fe(III). Nitrate levels and speciation depended, however, mostly on different loadings of the polycation, where the lowest loading (0.075 g/L) provided the highest efficiency in nitrate removal.

The working hypothesis to explain these results is that the tetrahedral coordination of Fe(III) in the smectite structure enhances the redox activity of the clay surface with nitrate. The purpose of this study was, therefore, to test this hypothesis by comparing the redox reactivity of SWa-1 and nontronite NAu-2, which have no tetrahedral Fe(III) and a high level of tetrahedral Fe(III), respectively.

The fine fraction ($<2\ \mu\text{m}$) of the Na-saturated forms of SWa-1 and NAu-2 were exchanged with chitosan in aqueous suspension, using four different loadings of chitosan (0.075, 0.25, 0.5 and 1.0 g/L) to form clay-chitosan, reversed-charge composites. All prepared composites were chemically reduced by sodium dithionite, then washed free of excess salts and reacted with sodium nitrate in an oxygen-free environment using a controlled atmosphere liquid exchanger (CALE) apparatus and inert-atmosphere reaction tubes (IRT). The final supernatant solutions were analyzed for NO_3^- -N and $(\text{NO}_3^- + \text{NO}_2^-)$ -N. The redox activity of smectite NAu-2, rich in tetrahedral Fe(III), was significantly lower than SWa-1, with no tetrahedral Fe(III).

SMECTITE FORMATION IN ACID SULFATE ENVIRONMENTS ON MARS

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Phyllosilicates of the smectite group detected in Noachian and early Hesperian terrains on Mars were hypothesized to form under aqueous conditions that were globally neutral to alkaline. These pH conditions and the presence of a CO₂-rich atmosphere should have been favorable for the formation of large carbonate deposits. However, large-scale carbonate deposits have not been detected on Mars. We hypothesized that Mars experienced acidic events caused by sulfuric acid that permitted smectite, but inhibited carbonate, formation. To verify this hypothesis, smectites were synthesized from Mars-analogue glass-rich basalt simulant in the presence of sulfuric acid of variable concentration (11-42 mM). Basalt simulant suspensions were prepared in batch reactors and incubated at 200 °C for 14d. Synthesized smectites were analyzed by X-ray diffraction, Mössbauer spectroscopy, visible and near-infrared reflectance spectroscopy and scanning electron microscopy. Basalt simulant suspensions were acidic at the beginning of incubation and varied from acidic (pH 1.8) to mildly alkaline (pH 8.4) at the end of incubation. Gradual neutralization of sulfuric acid during basalt weathering led to formation of the dioctahedral smectite at pH ~3 followed by trioctahedral smectite saponite at pH ~4 and higher. Anhydrite and hematite formed in the pH range from 1.8 to 8.4 while natroalunite was detected only at pH 1.8. The experimental results demonstrate that smectite formation through basalt alteration on Mars was not limited to neutral/alkaline pH conditions but could also occur under acidic conditions. Acidity modeling revealed that sulfuric acid produced by volcanic SO₂ degassing on early Mars could be the major source of acidity for the alteration of basaltic materials resulting in global-scale smectite formation.

URANYL PEROXIDE NANOCLUSTER INTERCALATION INTO SYNTHETIC HYDROTALCITE

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Uranyl peroxide nanoclusters are a class of polyoxometalates (POMs) that can exceed 3 nm in diameter and are connected by peroxide and hydroxide bridges equatorially coordinated to UO_2^{2+} ions¹. The very high aqueous solubility, large size relative to many transition-metal POMs, and stability of these nanoclusters has been of increasing scientific and industrial interest². Layered double hydroxides (LDHs), including hydrotalcite, are anionic clays composed of divalent and trivalent cations in positively-charged sheets separated by an interlayer containing water and polyatomic anions³. Synthetic LDHs have been extensively researched due to their expandable interlayer, which can accommodate transition metal POMs⁴. Intercalation of uranyl peroxide nanoclusters into anionic clays potentially allows for novel applications related to the nuclear fuel cycle. This could include application for radionuclide-contaminated sites, such as Fukushima Daiichi⁵, as the large size of the nanoclusters would remove a significant fraction of U from solution while potentially accommodating fission products in the expanded gallery (Figure 1).

The intercalation of uranyl peroxide nanoclusters into synthetic MgAl-hydrotalcite has been attempted using established intercalation techniques such as co-precipitation, anion exchange, and exfoliation. The resulting reaction products were then characterized using a suite of instruments: powder X-ray diffraction (PXRD) to measure the *d*-spacing of the interlayer, Raman spectroscopy to identify the interlayer species, and inductively couple plasma optical emission spectroscopy (ICP-OES) to determine the elemental ratios.

Early PXRD analyses have shown the clays to be well-formed (Figure 2) and Raman spectroscopy has implied the persistence of the nanoclusters after the reaction, as well as polyatomic anionic species. Further experiments will be conducted by first pillaring the LDHs to allow for greater uptake of the nanocluster species.

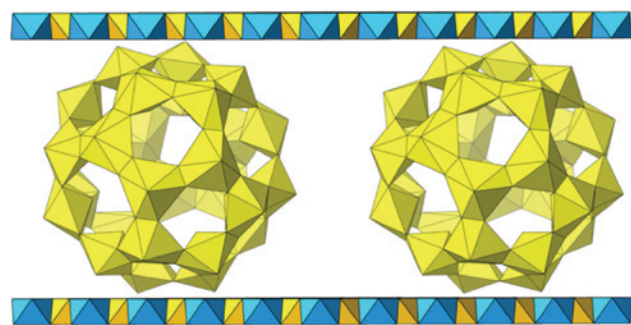


Figure 1. Schematic showing a hypothetical arrangement of $\text{Li}_{28}[(\text{UO}_2)(\text{O}_2)_{1.5}]_{28} \cdot 140\text{H}_2\text{O}$ into the interlayer space of the layered double hydroxide quintinite⁶, $\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3)(\text{H}_2\text{O})_3$.



Figure 2. Synthetic hydrotalcite after reaction with $\text{Na}_{44}\text{K}_6[(\text{UO}_2)_{24}(\text{O}_2)_{24}(\text{P}_2\text{O}_7)_{12}][\text{IO}_3]_2 \cdot 140\text{H}_2\text{O}$.

BACTERICIDAL EFFICACY OF SELECT CLAY MINERALS UPON A VIRULENT STRAIN OF *AEROMONAS HYDROPHILA*

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A highly virulent strain of *Aeromonas hydrophila* (VAH) is the causative agent of severe and widespread outbreaks of motile Aeromonas septicemia in farmed catfish in West Alabama and East Mississippi. While this disease is very common, field fish diagnostic observations and a review of 10 years of lab records identified an area that had not experienced VAH outbreaks. The only obvious component that was unique to this region was geology. Because of the documented bactericidal properties of clay minerals, we initiated a study to evaluate the in-vitro bactericidal efficacy of select clay minerals upon a virulent strain of *Aeromonas hydrophila* (VAH). The goal was to identify if clay components of ponds could influence VAH outbreaks and, if so, could they be used as feed or water additives to prevent disease.

Clay mineral samples were obtained from commercial sources, local deposits and synthetically produced. Clay minerals were evaluated in-vitro with a modified minimum bactericidal concentration (MBC) protocol. A natural clay mineral deposit was identified that exhibited bactericidal properties. However, the concentration (120 g/L) required for a 100% lethal concentration dose (LCD) is impractical for use in feeds or ponds. The synthetically produced samples were found to exhibit bactericidal properties. The 100 % LCD in nutrient rich media (2 g/L) and nutrient limited media (200 mg/L) were considered as practical treatments for incorporation into aquaculture feed. The synthetically produced sample was made palatable with the addition (0.002 ml/g) of menhaden fish oil and fed to channel catfish (*Ictalurus punctatus*) for 10 consecutive days. No remarkable findings were observed from histological examination of gastrointestinal tissues.

STUDY OF BASALTIC PIECES OF ROCKS BY ATTENUATED TOTAL REFLECTANCE SPECTROSCOPY (ATR) AND NEAR INFRARED (NIR) SPECTROSCOPY

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The aim of this work was to identify *in situ*, i.e. without any separation procedure, clay minerals present in basaltic rocks. FTIR spectroscopy was used. The samples are core materials representing the Ediacaran Volyn-Brest basalt trap province, located at the western margin of the East European Craton. The clay minerals in these basalts are products of their hydrothermal alteration, characterized in detail by Środoń et al. (2017).

The small pieces of rocks were studied as they are by FTIR in the middle infrared (4000–400 cm⁻¹) using ATR configuration and a single-reflection accessory. ATR spectra were acquired using a Nicolet iS50 FTIR spectrometer equipped with a KBr beam-splitter and a DTGS/KBr detector with an internal iS50 ATR device. Internal reflection element (IRE) was a diamond crystal with refractive index of 2.4. The contact and constant pressure between the sample and the diamond crystal were ensured by the pressure tower of the device. The refractive index of the samples was assumed to be 1.45. Then, the penetration of the IR beam, ranges from ~ 5 µm in the OH stretching region to ~ 0.5 µm at 400 cm⁻¹. The spectra were corrected using the ATR correction corresponding to the device. NIR spectra (4000–7500 cm⁻¹) were acquired with a Thermo-Scientific Integrating Sphere (diffuse reflectance) equipped with an internal InGaAs detector, set on a Thermo-Scientific Nicolet 6700 FTIR spectrometer. A white light source was used, associated with a CaF2 beam splitter. The small pieces of rocks were analyzed as they are, simply placed on the integrating sphere.

Diocahedral and trioctahedral smectites could be revealed in many samples in various amounts by both ATR and NIR. More precisely, the diocahedral smectite is montmorillonite and the trioctahedral smectite was identified as griffithite, an iron-rich saponite (Komadel et al., 2000).

The clay minerals identification in these geological and technical contexts may be useful in the issue of the origin of clays on Mars.

Authors acknowledge financial support from the Polish National Science Centre MAESTRO grant 2013/10/A/ST10/00050 and from the European communities (FEDER) and the “Région Nouvelle Aquitaine”.

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QUANTIFYING HYDROLYSIS OF KEGGIN-BASED AL-CLUSTERS FROM NMR SPECTROSCOPY

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Aluminum forms a number of large polynuclear clusters in aqueous solution, including the well-known ϵ -Keggin isomer of the “Al₁₃” tridecamer, and larger related clusters such as the Al₃₀. These Keggin-type clusters are thought to form during neutralization of acidic waters in contaminated sites or in soils, have found use as pillaring agents for clays, constitute a large fraction of aluminum chlorohydrates used as flocculants, and serve as molecular-scale models for mineral surfaces. The relatively high charge of the clusters, arising from full protonation of bound waters, prevents condensation, but partial deprotonation reduces the charge and promotes agglomeration through formation of bridging bonds between clusters. NMR studies of commercial Al-chlorohydrate and the γ -Keggin isomer of Al₁₃ reveal distinct spectroscopic changes upon deprotonation useful for inferring the extent of hydrolysis. In addition to the characteristic tetrahedral Al peak, the octahedral Al in ϵ -Keggin-like structural fragments yield distinct spectroscopic signatures characterized by large quadrupolar coupling arising from the electric field gradient between the equatorial bridging hydroxyls and the bound water to central oxo axis. For the sulfate salt of the γ -Al₁₃, in which one of the terminal waters is deprotonated, signals from each of the thirteen Al sites were resolved in ²⁷Al MQ/MAS NMR spectra and assigned with the help of DFT calculations. These results show that octahedral Al with a terminal hydroxyl exhibits a greatly reduced quadrupolar coupling, which can be readily identified. For Al-chlorohydrate, comparison of the intensities of the characteristic Al₃₀ tetrahedral signal with that for the ϵ -Keggin-like octahedral Al yields estimates for the ratio of intact vs. condensed clusters. Intact clusters in the solid are expected to remain highly reactive owing to the lability of the terminal waters and their presence appears to relate to coagulation efficiency.

GRAPHITIC CARBON NITRIDE INCORPORATED IN 2D NANOCLAY AS A NOVEL UV SCREENING AGENT

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Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) has received a great attention not only due to its high chemical and thermal stability, but also due to its photocatalytic property. In this study, we developed a novel soft chemical route to incorporating $g\text{-C}_3\text{N}_4$ nanosheet into the interlayer space of 2D nanoclay (Na-mica) through intercalation of cyanamide and subsequent pyrolysis. The $g\text{-C}_3\text{N}_4$ -mica nanohybrid as well as bulk $g\text{-C}_3\text{N}_4$ showed excellent UV absorption properties below 450 nm. However, the photocatalytic activity of $g\text{-C}_3\text{N}_4$ -mica hybrid was almost quenched, due to the effective screening of photoactive site by insulating mica. It is, therefore, concluded that the present $g\text{-C}_3\text{N}_4$ -mica could provide a key to new application of semiconductor for UV blocking polymer and related film industries, and sun screen cosmetic ones due to its unique properties like excellent UVA-UNB-UVC screening function without any photocatalytic degradation and phototoxicity.

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BENTONITE ALTERATION IN AQUEOUS SOLUTIONS RELEVANT TO THE UNDERGROUND DISPOSAL OF RADIOACTIVE WASTE INCLUDING THE EFFECTS OF MICROBIAL ACTIVITY

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The stability of bentonite, which varies in physical and chemical behavior, is investigated as a suitable geo-technical barrier material for underground radioactive waste containment. The suitability of these clays as effective long-term seals and the nature of the precise alteration mechanisms that may occur when subject to various groundwater remains a question of debate. Furthermore, the influence of microbial activity on the mineralogical and chemical behavior of bentonite is generally neglected in the context of experimental studies with aqueous solution. The aim of this research is to characterize the mineral stability of a set of industrial bentonites relevant to the underground sealing of radioactive waste. To study the microbial activity, two different bentonites (B36; Jelsovy Potok, Slovakia and SD80; Milos, Greece) were selected for the long-term experiments of the UMB Project, housed in the GRS laboratories in Braunschweig. These were reacted in laboratory batch-experiments with aqueous solutions to simulate i) Opalinus shale pore waters and ii) saline cap rock solutions in a water/solid ratio of 2:1 at temperatures of 25, 60 and 90 °C for one year. For the microbial batch-experiments, both bentonites were supplemented with substrate (50 mM lactate, 50 mM acetate, 3 mM methanol, 0.1 mM AQDS). The reacted samples were dialyzed and then analyzed by XRF and XRD. The CEC was also determined. Following alteration, samples containing substrate showed distinct color changes compared to controls, indicative of bacterial activity. XRD results of the non-fertilized bentonite show no new mineral phases but significant changes in the intensity and d-value of the (001)-reflection of smectite. Sample B36 shows irreversible loss of its swelling capability at temperatures above 60 °C following treatment with the saline cap rock solution. Batch-experiments supplied with substrate show similar effects at 25 °C. In contrast to the saline cap rock solution experiments, the Opalinus shale pore water resulted in minimal modification of the smectite (e.g. B36). The 16S rRNA-gene analysis revealed the dominance of spore-forming *Bacillus* species in sample B36 incubated with Opalinus shale pore water including substrates at 25 °C. Furthermore, sulfate-reducing microbes dominate the microbial community in sample SD80 with substrate, containing Opalinus shale pore water solution at 25 °C. Among the identified microbes, potential sulfate-reducing as well as iron(III)-reducing species occur. This opens up the possibility that the smectite may lose its swelling capability *via* layer-charge increase associated with the reduction of octahedral Fe³⁺.

AQUEOUS COMPLEXATION AND DISPROPORTIONATION OF MN(III) IN THE PRESENCE OF PYROPHOSPHATE: IMPLICATIONS FOR ITS ROLE AS A GEOCHEMICAL OXIDANT

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Dissolved Mn(III) species complexed by high affinity ligands have recently been recognized as a significant form of Mn in suboxic redox transition zones of various aquatic systems, but their speciation, stability and reactivity are poorly understood. Several previous studies suggested dissolved Mn(III) species as potent geochemical oxidants. In addition to acting as the intermediate for Mn oxidation and reduction, Mn(III) can also undergo disproportionation to produce insoluble Mn oxides. With pyrophosphate (PP) as the model ligand, we conducted experiments to evaluate the thermodynamic and kinetic stability of Mn(III) complexes as well as their interactions with As(III), a potential electron donor. Thermodynamic calculations using a selected set of Mn-PP complexation constants could predict the stability regime of Mn(III)-PP at circumneutral pH. With an initial lag phase, the kinetics of Mn(III)-PP disproportionation could be modeled as an auto-catalytic process in which the produced Mn oxide promotes further disproportionation. As(III) could not be oxidized by Mn(III)-PP complexes or by the Mn oxides formed from their disproportionation, which is in contrast to the traditional expectation of rapid oxidation of As(III) by Mn oxides. While the anticipated disproportionation of Mn(III)-PP would produce equally molar amount of solid Mn(IV)O₂ and aqueous Mn(II), the produced solids were not pure Mn(IV). X-ray diffraction of the produced Mn solids indicated a mixture of triclinic birnessite and δ -MnO₂, while the average oxidation state and the kinetic modeling of autocatalytic disproportionation indicated closer resemblance to triclinic birnessite. Rapid As(III) oxidation by externally added δ -MnO₂ in the presence of PP suggested that PP was not responsible for the lack of reactivity of the oxidants originating from dissolved Mn(III). Synthetic triclinic birnessite is a weaker but still capable oxidant for As(III). Instantaneous Mn(III) disproportionation upon dissolution of Mn(III)-acetate solids oxidized As(III) at similar rates as triclinic birnessite, disproving an overall inability of Mn solids from Mn(III) disproportionation to oxidize As(III). As(III) in the presence of instantaneous disproportionation of Mn(III)-acetate was oxidized at similar rates as triclinic birnessite. The As(III) oxidation results highlight an intriguing phenomenon that the reactivity of Mn oxides produced by Mn(III) disproportionation is modulated by the rate of disproportionation and the ligand that had complexed the Mn(III).

SMECTITE TO ILLITE TRANSFORMATION AS A GEOPRESSURE GENERATION MECHANISM, GULF OF SUEZ—MUD ROCK: A CASE STUDY

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Overpressure mud rocks is a serious problem in the drilling operation within the Gulf of Suez area, detection and prediction of overpressure intervals is an important in the oil and gas industry, the overpressure generation mechanism related to many factors, the compaction disequilibrium zones, lateral transfer, clay mineral transformation, osmosis and others mechanisms.

The paper highlight the geopressure formations and overpressure generation mechanisms in the studied field using the available data, Eaton's resistivity and sonic methods are used for pore pressure calculation with some modification in the Eaton exponent to be fit in the area of interest.

The overpressure generation mechanism investigated and defined in the studied area, where the compaction disequilibrium and smectite to illite transformation or clay mineral diagenesis are recognized as potential contributors to overpressure generation.

We aim to look at the relationship between overpressure generation and the smectite-to-illite transformation, so we study the reaction rate and the conditions such as temperature, kcl concentration and time that induce smectite-to-illite transformation.

The study revealed that the smectite to illite transformation is one of the main overpressure generation mechanism in the Gulf of Suez mud rocks, based on mineral composition results of cooked samples, it is clearly that illitization goes through three stages, the geopressure mud rocks need more inhibitions and using of suitable mud weight for safe drilling.

EFFECT OF THE CLAY MINERALS CHEMICAL STABILITY ON THE PORE PRESSURE MODEL CALIBRATION, GULF OF SUEZ, EGYPT

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Mud rocks drilling related problems spot the light on the importance of studying the mud rocks characteristics and behavior with the drilling mud in the oil and gas industry. It was noticed in the last wells especially in July field many caved shale problems while drilling the Late Miocene Zeit formation lower part, these cuttings was described as firm, which explain that is why there was no suspect for the chemical instability reasons in the studied interval, especially it was drilled using salt saturated kcl polymer. the main problem that this phenomenon was not affected by increasing the mud weight while drilling.

The main objective of this research is to identify the minerals composition of the studied mud rock intervals, delineate the reason of the caved shale occurrence in the drilled intervals and study of the chemical stability effect on the pore pressure modelling.

In this paper, we analyze the cuttings (drilled and caved) by XRD to help us using these failure as a calibration point, Liner swelling test was done using the same mud type used for the drilling. The study revealed that, the XRD analysis showed very high content of Smectite in the 4 selected samples ranged from 34 to 57 %, liner swelling test showed very high swelling ratio (20–27 %) with rapid rate after short time (1 min), although these samples assumed to be affected already by the swelling while drilling this section,

This study helped us for more understanding of the late Miocene Zeit formation nature, its mineral composition and swelling ratio, based on this study, we didn't use this caved shale problem as a calibration point for the unconfined compressive strength or the whole model, for any further caved shale problem in this section we will keep the designed mud weight as it is, just good hole cleaning with optimum mud additives to enhance the hole conditions.

EFFECT OF CLAY MINERALS IN OIL AND GAS FORMATION DAMAGE PROBLEMS: A CASE STUDY, GULF OF SUEZ, EGYPT.

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Formation damage can be observed from the production decline and injection rates, the diagnosis of formation damage required integrated data from the geological side and the engineering side, more understanding for the reservoir characteristic and minerals is essential to define the causes of formation damage and a good treatment for a studied well, clay minerals has high impact in the formation damage studies.

In this paper, two studied wells in the gulf of suez offshore was investigated to define the root causes of formation damage encountered problems, a detailed study about the studied reservoirs lithology, mineralogy and cementation, the scanning electron microscope used for studying the configuration, texture, and fabric of minerals, especially clays, in addition X-ray diffraction analysis used to detect the amount and types of clays in the studied reservoirs, revising of the used fluids and interaction between fluids and minerals investigated also.

In general, the X-ray diffraction results for the well A show high amounts of kaolinite reached up to 17% accompanied with the high quartz percentage of the whole samples, other clays are present also as illite with percentage ranged from 3 to 5%, chlorite also present from traces to 1% percent, while in well B Clays are present also as illite with percentage ranged from 4.4 to 8.2, Scanning electron microscopy analysis shows the presence of kaolinite, illite and chlorite in the studied wells.

The study revealed that, the formation damage in the well A may results from deflocculatabl kaolinite clay by non-equilibrium water-based fluids with the potential to severely reduce near wellbore permeability, or clay particle dispersion and pore plugging by movement with production, where the movement of fines affects on the production performance of a well, especially in the sandstone formation reservoirs. Salinity chock may be responsible for the clays dispersion.

The formation damage in the well B may results from the used stimulation fluid, where Hcl react with illite and break it to fines and this will block the pore throats and cause a severe permeability reduction in the studied well.

Our recommendation is core flooding test for the best stimulation and for more understanding of the problem, try Acid stimulation and chemical treatment for the perforated intervals in the studied well using clay stabilizer.

ALTERATION OF VOLCANIC SEDIMENTS ON MARS AND THE FORMATION OF CLAY MINERALS AND X-RAY AMORPHOUS MATERIALS

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The surface of Mars is dominated by basaltic volcanogenic sediments and sedimentary rocks that were deposited by wind, water, and impacts [e.g., 1,2]. Geomorphologic evidence for rivers and lakes suggests a more Earth-like climate early in Mars' history, but the nature of this climate has been a topic of debate: was early Mars warm and wet or cold and icy? Secondary phases in ancient martian volcanic sedimentary rocks can shed light on these early environments. Here, we focus on the secondary phases (specifically, clay minerals and X-ray amorphous materials) detected on the martian surface from orbital and rover observations, and investigate what these phases tell us about the temporal evolution of aqueous environments on early Mars.

Orbital visible/near-infrared (VNIR) and thermal-infrared spectroscopy have been essential for characterizing the global mineralogy of Mars. A variety of clay minerals have been identified by VNIR spectroscopy in ancient martian terrains, suggesting changing aqueous environments over time [e.g., 3]. For example, in Mawrth Vallis, both allophane and imogolite, which are common weathering products of volcanic ash, have been detected in a unit that overlies Fe/Mg-smectite- and Al-smectite/kaolinite-bearing units, indicating a change from wetter environments with slower weathering rates to rapid leaching environments [4]. Regional detections of allophane [5] and leached glass [6] further indicate rapid leaching of large deposits of volcanic ash/glass.

Measurements by the CheMin X-ray diffractometer on the *Curiosity* rover in Gale crater have identified smectite in most fluviolacustrine sedimentary rocks and X-ray amorphous phases in all samples analyzed to date. The smectite likely formed in lake waters [7], and a transition to more dioctahedral character moving up the stratigraphy indicates an increase in weathering intensity over time [8]. Calculations of the composition of the amorphous component demonstrate that it is not consistent with a primary glass and is likely made up of an assortment of secondary products [9]. Studies of modern mafic glacial sediments in Three Sisters, Oregon demonstrate that X-ray amorphous materials are the only secondary phases that form in these cold and icy environments, and the diversity of amorphous phases [10,11] suggests that amorphous materials detected by CheMin could have formed from similar cold and icy conditions.

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MOLECULAR SIMULATION STUDIES OF CO₂-GEOLOGICAL FLUIDS IN SWELLING CLAYS

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Shale gas production with water-based hydraulic fracturing may invoke high water consumption and formation damage. Carbon dioxide (CO₂) is a promising candidate for reservoir fracturing and enhanced gas recovery (EGR), plus benefit from long-term CO₂ sequestration. Swelling clays are important components of shales. Understanding the interaction between CO₂-geological fluids (especially CO₂-H₂O-CH₄ ternary mixture) and swelling clays is important for CO₂-EGR and CO₂ sequestration in shale gas reservoirs.

In this study, we employ the grand-canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulations to investigate CO₂-H₂O-CH₄ ternary mixture in Na-montmorillonite clay interlayer under geological conditions ($T = 323$ K, $P = 90$ bar) with relative humidity (RH) in the ranges of 5%–40%. We studied the effects of RH on the intercalation of different species. The stable clay interlayer distances at different RH values are determined based on the normal pressure and free energy curves of H₂O-CO₂-CH₄-Na⁺ complex in the montmorillonite clay interlayer. Simulation results show that there are two stable hydration states: monolayer hydrates (1W) with a basal spacing around 12 Å and bilayer (2W) H₂O-CO₂-CH₄ mixture with a basal spacing around 14.5–15.7 Å. In the range of RH investigated, 1W state is more stable than 2W state. In general, CO₂ and CH₄ intercalation in the clay mineral is strongly influenced by RH. Our simulation results show that high RH values facilitate water molecules entering clay interlayer and decrease the CO₂ and CH₄ intercalation. Different CO₂/CH₄ ratios in the ternary mixture are investigated. The presence of CO₂ may significantly influence the CH₄ sorption. CO₂ and CH₄ molecules are partially hydrated, especially at low RH, while sodium ions are fully hydrated due to its relatively high hydration energy with water molecules.

We further study force field parameters on the sorption of H₂O-CO₂ binary mixture in clays. The unlike-pair interaction parameters between H₂O and CO₂ are optimized to reproduce the mutual solubility of H₂O and CO₂. Subsequent GCMC simulations with the optimized parameters are performed to investigate the compositions of H₂O-CO₂ mixture in a Na-montmorillonite interlayer at $T/P/RH = 323$ K/90 bar/90%. Simulation results show that the optimized LJ unlike-pair interaction parameters result in more reasonable sorption results in clays.

DIFFERENTIATING DEHYDRATED HALLOYSITE FROM KAOLINITE USING XRAY DIFFRACTION METHODS

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The Kaolin group minerals, in particular, kaolinite and halloysite are important industrial minerals that are used in a wide range of applications due to their low surface charge, (mostly) low surface area, low ion exchange, particle size and shape and often bright white colour. Current worldwide production of kaolin is approximately 40 million tons per annum.

Poochera, located on northern Eyre Peninsula contains some of the largest resources of commercial-grade kaolin known in South Australia (Ferris and Keeling, 1993). Exploration and evaluation drilling of the resources showed the kaolin to be very high brightness and composed of variable platy and tubular forms of kaolin. Differences in the amount and morphology of the kaolin has direct effects on rheology for paper coating and strength for ceramics applications. While differentiating halloysite from kaolinite can routinely be done using formamide intercalation (Churchman et al., 1984), the tubular form of kaolin from the Poochera deposit showed little, if any swelling of dehydrated halloysite basal peaks (001) from $\sim 7.2\text{\AA}$ to $\sim 10.4\text{\AA}$ after intercalation.

A previous study of kaolin from Mount Hope, a similar deposit located approximately 240 km SSE of the Poochera deposit, successfully used SEM point counting and FT-IR with partial least squares (PLS) analysis to differentiate between the tubular and platy forms of kaolin (Janik and Keeling, 1993). The same samples and SEM point counting data were used to determine calibrations for quantitative mineralogy of the Poochera kaolin deposit using a variety of XRD-based techniques; i) Hinckley Index (Hinckley, 1963), ii) whole pattern fitting, iii) Rietveld QXRD, iv) XRD PLS analysis, and v) profile fitting of the kaolin 001 peak at $\sim 7.2\text{\AA}$.

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QUANTIFICATION OF PREDOMINANT MINERALS IN SEDIMENTARY ROCKS BY CHEMOMETRIC ANALYSIS OF INFRARED SPECTRA

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The chemometric analysis was applied on infrared spectra of samples of three types of sedimentary rocks (claystone, clay slates and sandstones) from several localities in the Moravian-Silesian area of the Czech Republic. Determination of chlorite, muscovite, albite and quartz was performed by chemometric methods (Principal Component Analysis and Partial Least Squares Regression) in these sedimentary rocks. A separate chemometric models were developed for quantification of content of each above mentioned minerals.

Results obtained by chemometric models were statistically evaluated. Accuracy, precision, repeatability, and uncertainty were selected as appropriate statistical parameters.

The infrared spectra of the sedimentary rock samples were measured by bromide pellets technique and also by diffuse reflectance technique.

MICROBIAL REDUCTION AND OXIDATION OF Fe(III)-OXIDES AND Fe(III)-PHYLLOSILICATES IN SOIL AND SEDIMENTARY ENVIRONMENTS

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Insoluble Fe(III)-oxides and Fe-bearing phyllosilicates are abundant redox active components in soils and sediments. Microorganisms play a key role in both the reduction and oxidation of such phases, with broad impacts on the fate and cycling of organic and inorganic compounds of both natural and anthropogenic origin. Dissimilatory Fe(III)-reducing bacteria (FeRB) utilize Fe(III)-oxides and Fe(III)-phyllosilicates as electron acceptors for respiration, whereas Fe(II)-oxidizing bacteria (FeOB) utilize Fe(II) end-products of DIRB metabolism as an energy source for chemolithotrophic metabolism. FeOB can also utilize primary Fe(II)-bearing silicate and sulfide phases as lithotrophic energy sources. In all cases, the Fe redox transformations take place *outside* of the bacterial cell via specialized biochemical mechanisms known collectively as “extracellular electron transfer” (EET). This presentation will review and synthesize our research on reductive and on oxidative transformations of specimen and natural Fe(III)-oxides and Fe-phyllosilicates relevant to soil and sedimentary environments. The model FeRB *Geobacter sulfurreducens* was used to examine the pathways of Fe(III) reduction in native and Fe(III)-oxide stripped subsurface sediments, in some cases materials that were coated with different amounts of synthetic high surface area (HSA) goethite. Cryogenic (12K) ⁵⁷Fe Mossbauer spectroscopy was used to determine changes in the relative abundances of Fe(III) oxide, Fe(III)-phyllosilicate, and phyllosilicate-associated Fe(II) [Fe(II)-phyllosilicate] in bioreduced samples. A Fe partitioning model was developed to analyze the fate of Fe(II) and assess the potential for abiotic Fe(II)-catalyzed reduction of Fe(III)-phyllosilicates. Parallel studies demonstrated the potential for chemolithotrophic Fe(II)-oxidizing microorganism to oxidize Fe(II)-phyllosilicates, and for cyclic coupling of Fe-phyllosilicate reduction and oxidation. Ongoing genomic and metagenomic sequencing efforts shed light on previously unrecognized EET mechanisms whereby microorganisms may oxidize insoluble Fe(II)-bearing mineral phases. Such pathways share key characteristics with known EET pathways in both FeRB and FeOB, and open up the possibility for development of molecular biological tools to study the abundance, distribution, and activity of Fe-redox cycling microorganisms in a variety of natural and engineered environments.

CONSPIRATION OF MINERALS AND ORGANICS IN ORIGINS OF LIFE

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The condensation of oligomers (amino acids, nucleotides) into the corresponding biopolymers on mineral surfaces, with or without activators, is a part of many prebiotic scenarii [1,2,3]. While it has long been evidenced experimentally, a satisfactory physico-chemical description is still lacking, and would constitute a prerequisite to determine the likelihood of “surface scenarii”. The corresponding polymerization reactions in aqueous solutions are endergonic and therefore do not occur spontaneously.

What makes them thermodynamically allowed on surfaces is simply the possibility of working in conditions of very low water activity, as all reported successful instances of polymerization involve drying steps. Since these condensation reactions result in the production of one water molecule ($R-COO^- + R'-NH_3^+ = R-CO-NH-R' + H_2O$), simple thermodynamic arguments (Lechâtelier's principle) ensure that decreasing water activity will favor condensation. This is of course not a catalytic effect since catalysis cannot change the thermodynamics.

The same argument holds for several reactions of fundamental importance in current bioenergetics, such as the formation of ATP (P-O-P from P-OH condensation) or various phosphorylations (C-O-P from C-OH and P-OH).

Therefore we have compared on the same supports the dimerization of the simple amino acid with the formation of ATP from ADP and inorganic phosphate, and with the formation of an inorganic activated molecule (pyro- and/or metaphosphates from orthophosphate). The investigated systems are characterized both macroscopically, from thermogravimetric analysis, and at the molecular level with ¹³C, ³¹P solid-state NMR, transmission IR and Raman spectroscopy of the dried powders in order to unequivocally identify the formation of so-called “high-energy” bonds (P-O-P, C-O-P but also amide bonds).

Not all mineral surfaces are efficient to promote endothermic condensations, although the thermodynamic argument should be the same for all of them. Some surfaces provide an intermediate strength interaction with the adsorbed biomolecules, probably by H-bonding, and in this way open new reaction pathways with lower activation energy, resulting in condensation at measurable rates for moderate temperatures (100-200°C).

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NOBLE GAS AND LIGHT HYDROCARBON INTERACTIONS WITH MONTMORILLONITE: ACCESSIBILITY OF THE INTERLAYERS

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Fluid-solid interactions of pure and mixed geofluids confined in the narrow pores of earth materials play important roles in the uptake, mixing, storage, extraction, and transport of these fluids. Fluid-pore interactions play out at the molecular to microscopic levels, and include sorption, wetting, diffusion, and flow, all impacted by confinement effects. Fluid-solid interactions play out at the surfaces, and clays have some of the largest surface areas of minerals. In addition, clay fractions often show significant intergranular porosity, and swelling clays in hydrated state have appreciable pore volumes in interlayer pores. Therefore, clay-fluid interactions may control the properties of fluids in shale and other clay-rich rocks. I will discuss excess sorption and neutron diffraction data we have collected to gain insight into clay interactions with noble gases, light hydrocarbons, water, and CO₂. This work aims at obtaining a basic understanding of the sorption capacity and fluid recovery amounts and rates of shales, and their dependence on shale composition, structure, and pore size distribution. Of great interest are the accessibilities of clay interlayer pore spaces, which contain large fractions of the clay and shale internal surfaces, to different fluids. The experimental data are interpreted to yield the mean fluid densities in the interlayer spaces, and their possible coordinations with the interlayer cations and their hydration shells.

EFFECT OF MICROBIALLY PRODUCED ORGANIC COMPOUNDS ON THE REDOX REACTIVITY OF FE-BEARING CLAY MINERALS

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Clay minerals are ubiquitous in the environment and most clay minerals contain Fe in their structure, which can be reduced both microbially and chemically. In addition, aqueous Fe(II), which is produced by microbial activity in anoxic environments, is also capable of transferring electrons to structural Fe in clay minerals. As a result, clay mineral Fe(II) and an Fe(III) oxidation product are formed. We showed that regardless of the Fe(III) oxidation product, the resulting reactive species for contaminant reduction was structural Fe(II), which exhibited the same reactivity as that in chemically reduced clay minerals. In natural environments, microbial activity releases not only Fe(II) but also a range of organic compounds such as ligands and electron shuttling compounds, which could affect the Fe(II)-reduced clay mineral reactivity.

To determine the effect of microbially produced organic compounds, we chose citrate, salicylate, tartrate, and oxalate as our model organic ligands and used anthraquinone-2,6-disulfonate (AQDS), juglone, riboflavin, flavin mononucleotide and flavin adenine dinucleotide as electron shuttling compounds spanning a broad range of reduction potentials (-0.216V to +0.530 V). We used a nitroaromatic compound (NAC) as reactive probe molecule and assessed its degradation kinetics as a measure of redox reactivity of the system.

When organic ligands were added to Fe(II)-amended nontronite NAu-1, NAC reduction kinetics were slightly slower compared to Fe(II)-organic ligand complexes alone, suggesting that the complexed Fe(II) was the dominant reactive species rather than clay mineral Fe(II). Interestingly, pre-reduction of NAu-1 changed the NAC transformation kinetics from pseudo-first order to biphasic, second order and strongly increased the rate compared to chemically reduced NAu-1 alone, pointing towards clay mineral Fe(II) contribution to contaminant transformation. Similarly, when we added the electron shuttling compounds to Fe(II)-reacted NAu-1, we observed a significant increase in NAC reduction rate. Pre-reduction of clay mineral Fe further increased the reaction rate, suggesting that clay mineral Fe(II) served as a source of reduction equivalents for electron shuttling compound reduction. Our combined results indicate that clay mineral Fe might provide redox buffering and reduction equivalent storage in natural systems.

CARBON-SILICATE COMPOSITES: THE ROLE OF FIBROUS CLAYS

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Clay minerals and carbon are present as abundant deposits in our Planet. Both of them constitute natural resources applied by humans since the prehistory for basic materials and energy developments. Although in some cases they can show certain similitude, as for instance their structural organization in the form of 2D solids, such as graphite and smectite minerals, they exhibit very different properties regarding their chemical reactivity, electrical and thermal conductivity, rheological characteristics, etc. In spite of these differences, clays and carbon can be deliberately assembled at the nano- or micro-meter range giving rise to functional materials provided of synergistic properties of interest in diverse application fields. In this way, carbon-clay hybrids can be applied from the fabrication of conventional pencil cores to the development of advanced composites for energy production and storage, active phases of sensing devices, specific sorbents of pollutants and improving catalytic systems (Darder et al., 2018; Ruiz-García et al., 2018). In particular, fibrous clays such as palygorskite and sepiolite have been involved to prepare carbon-clay functional composites (Ruiz-Hitzky et al., 2016), the assembly of both components being reached through top-down and bottom-up synthetic strategies. Following the top-down approach, the individual carbon (*graphenic*) components such as multiwall carbon nanotubes (MWCNT) and graphene nanoplatelets (GNP) can be assembled to fibrous clays by sonomechanical treatments (Ruiz-García et al., 2014). The bottom-up approach used as a second strategy of carbon-clay composite synthesis makes use of diverse organic precursors that in a controlled atmosphere can be thermally transformed into carbonaceous materials in the presence of clays including sepiolite and palygorskite.

This communication intends to introduce the latest advances on this topic, scarcely known at the moment but showing a promising future towards new functional materials based on fibrous clays for advanced applications.

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THE QUALITY OF MG-Fe LAYERED DOUBLE HYDROXIDE DERIVED FROM MAGNESITE AND HEMATITE

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Layered double hydroxides (LDH) are crystalline phases classified as non-silicate oxides and hydroxides of the following general chemical formula: $[M^{II}_{1-x}M^{III}_xOH_2]^{x+}[A^{n-}]_{x/n} \cdot yH_2O$. The LDH are called “anionic clays” due to evident similarities to clay minerals. These include: layered structure, variable layer charge, rheological and colloidal properties. However the main difference is their ability to exchange anions in contrast to clay minerals which possess cation exchange properties. LDH are rare in nature, however their synthesis can be easily carried out in the laboratory. The disadvantage of this approach is a relatively high cost of used pure chemical reagents. To overcome this problem a synthesis protocol involving transformation of abundant and widely available minerals into hydrotalcite-like phases is proposed in the research.

For the experiments, magnesite [M], hematite [H], $MgCl_2 \cdot 6H_2O$ [Mg] and $FeCl_3 \cdot 6H_2O$ [Fe] were used as sources of magnesium and iron in order to obtain Mg-Fe LDH. The LDH was synthesized in four variants using different reagents or minerals: Mg–Fe, M–Fe, Mg–H, M – H. Before synthesis, M and H were dissolved in hydrochloric acid to obtain solution with Mg^{2+} and Fe^{3+} , respectively. Firstly, the pH of solution containing Mg^{2+} was set to 10 by aqueous NaOH. Secondly, the solution containing Fe^{3+} was added dropwise to the Mg^{2+} solution. During this process the pH was constantly controlled in the range of 9-10. Finally, the suspensions were aged at room temperature for 2 h and afterwards washed with water and dried overnight at 60°C. All samples were characterized by XRD, FTIR and SEM. The XRD patterns confirmed the formation of LDH in all synthesis routes when compared to pyroaurite standard (JCPDS #14-0293) which is a magnesium iron carbonate hydroxide (Millis et al., 2012). However, for all samples with exception of the M–H sample, the presence of brucite (JCPDS #44-1482) was noticed. The FTIR spectra showed characteristic bands attributed to the water content and presence of CO_3^{2-} , Mg-O and Fe-O. Also, in all samples except M–H sample, a band at 3700 cm^{-1} indicating the additional formation of brucite (Fahami, Beall 2016) was observed. The SEM showed that compared to the starting materials (M and H samples), the morphology of products has clearly changed. The images enabled to observe characteristic layered morphology for all the synthesized materials.

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FTIR BASED QUANTIFICATION OF ADSORBED COMPOUNDS ON CLAYS

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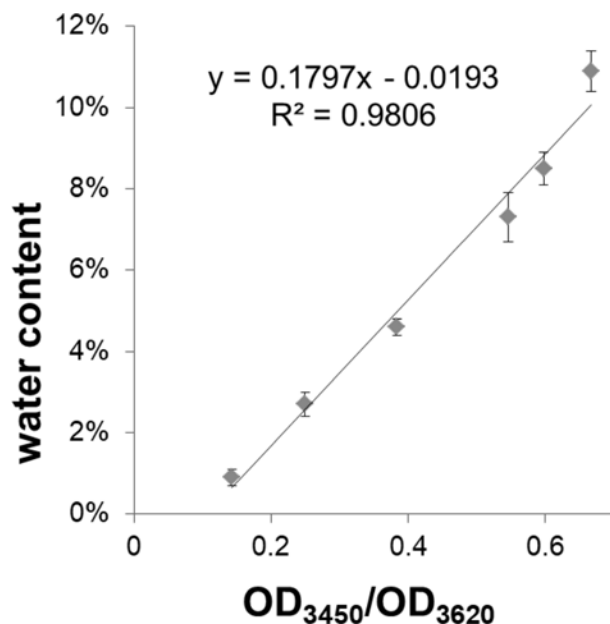
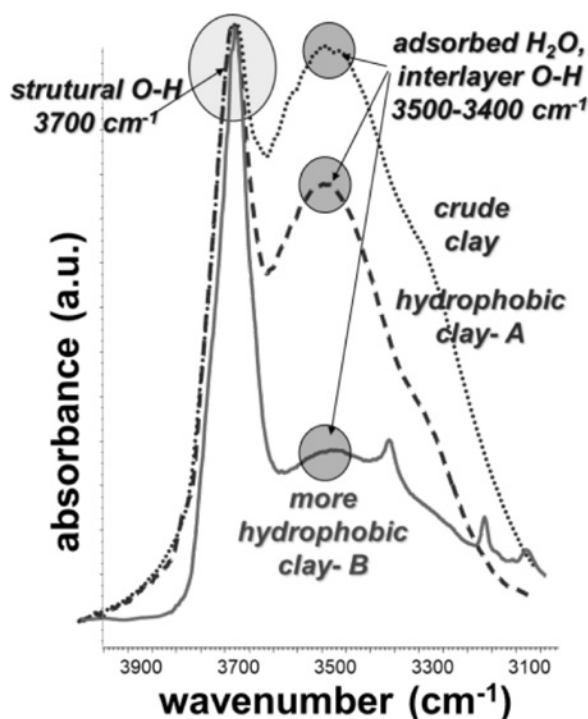
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In the preparation of hybrid clay-organic compounds the first question to be answered is “what is the ratio between the components”. In several cases the amount of organic material combined with the clay mineral must be determined after performing the initial “mixing” by a specific “indirect” or “direct” method. In indirect methods measurement the remaining organic compound is measured in a procedure known as “mass balance”. However, in such techniques other processes that influence concentration in equilibrium solution might be wrongly ascribed as “adsorption”, yielding overestimates (due to degradation, precipitation or evaporation of the adsorbate) or underestimates (due to ineffective separation).

Attenuated Total Reflectance (ATR) -FTIR can be used to quantify directly the amount of organic compounds adsorbed on clay minerals, yielding similar results when compared with other techniques (gravimetric, UV-Visible, CHNSO) and even describing similar effects of saturation or desorption. Its main advantage is that it allows measurement of dispersions, gels, liquids and pastes very fast, with no extra preparation procedures. For example (left figure), ratios of absorption between clay O-H band (at 3620 cm⁻¹) to the absorption of adsorbed water (at app. 3450 cm⁻¹) can be used to evaluate hygroscopic water content. After calibration done gravimetrically (right figure), water content of unknown samples might be directly evaluated.

The advantages of the procedure are (a) it evaluates directly the adsorbed amount on the sorbent (b) it might measure accurately chemicals “not seen” with other simple methods as UV-Visible spectroscopy.



MOLECULAR SCALE MECHANISM OF CHROMIUM INTERACTION WITH METAL OXIDES: MICROBIAL AND STRUCTURAL ASPECTS

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Chromium (Cr) is a significant heavy metal and radionuclide contaminant. Common oxidation states of Cr are Cr(VI) (highly mobile, toxic, and bioavailable) and Cr(III) (typically insoluble in circumneutral conditions, and a micronutrient). The environmental and geological fate of Cr is heavily influenced by common metal oxides such as iron (Fe) and manganese (Mn) oxides.

For example, traditional remediation strategy for Cr(VI) contamination employs the reduction of Cr(VI) to Cr(III) and the subsequent precipitation of the insoluble Cr(III)-Fe(III)-(oxy)hydroxides. Yet, the role of microbial organic molecules on the transformation of these remediation products has generally been overlooked. Our research investigated the stability of Cr(III)-Fe(III)-(oxy)hydroxide solid solution series in the presence of representative microbial exudates, siderophores (e.g. desferrioxamine B; DFOB) and small organic acids (e.g. oxalate). In the presence of DFOB, Fe was preferentially released relative to Cr from all solid phases. Oxalate acted synergistically with DFOB to increase the Fe release rate. The remaining solids became enriched in Cr relative to Fe, leading to increased solubility relative to the initial solid phases. Thus, the presence of microbial exudates can promote the release of Cr(III) from remediation products via both ligand complexation and increased solid solubility, producing dissolved Cr(III) or Cr(III)-ligand complexes that are susceptible to subsequent oxidation to Cr(VI), leading to the occurrence of recontamination.

On the oxidation side, the most significant environmental oxidant of Cr(III) is Mn oxides, the formation of which also require microbial activities. Our study demonstrated that Cr(III) oxidation by bacterial Mn oxides are affected by the presence of light and organics, and the Mn(II) produced during the redox reaction can be cycled in the system, leading to continuous Cr(III) oxidation even in the presence of small amounts of biogenic Mn oxides. Taken together, our study demonstrated the importance of taking into account microbial activities on the transformation of Cr-containing phases in the presence of common metal oxides, and have important implication for the environmental and geological processes involving Cr.

MODIFICATION AND CHARACTERIZATION OF A NIGERIAN CLAY FOR IMPROVED RHEOLOGY IN WATER-BASED DRILLING FLUID

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Nigeria is one of the major oil producing countries in the world and as a result, embarked on substantial deep well drilling activities. Presently, there is no significant exploitation of Nigerian clays especially bentonitic clay for drilling fluid production despite its proven large deposits at different locations in the country. Several researches have shown that most Nigerian local bentonite samples are not suitable for drilling mud production. Hence, bentonite samples are imported into the country to produce drilling fluids. Importation of clays and additives add to the cost of drilling which is undesirable. Improving the qualities of Nigeria clay is therefore imperative for them to serve as substitute for the imported bentonite.

A Nigerian clay sample obtained from Abia state was pre-treated using NaOH, Na₂CO₃, NaHCO₃ and KOH at various concentrations and pre-treatment time to improve their suitability for drilling fluid production. Response Surface Methodology (RSM) was adopted to design the experiment using two factors and three-levels Central Composite Design (CCD). The raw and beneficiated samples were tested for rheology, pH and mud weight. Selected pre-treated sample was analyzed using X-ray Diffractometer (XRD), X-ray Fluorescence (XRF), Fourier Transform Infrared (FTIR) and Scanning Electron Microscope (SEM). The selected pre-treated sample was nano-sized using ball milling machine. Drilling fluid was developed using the nano-sized clay sample and bio-polymers (non- synthetic polymers).

Viscosities of the pre-treated samples increased with increasing shear rate which shows that the investigated samples exhibited shear thickening properties. pH values of the clay slurry increased in all the pre-treated samples compared to the raw samples. Na/Ca ratios and rheological properties were significantly increased after treatment. Modification using KOH resulted in total removal of the Ca content in Ubakala clay. XRD results shows that the pre-treated clay contains high quality montmorillonite, albite and quartz.

The research has shown that pre-treatment has significant effect on the mineral, chemical and morphology of the clay sample. Drilling fluid developed using the nano-sized pre-treated Nigerian clay and locally sourced additives (bio-polymers) have viscosities that compared favourably to the American Petroleum Institute (API) stipulated standard.

STRUCTURE CHANGE IN OIL SANDS FLUID FINE TAILINGS DUE TO FLOCCULATION WITH A HIGH MOLECULAR WEIGHT ANIONIC POLYACRYLAMIDE

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Water based extraction of bitumen from Alberta's oil sand deposits creates large volumes ($\sim 10^9$ m³) of a slow settling slurry referred to as Fluid Fine Tailings (FFT). Treatment of FFTs using polymeric flocculants represent one of the most effective approaches to accelerate their consolidation and minimize volume. In this study, we used rheological tests to examine FFT interactions of three different FFTs representing different extraction processes with a polymeric flocculant. Dynamic amplitude sweep tests (Fig. 1) were performed on both the untreated and the polymer treated FFTs over a range of clay to water ratios. The latter were tested both in the intact state as well as after different degrees of destructuring. The results of the rheological tests highlight structural changes that occur in the FFT as a result of flocculation, and are used to elucidate how the polymer interacts with clay particles in the FFTs.

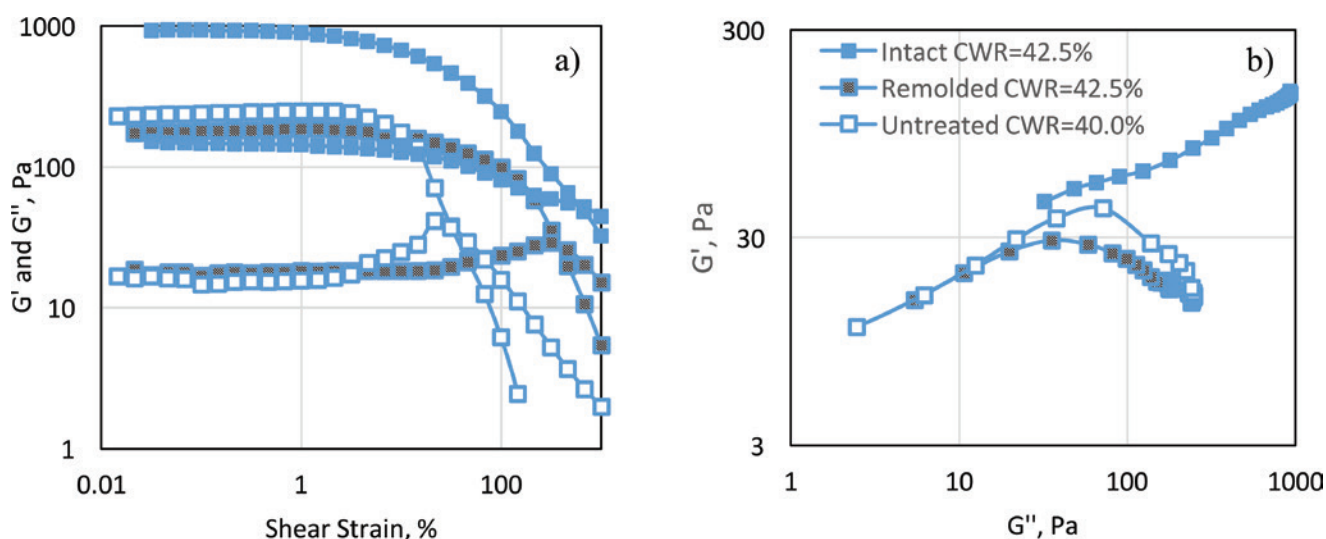


Figure 1. a) Dynamic amplitude sweeps on untreated and polymer treated FFT at similar clay to water ratios (CWR); b) Cole-Cole plots of the data shown in Fig.1a

ENVIRONMENTAL TRANSFORMATIONS OF SILVER AND ZINC OXIDE NANOPARTICLES DRIVE RISK ASSESSMENT UNDERSTANDING

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Over the past decade, a tremendous amount of effort has been put forth to investigate the potential release of engineered nanomaterials (ENMs) to the environment. The rationale behind this endeavor is based on the wide-spread application of ENMs in consumer products such as metallic silver ENMs as antimicrobial agents in medical equipment, cleaning products, and fabrics to control odors; as well as zinc oxide ENMs in cosmetics and ultraviolet coatings. In themselves relative to the concentration in consumer products, metallic silver and zinc oxide ENMs pose very little threat to humans; however, a legitimate concern is exposure to ecosystem receptors, if released to the environment. As consumers, we purchase ENM-laden products and bring them into our homes where they are used and disposed. Two common disposal options are wastewater leaving the home via hygiene washing and laundry or landfill through discarding trash. Predictive modeling indicates that the vast majority of ENMs in consumer products brought into the home leave the home via the wastewater disposal pathway.

Once ENMs enter wastewater and flow to the community wastewater treatment plant (WWTP), they undergo a unique chemical and physical adventure to transform into relatively inert products, and are generally captured in the sludge or biosolids within the WWTP. To emphasize, they are no longer pristine metallic silver and zinc oxide ENMs. Metallic silver ENMs convert to silver sulfide and silver chloride moieties of various size; likewise, zinc oxide changes to zinc sulfide with potential to alter to other phases upon aging. These transformations are very important for risk assessment. It is prudent to understand that the risk assessment of silver sulfide is tremendously different than metallic silver ENMs. However, this adds complexity to regulatory agencies and policy development to provide comprehensive risk analysis of ENMs.

This presentation will highlight the transformation of metallic silver and zinc oxide ENMs found in consumer products and disposal scenarios. Imperative to the discussion will be relevancy of experimental studies to fall in line with conditions observed at WWTPs so that risk assessment can be based appropriate and applicable guidelines.

ACTIVITY OF ANTIBACTERIAL CLAY AGAINST DRUG-RESISTANT BACTERIA

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Oregon Mineral Technologies (OMT) Blue Clay has shown antibacterial properties in preliminary studies. Here, we assessed its *in vitro* activity against planktonic and biofilm bacteria.

Twelve bacterial strains representing species frequently associated with wound infections, including antibiotic resistant strains, were studied. For planktonic studies, bacteria were grown to 1.5×10^8 cfu/mL in 20% (5g/L) Luria broth (LB), diluted to 10^7 cfu/mL, and combined in a 1:1 ratio with OMT clay (200 mg/mL), OMT leachate, or water. Samples were incubated at 37°C with shaking, and quantitatively cultured at 0, 4, 8, 12, and 24h. For biofilm studies, biofilms grown on Teflon discs were incubated for 24h with either OMT Blue Clay (200 mg/mL), OMT leachate, or 10% LB, followed by quantitative culture. All testing was performed in triplicate. Statistical analyses were performed using the Wilcoxon rank sum test.

Planktonic studies. Within 4h, the clay and leachate significantly reduced planktonic bacterial populations of all strains tested compared to controls ($p \leq 0.05$). By 24h, there was a $\geq 3 \log_{10}$ cfu/mL reduction for all strains tested, with the exception of leachate-treated *Staphylococcus aureus* IDRL-6169, for which there was a $2.5 \log_{10}$ cfu/mL reduction that was statistically significant compared to the control ($p=0.0369$). At 24h, *S. aureus* IDRL-6169 and *Escherichia coli* IDRL-10366 exhibited greater reductions when treated with clay *versus* leachate ($p = 0.0369$ and 0.0463 , respectively); for the remainder of the strains there was a less than $0.5 \log_{10}$ cfu/mL difference between the clay and leachate, a statistically non-significant difference.

Biofilm studies. Clay exposure reduced population densities of all organisms tested compared with controls, of statistical significance. Leachate treatment also resulted in statistically significant population reductions compared with controls for all organisms except for *S. aureus* IDRL-6169. Clay *versus* leachate formulations supported statistically significant population reductions of greater magnitude for four of the twelve organisms tested: *S. aureus* IDRL-6169 ($p=0.0369$), *Staphylococcus epidermidis* RP62A ($p=0.0253$), *Enterobacter cloacae* IDRL-10306 ($p=0.0495$), and *E. cloacae* IDRL-10375 ($p=0.0495$).

OMT Blue Clay exhibited antimicrobial activity against all 12 bacterial strains tested in planktonic studies, and in addition, demonstrated activity against biofilms *in vitro*.

LANDSHED POSITION AND MANAGEMENT AND THEIR RELATION TO MINERAL AND CHEMICAL WEATHERING AS ASSESSED BY HIERARCHICAL CLUSTER ANALYSIS OF REGOLITH ELEMENTAL DATA

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Chemical denudation and chemical weathering rates vary under temporal, climatic, bedrock, biotic, and topographic conditions. Constraints for landscape evolution models must consider changes in these factors on human and geologic time scales. Metrics to evaluate the states of landscape evolution include landscape position, landscape management (i.e., agricultural crops and their rotations), soil profile properties, and regolith mineralogy/chemistry. This study examined deep (~8 m) weathering profiles situation at the Calhoun Critical Zone Observatory (CCZO) located on granitic gneiss in the Piedmont of the S.E. United States. Sites were located on various interfluvial-landshed[#] system orders (Brecheisen et al., 2017), which have been managed for nearly a century as either hardwood, pine, or cultivated crop covers. The CCZO trends up to 5th order within a 150km² landscape. Plotting of elemental metrics such as the traditional chemical index of alteration (CIA) shows depth trends of intense weathering at the surface and subsurface pedogenic clay accumulations (50 to 300 cm). Cultivated plots display the deepest weathering fronts, as seen in CIA values of >90% to 5 meters. Although CIA varies with depth, there is a general trend of increased weathering with increased interfluvial order. In three of the four paired pine-hardwood sites, pines have slightly lower CIA values relative to hardwoods. Hierarchical cluster analysis of the chemical data in the context of depth of samples in profile, landshed order location, and vegetative cover suggests that management of the landscape exerts an influence on weathering rate in the CCZO (assuming degree of management decreases in the order of hardwood → pine → cultivated). This approach using elemental data can be further constrained by quantitative mineral analysis using X-ray diffraction. Agreement between elemental and mineral quantification provides an accurate means for understanding mass balance of materials fluxing into and out of the Critical Zone.

[#]A landshed system is defined by the narrowest and most highly dissected ridges and isolated hilltops that are considered 1st order, which then increase in order dendritically as branches join uphill to become more voluminous.

Reference: Brecheisen, Zachary, Seulgi Moon, Daniel Richter, Patrick Halpin (2017): Ordering interfluvies: an analytical framework for hierarchical patterns in landscape structure and function. American Association of Geographers Annual Meeting, Boston, MA, 7 April 2017.

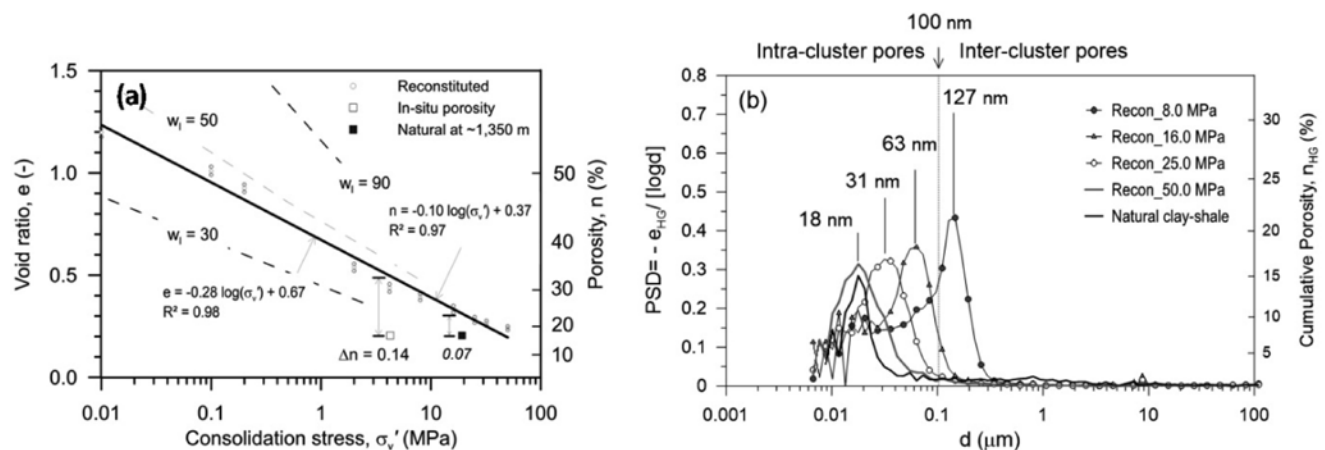
DIAGENETIC CEMENTATION EFFECTS ON THE PORE STRUCTURE AND MECHANICAL PROPERTIES OF OPALINUS CLAY-SHALE

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Diagenetic processes of lithification and concomitant precipitation of cementing agents act to increase the strength and stiffness of Opalinus clay-shale: a potential host rock for deep geological storage of nuclear waste in Switzerland. These processes are offset by the creation of fractures that lead to fissility of the natural material. Reconstituted shales can provide new insights into the nature of the pore structure in natural materials. Here we investigate the effects of burial diagenesis on the pore structure and mechanical behavior of Opalinus clay by comparing the reconstituted and natural materials through different techniques including N₂ adsorption and mercury intrusion porosimetry as well as the nanoindentation and uniaxial compressive loading. We reconstituted the parent material through multiple grinding operations, sedimentation from a dispersed slurry, and one-dimensional isothermal consolidation to produce uniform specimens with no cementation bonding. Results show that even at large consolidation stresses more than twice the estimated maximum in situ effective stress the total porosity and the dominant pore size of reconstituted specimens did not converge to those of the natural clay-shales. Also, despite a brittle to semi-brittle response observed in the natural Opalinus clay-shale, the reconstituted material exhibited a strain hardening behavior followed by a brittle failure and a significantly lower uniaxial compressive strength. The observed discrepancies in terms of pore structure and mechanical response of reconstituted and natural materials indicated that the mechanical consolidation itself was insufficient to modify the microfabric and increase the material strength, and instead a chemical cementation process at a submicron scale was responsible for such modification.



MECHANICAL PROPERTIES OF BENTONITE BARRIERS— THE BEACON PROJECT

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The sealing ability is essential for the engineered clay (bentonite) barriers in all geological repository concepts. This is normally achieved by a swelling pressure and a low hydraulic conductivity. The swelling pressure may also impact the barriers in the repository. The mechanical properties of the installed EBS, that may consist of a mixture of blocks, pellets and engineering voids, will be entirely different from the situation after full saturation. It is therefore important to understand:

1. The mechanical evolution during the saturation phase
2. The final situation after reaching equilibrium

The understanding of the mechanical processes in bentonite is incomplete, even though the material intended as buffer or seal in geological repositories has been studied for decades. The focus of earlier studies has often been on the hydraulic and geochemical/mineralogical issues, while the mechanical issues have been treated as a secondary issue. At this stage, when implementation of geological disposal is getting imminent, the mechanical issues have become more important, since they often represent the connection between the long-term performance and the design and construction of a repository. In the EU-funded project BEACON is studying these issues.

There are data currently available from a number of laboratory as well as large scale field experiments. Many of these experiments have not been analysed in detail. One objective of the current project is to study available experimental results in more detail.

Experimental data as well as model results show that the homogenization process is not complete and that some heterogeneities (i.e. dry density gradients) will remain. In the used models, this is caused by hysteresis effects and non-isotropic stress fields.

The first step is to verify and validate models on well constrained laboratory tests. Those tests are selected since they are very well instrumented and they contribute to understand the role of heterogeneity in swelling clay behaviour. The second step is to apply the models on large scale experiments. A focus is done on experiments well described, in preference dismantled to get details (for example on final water saturation state) and highlighting heterogeneity effects. The third step will be dedicated to predictive simulations. One of challenge is to be able to perform predictive simulations for swelling materials integrating initial heterogeneities.

POLYCYCLODEXTRIN-MONTMORILLONITE COMPOSITES: REGENERABLE DUAL-SITE SORBENTS FOR REMOVAL OF BISPHENOL A FROM WASTEWATER

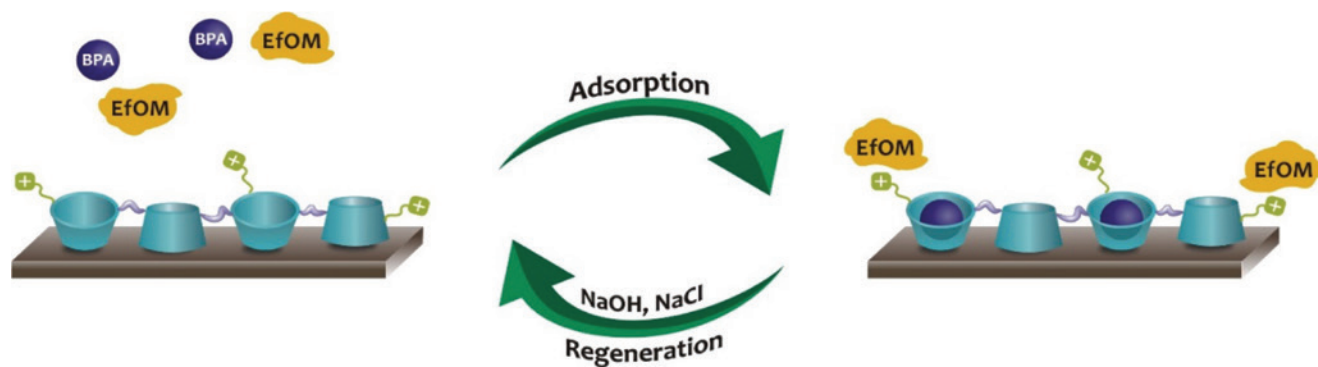
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Adsorption of emerging micropollutants from wastewater is challenging due to sorbent inefficiency in the presence of effluent organic matter (EfOM). Further, sorbent regeneration, a requisite in efficient wastewater treatment, is often overlooked. In this study, we addressed both challenges by designing regenerable, dual-site polymer-clay composites, for the simultaneous removal of bisphenol A (BPA), a micropollutant, and EfOM, from treated wastewater. We designed composites based on β -cyclodextrin, which was polymerized and modified with a cationic group (pCD⁺) or not (pCD⁰) and adsorbed to montmorillonite (pCD⁺-MMT and pCD⁰-MMT, respectively). We tailored the composites as dual-site sorbents to target BPA through hydrophobic size inclusion in β -cyclodextrin cavities and anionic EfOM compounds by the cationic groups. We confirmed β -cyclodextrin polymerization and composite fabrication using a suite of analytical tools.

Adsorption of pCD⁺, characterized by low M_w and positive charge, to montmorillonite, produced an intercalated composite with positive zeta potential. While adsorption of uncharged pCD⁰, characterized by very high M_w , produced an exfoliated composite. The contrasting composite structures were likely induced by polymer size and conformation at the adsorbed state. Further, the planar conformation of pCD⁺ on the clay surface, in comparison to the globular one of pCD⁰, resulted in more rapid adsorption of BPA by pCD⁺-MMT. The dual-site property of pCD⁺-MMT enabled the simultaneous removal of BPA and EfOM from wastewater, which was as high as that of each pollutant separately. Thus, pCD⁺-MMT simultaneously removed BPA and EfOM without compromising BPA removal kinetics. pCD⁺-MMT was employed in filtration columns and demonstrated efficient simultaneous filtration of BPA and EfOM from wastewater. Furthermore, highly effective, in-column regeneration was obtained by selectively eluting EfOM and BPA, with brine and alkaline solution, respectively. Sorbent reuse was demonstrated in two filtration/regeneration cycles, during which sorbent performance remained uncompromised. This study highlights the potential to design novel dual-site clay composites as selective and regenerable sorbents for advanced wastewater filtration.



MODELING MICROSCALE ARSENATE ACCUMULATION IN COMPLEX SOIL MINERAL ASSEMBLAGES

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Soil solids contain complex assemblages of (phyllo)silicate and (hydr)oxide minerals, non-crystalline solids, organic matter, and biota that affect the fate of plant nutrients and potentially toxic elements. Mechanisms of trace-element binding in soils are typically determined by studying pure, model analogues of soil minerals, which do not capture the multi-component complexity of soil mineral assemblages. Our goal is to determine how micro- and nano-scale complexities affect arsenate binding in soil matrices. The specific objective was to determine which soil matrix elements (as proxies for soil minerals) describe the microscale spatial distribution of As binding in soil matrices developed under different pedogenic (weathering) environments. Five quartz sand-grains (<2 mm) selected from soil environments with different redox conditions and organic carbon contents were imaged using micro- X-ray fluorescence spectrometry (μ -XRF) on the Submicron Resolution X-ray Spectroscopy (SRX) beamline at NSLS-II. Images were collected across a 100 μ m x 100 μ m region using an \sim 1 μ m x 1 μ m spot-size, before and after treating the oxide-coated quartz sand grains with 0.1 mM As(V) solution. Preliminary results from spatial likelihood linear model suggest that regardless of the other elements imaged (Ca, Cr, Cu, Mn, Ni, Si, Ti and Zn), Fe was the dominant element accounting for accumulation of As(V), and these other elements had only minor effects. In one grain coating, we found a significant correlation between Fe and Al from Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). Collectively, our results indicated that iron and perhaps aluminum (hydr)oxides were dominant sorbents for As(V) in the soil matrices evaluated, consistent with inferences from research on model mineral systems.

COUPLED KINETIC REACTIONS AT MINERAL-WATER INTERFACES: DEVELOPING QUANTITATIVE MODELS

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Understanding the kinetics of coupled reactions of ions on mineral particles (e.g. adsorption/desorption and redox reactions) is crucial for predicting the dynamic behavior of contaminants in soil environments. Ferrihydrite is one of the most important mineral adsorbents to control the reactivity and fate of both cation and oxyanion contaminants, while manganese (Mn) oxides exhibit high reactivity with redox sensitive elements such as arsenic (As). Currently, there is still a lack of quantitative understanding on the role of mineral binding sites and coupled reactions in controlling the kinetic behavior of ions in soil minerals.

In this talk, we will first describe the development of a unified kinetics model for both cation and oxyanion adsorption/desorption on ferrihydrite based on the CD-MUSIC model. The key idea of our model is to constrain the adsorption and desorption rate coefficients for each specific binding site and the variations of adsorption or desorption rate coefficients among different binding sites. We quantitatively demonstrated how the equilibrium binding of cations and oxyanions with various ferrihydrite binding sites affected the adsorption and desorption rates. Then, we will introduce a novel quantitative model for the coupled kinetics of As adsorption/desorption/oxidation on MnO₂. The model was able to account for the variations of As concentrations, different binding behavior of As(III) and As(V), and flow rates. Our model quantitatively shows that the coupled As adsorption/desorption/oxidation processes are highly dependent on As mass loading rates on MnO₂.

DIFFERENT POOLS OF BIOAVAILABLE IRON IN NONTRONITE NAU-1: INSIGHTS FROM IRON STABLE ISOTOPES

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We have previously shown that 10% of Fe in unaltered nontronite NAu-1 is bioavailable, Shi et al (2016) ES&T. However, whether or not the bioavailable Fe fraction of the clay remains constant over multiple redox cycles is unclear. We carried out three redox cycles of NAu-1 to monitor the accompanying changes in Fe bioavailability. NAu-1 was reduced by *Shewanella oneidensis* MR-1 coupled to lactate oxidation in anoxic conditions and re-oxidized by O₂. The extent of Fe reduction from the 1st to 3rd reduction half-cycle (RHC) decreased from 9.7 to 5.7%, which we attribute to the preferential reductive dissolution of Fe(III) from small clay particles. This explanation is supported by increasing average particle size, the relative dissolution of Fe, Si and Al, and diminished Fe isotope fractionation factors [$\Delta^{56}\text{Fe}_{\text{aq Fe(II)}-\text{struc Fe(III)}}$ and $\Delta^{56}\text{Fe}_{\text{edge Fe(II)}-\text{struc Fe(III)}}$] from the 1st to 3rd RHC. We predict that after the complete consumption of the bioavailable Fe in the small particles, Fe located on the edges of large particles remains as a renewable pool of reducible Fe which oscillates between Fe(II) and Fe(III) during the experiment. Renewable Fe at the edges of larger particles accounts for 4.2% of total Fe in the experiment. This study, for the first time, reports Fe isotope variations during the redox cycles of Fe-containing clay, and contributes to the knowledge on the bioavailability and redox reversibility of Fe-rich clay minerals in the environment.

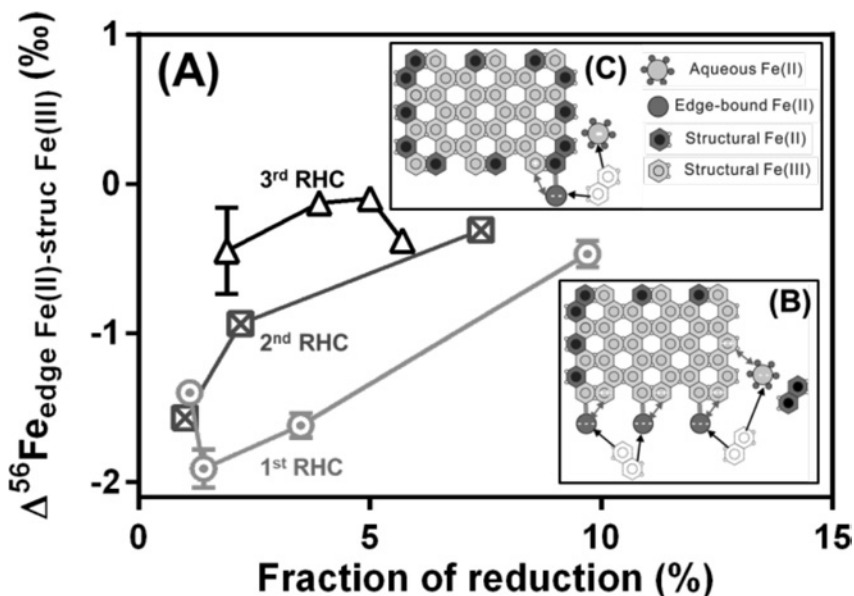


Fig.1. (A) At the same extent of Fe reduction, $\Delta^{56}\text{Fe}_{\text{edge Fe(II)}-\text{struc Fe(III)}}$ decreases from the 1st to 3rd RHC. (B) During the 1st RHC, small particles were abundant and preferentially dissolved (long arrows), large Fe isotope fractionation was produced by the electron transfer and atom exchange (ETA) between the edge-bound Fe(II) and structural Fe(III) (short arrows). (C) Due to the removal of Fe from small particles during the early RHCs, more structural Fe(III) on the edge of large particles was reduced, which decreased the exchangeable edge surface, inhibited ETA between the edge-bound Fe(II) and structural Fe(III), and minimized $\Delta^{56}\text{Fe}_{\text{edge Fe(II)}-\text{struc Fe(III)}}$.

STABILIZATION OF NEUTRAL MOLECULES INTO INTERLAYER MODIFIED LAYERED DOUBLE HYDROXIDES THROUGH PI-PI ATTRACTION

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During past decades, intercalation chemistry on layered double hydroxides (LDHs) has been developed to encapsulate various organic anions taking advantages of positively charged LDH layers. However, there has been distinct limitation in LDH that neutral molecules were rarely stabilized in LDH's gallery space. Intercalation of neutral molecules is only possible through weak physisorption which does not assure high loading amount or stability. To overcome this limitation, we preliminarily modified the interlayer space of LDHs with aromatic carboxylate derivatives of target neutral molecule. In this strategy, the neutral molecules would be stabilized through pi-pi attraction with aromatic carboxylates. To prove this hypothesis, we utilized cinnamate (CA) and cinnamaldehyde (CAD) as aromatic carboxylate derivative and aromatic neutral molecule, respectively. Furthermore, we tried to control the loading capacity of neutral CAD by adjusting intermolecular space among carboxylate (CA). The intermolecular space was controlled by intercalating CA into charge density controlled ZnAl-LDH. Three kinds of ZnAl-LDH with Zn(II)/Al(III) ratios 2, 4 and 7 will have demanded area per charge values of 23.7 Å²/(+), 40.5 Å²/(+), and 95.1 Å²/(+), respectively. The CA intercalated LDHs were first prepared through conventional coprecipitation method (CL hybrids). From the X-ray diffractions and Fourier transform infrared spectra, it was revealed that carboxylate moiety of CA was well anchored on LDH layers through electrostatic interaction. The CL hybrids were then subjected to CAD stabilization by simply soaking hybrids into CAD solution. The CAD stabilized CLs (CLC hybrids) were determined to have 4.89, 11.4, 13.9 wt/wt% of CAD content for Zn₂Al-, Zn₄Al- and Zn₇Al-LDH hybrids, respectively, through CHNS elemental analysis and high performance liquid chromatography (HPLC). Scanning electron microscopic images showed that the layered structure of LDH did not change significantly upon successive intercalation, although the surface morphology seemed to be slightly modified due to surface adsorbed organic moiety. The time-dependent release of both neutral molecule and carboxylate derivative in aqueous media was evaluated by HPLC quantification. It was shown that the CA release was suppressed due to the pi-pi interaction between LDH's gallery.

SECONDARY CLAY MINERALIZATION IN THE CHICXULUB IMPACT CRATER PEAK-RING: AN ISOTOPIC PERSPECTIVE.

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In 2016 the joint International Ocean Discovery Program (IODP)-International Continental Scientific Drilling Program (ICDP) Expedition 364 recovered core from the Chicxulub impact crater peak-ring between ~506 and 1335 metres below the seafloor (mbsf) at Site M0077A, located at 21.45°N, 89.95°W [1]. Preliminary lithologic characterization has revealed a hydrothermal system was generated by the impact that may have been spatially extensive and long-lived [2]. Clay and zeolite mineralization is especially pervasive throughout the uppermost part of the core sequence, which contains a layer of impact melt-bearing breccia overlying clast-poor impact melt rock, above highly fractured and altered crystalline basement. Within these breccias, clays are most commonly associated with the remnants of silicate impact glass, possibly suggesting a dissolution-precipitation model for their origin. The formation and subsequent preservation of clays is not well characterized in terrestrial impact settings; these mineralogies are of interest within the planetary science community as they are ubiquitous across the surface of Mars and not only indicate the presence of water within an environment, past or present, but they may also act as templates for prebiotic organic materials synthesis.

An initial sample set including four melt-bearing impact breccias and one clast-poor impact melt rock was selected for $\delta^{18}\text{O}$ analysis at the Laboratory for Stable Isotope Science (LSIS), following separation and X-ray diffraction characterization of the <2 μm size-fraction from bulk rock powders [3]. *p*XRD showed that trioctahedral smectite is the dominant clay mineral, together with other minor unidentified phases. Electron microprobe analysis revealed these clays occur along fractures and alteration fronts within remnant impact glasses, and in some instances completely replaced clasts.

The $\delta^{18}\text{O}$ results are best interpreted based on the likely fluid reservoirs circulating at different core depths. These fluids are hypothesized to be a mixture of seawater and basinal brines. Results for melt-bearing impact breccias from ~629 to 663 mbsf suggest formation between 95 and 115°C as calculated [4] assuming an ancient seawater source (~-3 to -2‰, VSMOW). The result for a clast-poor impact melt from ~714mbsf suggests higher temperatures 145-175°C assuming a fluid source more influenced by basinal brines (+3 to +6‰, VSMOW). The range of clay $\delta^{18}\text{O}$ likely reflects depth-dependent fluid mixing and differences in lithology. Forthcoming $\delta^2\text{H}$ results for these clays should help resolve some of the ambiguity surrounding our interpretations.

[1] Morgan J. V. et al. (2016) *Science*, 354, 878–882; [2] Simpson S. L. et al. (2018) *49th LPSC*, #2518, [3] Libbey, R. et al. (2013) *Clays and Clay Minerals*, 61, 204-217. [4] Sheppard and Gilg (1996) *Clay Minerals*, 31, 1-24.

APPLICATION OF HIGH GRADIENT MAGNETIC SEPARATION FOR CHARACTERIZATION OF GLAUCONITE WEATHERING PRODUCTS FORMED IN SOILS UNDER DIFFERENT PH CONDITIONS

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The aim of the present research was to compare products of glauconite weathering occurring in two soils formed under temperate climate in different pH conditions. Previous research indicated that both in acidic and in alkaline soils glauconite weathered into smectite-rich glauconite-smectite mixed-layered minerals. Kaolinite and likely iron oxyhydroxides may have also been formed at the expense of glauconite. For better characterization of the weathering products from the studied soils high-gradient magnetic separation was applied. Na-saturated clay fractions from C and B soil horizons were separated into magnetic and nonmagnetic subfractions using a Frantz LB-1 Magnetic Barrier Laboratory Separator. The obtained subfractions were analyzed using XRD and EDS methods.

Magnetic fractions from both soil profiles were dominated by glauconite. A 10 Å phase was also identified in nonmagnetic fractions. It was especially abundant in nonmagnetic material from acidic soil. Smectite concentrated in nonmagnetic fractions, however, in magnetic fraction from alkaline soil it was also identified. A 7 Å phase was detected in both magnetic and nonmagnetic fractions but it clearly concentrated in nonmagnetic fractions, especially in the material from alkaline soil. In magnetic fraction from alkaline soil goethite was identified, whereas magnetic fraction from acidic soil contained lepidocrocite. As expected, nonmagnetic fractions contained less Fe relative to magnetic ones. This may be possibly caused by the fact that both smectites and micas in magnetic fractions contained more Fe than those from nonmagnetic ones.

Magnetic separation of clay material from the studied soils revealed differences between the two profiles, which may be due to different pH conditions. The observed distribution of minerals between magnetic and nonmagnetic fractions may result from different chemical composition of minerals which influences the magnetic susceptibility. The distribution can be, at least in part, affected by incomplete separation, although this effect should be minimized due to repeated separation of each sample.

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ARE AMORPHOUS PHASES ON MARS PRECURSORS TO CLAY MINERALS?

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The Mars Science Laboratory (MSL) rover has investigated several hundred stratigraphic meters of fluviolacustrine sedimentary rocks within Gale crater. Mineralogic analyses imply a basaltic parent material composition for the sediments, and most fluviolacustrine rock samples contain smectite. All of the samples measured by the CheMin X-ray diffractometer (XRD) instrument also contain high abundances of an X-ray amorphous component (AmC) of unknown origin. X-ray amorphous weathering products are frequently found in volcanic soils on Earth, and are thought to be precursors to clay minerals. Could the X-ray amorphous materials on Mars similarly represent pedogenic weathering materials formed under an early Mars climate, and could they have helped form some of the clay minerals detected within the crater? Here, we investigate secondary amorphous weathering products from a variety of Mars analog sites on Earth to compare to data returned from MSL.

The climate of early Mars has been a topic of debate: “warm and wet” or “cold and icy”? Therefore, our terrestrial analog sample suite includes: sediments from recently de-glaciated volcanoes (Oregon; “cold and icy”), modern volcanic soils (Hawaii; “warm and wet”), and volcanic paleosols (Oregon; “cool and moderately wet”) in order to determine how formation environment, climate, and diagenesis affect the abundance and composition of the AmCs. The AmCs are characterized using methods similar to those used for MSL samples; XRD mineralogy is combined with bulk chemistry in a mass balance equation to calculate the bulk AmC composition. We also utilize transmission electron microscopy (TEM) to study the individual amorphous phases at the nanometer scale.

The composition of the bulk AmCs for the “warm and wet” samples are depleted in mobile elements (i.e., K, Na, Ca, Mg) and enriched in less mobile elements (Al, Fe(III), and Ti), consistent with substantial weathering in an open system. In contrast, the glacial sediment and paleosol samples have bulk AmC compositions with higher abundances of mobile elements and substantially less Al and Ti. Many of the individual phase compositions in the cooler climate samples are consistent with smectite clays, indicating proto-smectite materials. Similar materials recently documented in soils on the Falkland Islands were hypothesized to be important, yet overlooked, components of volcanic soils formed in environments with low water activity. The glacial and Hawaiian samples do not contain clay minerals, while the paleosols do, suggesting kinetic barriers inhibiting clay formation. Chemical analyses of the AmCs on Mars show that these materials are more consistent with the “cold and icy” climate AmC compositions and are thus more consistent with a weathering environment that restricted the leaching of mobile ions. We hypothesize that the silicate portion of the amorphous materials could have served as precursors to the smectitic clays found in most fluviolacustrine rock samples in Gale crater.

MINERAL/WATER INTERFACIAL REACTIVITY IN A CHANGING ENVIRONMENT

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Major environmental challenges, due to climate change, are having a profound impact on humankind. Rising seas and temperatures are causing increasing flooding and melting of ice and permafrost soils. The impact of these processes on interfacial processes and reactivity in natural systems such as minerals and soils is not well understood. For example, how do rising seas, that cause inundation of soils with saline water, followed by retrenchment, affect cycling of redox active elements such as arsenic (As) and chromium (Cr)? What will be the effect of redox changes and sorption process on the sequestration of carbon (C) on mineral surfaces of iron (Fe) and manganese (Mn) minerals in soils, a major mechanism for preventing loss of C from soils to the atmosphere. This presentation will explore these questions over a range of spatial and temporal scales.

MY LIFE WITH ILLITE-SMECTITE

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Clay science—as we know it today—was born just after the proper tool needed for studying so finely dispersed materials became available. X-ray powder diffraction was discovered by Peter Debye and Paul Scherrer in 1916, the first paper confirming crystalline structure of clays was published in 1923 in Sweden by Hadding, basic clay structures were solved in the thirties, and the phenomenon of mixed-layering was described by Hendricks and Teller in 1942. I was born in 1947, so for good reason I could not have been a pioneer, but a grandson of pioneers. When I first heard about clays in the seventies, the clay science was already quite mature, with major lines of research well established, clay societies and clay journals already in place, and the second generation of clay scientists already in their mature years. I had the privilege to meet real pioneers: Brindley, Grim, and Jackson in the US and Georges Millot in France. However for me as a geologist by training the most appealing was the type of research conducted those days by John Hower and Bob Reynolds. One postdoc year with John Hower at Case Western Reserve U. in Cleveland was decisive for my future involvements.

Most scientists in their research are concentrated either on a specific method or on a subject. I belong to the latter type: all my life I tried different approaches to address problems related to the illite-smectite clay group, which is the most abundant among clays, accounting for ca. 30% of the mass of sedimentary rocks, and affecting so strongly rock properties. I did not work alone: I owe a lot to my main scientific partners: Denny Eberl, Victor Drits, and Dougal McCarty in the US and Norbert Clauer and Francoise Elsass in France. Latter also to my students, in particular Krzysztof Mystkowski and Marek Szczerba.

Milestones of the illite-smectite research, which I was involved in, were methodical papers. First the measurement of illite-smectite layer ratio, which accounted for the variable thickness of ethylene glycol complex and for the admixture of pure illite, ubiquitous in common geological materials. This allowed me to publish in 1978 one of the first papers comparing clay and organic diagenesis, and to study with Denny Eberl the illitization via wetting and drying, hydrothermal illitization, and the chemical evolution of illite-smectite in the course of diagenesis. In the next phase, we got interested in the size and shape of the illite-smectite crystals and fundamental illite particles, inspired by papers of the Macaulay team. We found that illite crystal thickness distributions are lognormal, they can be measured by XRD, they form in a nucleation and growth process, and thinner particles can be physically separated from thicker by supercentrifugation. The last two findings generated new approach to the K-Ar dating of illite and to interpreting such dates. The regional studies which followed documented thermal histories often more complex than expected and involving large scale thermal events. The third methodological contribution of a broader resonance was the XRD technique of quantifying mineral composition of clay-bearing rocks, which inspired us to organize the Reynolds Cup and allowed diverse applications: the calibration of borehole logging data, N and B capture by illite in the course of diagenesis, distinguishing sedimentary sorting from climatic effects in sediments, tracing hydrothermal alteration of basalts, development of the Ediacaran paleosols, and provenance of the Ediacaran glacial sediments. The mix of developing and applying new techniques makes research very rewarding.

ADDING HYDRATION, TAUTOMERIZATION, AND NUCLEOPHILIC ATTACK TO OUR CONCEPTUALIZATION OF REDOX REACTIONS AT OXYHYDROXIDE MINERAL SURFACES TO IMPROVE REACTIVITY PREDICTIONS

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When a new plant-, fungal-, or microbe-derived natural product is identified in soils, or when a new pesticide or other agricultural amendment is introduced, we want to be able to predict predominant transformation pathways, rates, and products. Recent work with aliphatic organic compound and phosphorus(III)-containing oxyanion reductants has motivated us to add new concepts to our chemical repertoire. “Hydration” has two meanings, both important to us. First, hydration refers to layers of water molecules surrounding dissolved species and covering surfaces. Adsorption, the first step in any interfacial reaction, requires partial loss of these waters of hydration. “Hydrophilic” reactants and surfaces, with strong interactions with their hydration shells, experience a disincentive towards adsorption, while “hydrophobic” reactants and surfaces experience a push towards adsorption. Second, hydration refers to nucleophilic attack by water and hydroxide ions. The $\text{CH}_3(\text{C}=\text{O})\text{H}$ form of acetaldehyde, for example, undergoes a hydration reaction that forms $\text{CH}_3\text{CH}(\text{OH})_2$. It is interesting to speculate about which of these two forms adsorbs more strongly, and which, once adsorbed, is oxidized more quickly. Tautomerization must also be considered. The enol form of aldehydes and keto acids, for example, is more susceptible to oxidation than the keto form. The phosphite anion $\text{P}(\text{OH})_2(\text{O}^-)$ is more susceptible to oxidation than the more abundant H-phosphonate tautomer $\text{H}(\text{P}=\text{O})(\text{OH})(\text{O}^-)$. These new concepts may apply to mineral surfaces as well. Inorganic oxyanions in solution are known to possess anhydride forms (e.g. pyrophosphate formed from orthophosphate, dichromate formed from chromate), and some even form mixed anhydrides and esters with organic compounds. In the materials science literature, some adsorbed species are referred to as anhydrides and esters. Within such a context, the nucleophilicity and electrophilicity of surface sites become interesting subjects for investigation as well.

THERMAL BEHAVIOR OF DIFFERENT TERMS OF THE SEPIOLITE-PALYGORSKITE POLYSOMATIC SERIES.

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The thermal behavior of a group sepiolite-palygorskite samples with different composition (different terms of the polysomatic series) has been studied with the aim of knowing the relation between the mineral crystal-chemistry and the *folding* process of these fibrous minerals. The samples have been studied by X-Ray Diffraction (Fig.1) and thermal analysis (DTA and TG) in the 25-500°C temperature interval. The results obtained show that intermediate terms need higher temperatures to fold.

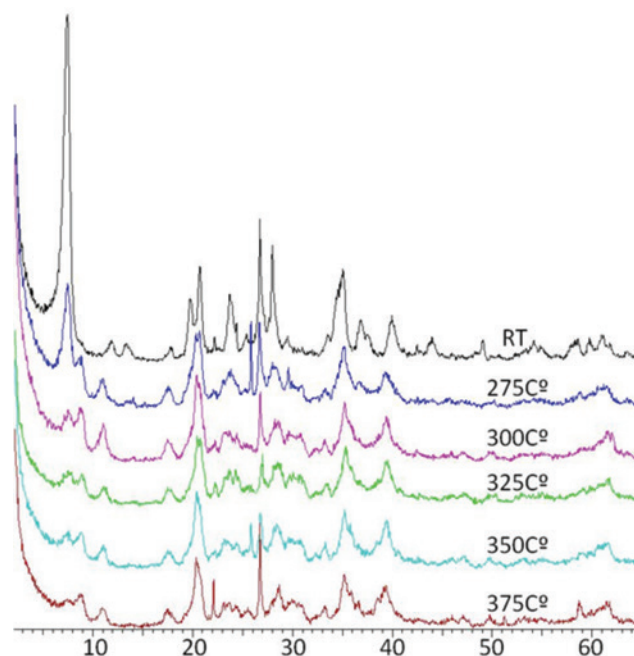


Figure 1. X-Ray diffraction patterns of sepiolite from Vallecas (Spain) heated at different temperatures.

IRON/MAGNESIUM SMECTITE FORMATION UNDER ACIDIC CONDITIONS ON EARLY MARS: AN EXPERIMENTAL FLOW-THROUGH ASSESSMENT

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Orbital observations have detected significant deposits of the phyllosilicate mineral smectite on Mars; however, the detection of carbonate deposits is limited. Early Mars may have experienced mildly acidic conditions derived from volcanic SO₂ outgassing and sulfuric acid formation that allowed smectite formation but prevented widespread carbonate formation. The detection of acid sulfates (e.g., jarosite) associated with smectite in Mawrth Vallis supports this hypothesis. Formation of smectites together with sulfates has been demonstrated in basaltic glass alteration experiments in sulfuric acid at pH 3 to 4 at 200°C in a *closed hydrologic system* (batch reactor, 14 days) (Peretyazhko et al., 2018 GCA; this meeting). The objective of this work was to evaluate smectite formation from basaltic glass under alkaline to acidic conditions in an *open hydrologic system* (flow-through reactor, 0.25 ml min⁻¹, 6–7 days, 190°C, 17 bar). Mineralogical analyses demonstrated that basaltic glass exposed to deionized water at pH 9.5 yielded serpentine and hematite while sulfuric acid solutions at pH 3 with 0, 10 and 50 mM MgCl₂ formed boehmite and hematite. Our results showed that smectite did not form in any flow experiments despite pH values (Fig. 1a). that are known to permit smectite formation (Peretyazhko et al 2018). Equilibrium calculations suggested Si concentration were favorable (~ 1 mM) for smectite formation at 24 h but became unfavorable beyond 48h (Fig. 1b). Previous closed-hydrologic experiments did not permit Si removal and resulted in ~ 10 mM Si which was sufficient for smectite formation (Peretyazhko et al., 2018 GCA; this meeting). Leaching rates lower than those replicated by our experimental conditions were likely required to maintain Si concentrations high enough to permit smectite formation on an acidic Mars. The production of smectite at low pHs would yield a significant paradigm shift regarding the geochemical evolution of early Mars: Early Mars geochemical solutions were mildly acidic, not neutral/alkaline. This could have profound implications regarding early martian microbiology where acid conditions instead of neutral/alkaline conditions will require further research in terrestrial analogs to address the potential for biosignature preservation on Mars (Johnson et al., 2016, LPSC).

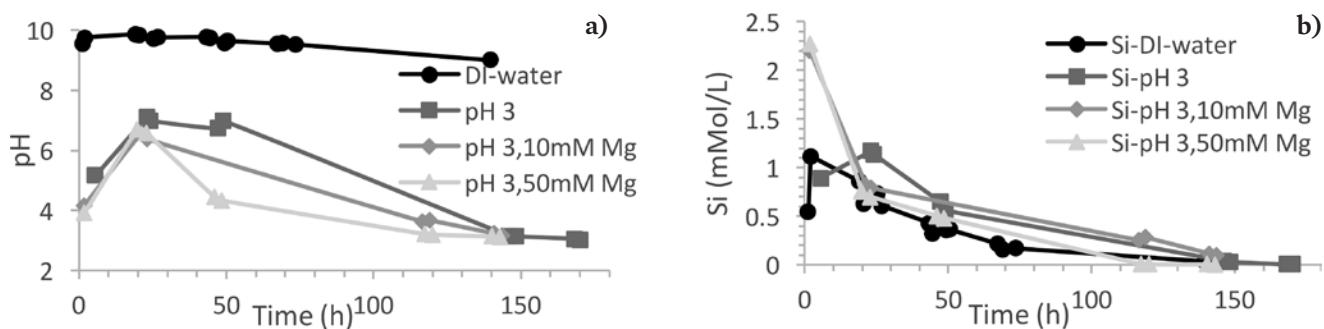


Fig. 1 a) pH and b) Si concentration versus time.

DEVELOPMENT OF INDUSTRIAL SCALE QUALITY CONTROL OF BENTONITE FOR BUFFER IN A KBS-3 HIGH LEVEL RADIOACTIVE WASTE REPOSITORY

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Bentonite is planned to be used as a barrier material in repositories for final storage of highly radioactive spent nuclear fuel in order to limit transport rate and protect the canister holding the waste for 100,000 to 1,000,000 years. The SKB concept is called KBS-3 and is based on a copper canister in compacted bentonite in crystalline rock. In order avoid microbiological activity and corrosion the bentonite should be low in sulphur and organic carbon. As determination of these components are not clay specific they will not get more attention here.

The other requirements on the bentonite are related to the barrier functions and hence the properties of the bentonite, e.g. swelling pressure, hydraulic conductivity, thermal conductivity and shear strength. Several of these properties are difficult and/or time consuming, making it difficult to test every property on a sample from every deposition hole every single day. Hence, instead the strategy is to test the properties of a sample from a big batch, and later only verify that the bentonite composition keeps constant within some given limits. This assumption should be valid, assuming that no relevant parameter is missed out. Currently X-ray diffraction (XRD; mineralogy), X-ray fluorescence spectroscopy (XRF; chemical composition), and Cation exchange capacity (CEC) are planned to be used as the key methods for continuous control of the bentonite. The bentonite swelling properties are related to the montmorillonite content and type, while properties such as thermal conductivity are more complex and depend on all included phases of the clay.

The accepted swelling pressure interval is currently 3-10 MPa, when tested with a specific method and fixed conditions, using consecutively, deionized water and 1 M calcium chloride as external solutions (corresponding to worst case scenarios). The swelling pressure vs density curve is different for different bentonite clays, and hence the corresponding density interval will be thinner or wider for different bentonites. The optimal case is a relatively slow increase in swelling pressure with increasing density, broadening the accepted density interval of the installed components, making installation more practical and economically efficient.

By adding different amounts of finely grinded sand to the bentonite (dominated by quartz, feldspar and mica) at 1,5 and 10 wt% we intend to simulate different qualities of the bentonites, making it possible to study how the properties are affected by the different levels of montmorillonite in the blends, and by that determining the accepted variation of montmorillonite.

HYDROTHERMAL ALTERATION OF CRATER LAKE DEPOSITS AT THE RIES IMPACT STRUCTURE, GERMANY.

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The 22-24 km diameter, 14.8 ± 0.1 Ma Ries impact structure occurred in southern Germany, in sedimentary Mesozoic rocks unconformably overlying a crystalline Hercynian basement. The Ries is a complex impact structure with a central basin existing within the tectonic rim. Ries' central basin is bounded by a prominent "inner ring", ~12 km in diameter. A series of impact melt-bearing breccias termed "suevites" infill the central ring and are overlain by ~336 m of post-impact sedimentary rocks. Some post-impact lacustrine deposits have been documented on the periphery of the inner ring; characterized by limestones and calcitic spring mounds (e.g. Erisberg spring mound).

The objective is to characterize and document the extent of hydrothermal alteration affecting the Ries crater-lake deposits. If a crater-lake developed in parallel with hydrothermal activity, it would have implications for the duration of the hydrothermal system, and post-impact biological successions. We applied optical microscopy, XRD of $<2\mu\text{m}$ clay separates, visible / near infrared reflectance (VNIR) spectroscopy, and electron microprobe analysis (EMPA) to altered samples from the Wörnitzostheim drill core samples, which were loaned from the Centre for Ries Crater and Impact Crater Research (ZERIN) in Nördlingen.

Alteration halos in the post-impact deposits were apparent in the Wörnitzostheim drill core at depths of 9.6 m and 14.33 m. A structure highly reminiscent of de-gassing pipes observed elsewhere at the Ries was also observed at 27.3 m. The sampled material contained mm scale grains comprising micas, feldspars, calcite dolomite and quartz. Fully quantitative EMPA work suggests that the clays making up the interstitial material consist of mostly smectite and illite. Other components of the interstitial material include μm -scale quartz, feldspars, pyrite, gypsum, calcite and dolomite. *p*XRD results for oriented $<2\mu\text{m}$ clay samples saturated with Ca and analyzed first at 54% RH at room temperature and then following treatment with ethylene glycol, plus *p*XRD of separate aliquots saturated with K, and analyzed at 0% RH and 54% RH at room temperature, followed by heating to 300°C and then 550 °C confirm the presence of smectitic clay, illite, and kaolinite. The results also suggest that the smectitic clay is interstratified with illite in amounts consistent with formation at ~100 to 130 °C. The clay mineral assemblage is consistent with argillic alteration, and the de-gassing pipe-like structure suggests the alteration may be predominantly hydrothermal in origin. This work provides the first detailed study of the alteration mineralogy of the basal lacustrine sediments at Ries and shows that impact-generated hydrothermal alteration and sediment deposition were concomitant.

NEW MODEL OF ETHYLENE GLYCOL LAYERS INTERCALCATED IN SMECTITES FOR XRD MODELLING

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Models of ethylene glycol (EG) intercalate used for XRD modelling of clay minerals assume increased temperature coefficients for EG molecules ($B = 11 \text{ \AA}^2$), but for water and Ca^{2+} ions it is however equal to that of regular crystal structures (approximately: $B = 1 \text{ \AA}^2$). This assumption is not confirmed by recent molecular dynamics (MD) simulations describing the distribution of water and EG atoms in the interlayer space of smectites. Therefore the aim of this study was to provide new adjustable models of one and two EG layers that are based on the MD simulations results.

A wide range of EG and water contents in the simulated structure was considered. For all the simulations, the average atomic density profiles along the z direction were calculated. Subsets corresponding to certain basal spacing were chosen as representative for one- and two-layers intercalates. The electronic density profiles of EG, water and Ca^{2+} ions were fitted with Gaussian functions. The aim was to minimize the number of functions and to achieve a maximally simple but yet flexible model of the interlayer structures.

The received new models show significant differences comparing to models implemented in programs for XRD modelling. The position of atoms in the interlayer space is generally different. It was also possible to determine the relationship between position of the atoms and the basal spacing. For some atoms also a relationship between the basal spacing and the ratio of Gaussian distributions were found. The thermal factors are generally larger and Ca^{2+} ions can exist both in inner-sphere and outer sphere complexes and its ratio can be optimized. All the relationships were implemented in the Rietveld software BGMN.

Using the new model makes it possible to receive slightly better or similar matchings between experimental and theoretical diffractograms, compared to the old models. The limitation of the new model is connected with the fact that distributions of water and EG molecules in the interlayer space are quite similar. Therefore, during minimalization procedure, EG and water molecules in the interlayer space are not treated fully separately.

ROLE OF SOLUBLE Fe(III) COMPLEXES IN IRON REDOX REACTIONS

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Fe(III) in aquatic systems is often assumed to exist either in the form of minerals or nanoparticles. Ferric iron, however, is easily stabilized by organic ligands in solution, and Fe(III)-containing proteins or Fe(III)-siderophore complexes represent good examples of naturally-occurring species that stabilize Fe(III) in a soluble form. Our research has demonstrated the existence of soluble organic complexes of Fe(III) in a variety of sedimentary environments. Yet the pathways by which these complexes are formed in sediments remained poorly understood. These complexes may be formed by aerobic oxidation of Fe(II) in the presence of organic ligands, but this process does not explain the presence of these organic-Fe(III) complexes in reduced sediments. Although non-reductive dissolution of poorly crystalline Fe(III) oxides by multidentate organic ligands may occur in reducing environments at circumneutral pH, this process cannot explain the simultaneous production of Fe(II) and organic-Fe(III) complexes in most sediments. In turn, these Fe(III) complexes may be produced simultaneously with Fe(II) as intermediate products in the bacterial reduction of Fe(III) oxides as demonstrated by incubations of *Shewanella* species on a variety of Fe(III) oxides. It was also recently proposed that bacterially-produced Fe(II) may be chelated by dissolved organic matter and oxidized abiotically by Fe(III) oxides to generate organic-Fe(III) complexes in marine sediments. New evidence suggests that soluble organic-Fe(III) complexes are also produced abiotically in the presence of dissolved organic matter without dissolved oxygen. Finally, experiments conducted with Fe(II)-oxidizing bacteria demonstrate the catalytic effect of dissolved organic matter on the precipitation of Fe(III) oxides, suggesting that Fe(II)-oxidizing bacteria may depend on the presence of natural organic ligands to grow. Alternative pathways that could result in the production of these complexes and the implications of these findings on the transformation of Fe(III) in sedimentary environments will be presented.

DESIGN AND CHARACTERIZATION OF NOVEL (POLYMER/CLAY NANOTUBE) HYBRIDS

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Surface functionalization of tubular nano-clays of imogolite and halloysite using the selective binding of organophosphonic acids and organosilane compounds, and the use of the surface modified nanotubes in polymer hybrids were studied. Surface modification of imogolite with alkyl phosphonic acid salt through the specific interaction of phosphonic acid and the exterior alumina sites of imogolite was presented. SI-ATRP was performed with the selectively adsorbed phosphonic acid functionalized ATRP-initiator to prepare polymer brushes on the imogolite surface. Selective modification of halloysite nanotube exterior and inner surfaces was demonstrated. Aqueous phosphonic acid binds to alumina sites at the tube lumen to make the lumen hydrophobic. Subsequent modification with organosilane affords bifunctionalized halloysites which both the lumen and exterior surface were modified. Loading of hydrophobic organic compounds to the modified lumen was confirmed. SI-ATRP was performed through the selectively adsorbed ATRP-initiator to prepare polymer brushes on the nanotube lumen. Also, surface modified halloysite was applied for preparation of novel intelligent polyurethane nanocomposites with improved thermal stability and mechanical properties.

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STUDY ON THE ADSORPTION OF NANO-FIBER REINFORCED POROUS CARBON ON EMULSIFIED OIL IN WASTEWATER

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In order to treat the highly concentrated emulsified oil wastewater discharged from the mechanical processing industry, in the present dissertation, attapulgite nanofiber reinforced porous carbon composite was used as the adsorbent to study the related regulation of the concentration of emulsified oil in wastewater, adsorption temperature, time and pH on the adsorption capacity of the porous carbon composite, removal rates of emulsified oil and COD. Meanwhile, the adsorption behavior of porous carbon composite on emulsified oil was investigated based on related theories. The micro morphology, crystal structure and surface functional groups of the porous carbon composite were studied by the transmission electron microscopy (TEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The results showed that the adding of attapulgite could increase the adsorption capacity of porous carbon composite on emulsified oil in wastewater. When the dosage of the adsorbent (g) was 0.35% of the volume of wastewater (mL), it only took 30 min to approach the adsorption equilibrium at 25°C and the removal rates of emulsified oil and COD reached 98.95% and 95.59% with the emulsified oil and COD concentrations of 2020 and 1999.5 mg/L, respectively. Furthermore, the adsorption kinetic process of adsorption on emulsified oil was also studied using the pseudo-first-order and the pseudo-second-order kinetic models, and the thermodynamic calculation showed that the ΔG^0 was less than 0, indicating that the adsorption of porous carbon composite on the emulsified oil was a spontaneous physical-chemical process. At the same time, it was found that the emulsified oil was adsorbed on the surface of the porous carbon composite and then diffused into the pores of the composite through capillary action according to the intraparticle diffusion model. The adsorption isotherms were well fitted by the Freundlich model, indicating that the adsorption process was multi-layer adsorption.

HYDROTHERMAL REACTIVITY OF MIXED METAL OXIDES WITH SILICATE ANIONS UNDER ALKALINE CONDITIONS

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Mixed Metal Oxides are a common kind of materials in nature, in which Mg-Al mixed oxides (hereinafter short for MMO) is widely distributed in the basic-ultrabasic magmatic rocks, evaporation of rivers-lakes and marine sedimentary rocks. In present study, MMO was obtained by calcining of Mg-Al Hydrotalcite. Its rehydration features and the related transformation mechanism in silicic alkaline solution under hydrothermal condition, were investigated by altering reaction time. X-ray diffraction (XRD) patterns showed that MMO reconstructed to form Hydrotalcite firstly; after that hydrotalcite transformed to saponite gradually, along with the formation and convention of impure phases (e.g. natrodavyn etc.). ²⁹Si and ²⁷Al MAS NMR results suggested that Al³⁺ cations preferred to occupy the tetrahedral sites on tetrahedral sheets. The formation of saponite was through a rehydration—dissolution—precipitation pathway, involving the critical steps, such as the reconstruction of MMO to hydrotalcite (Ht), exsolution of Al³⁺ from Ht, condensation of metasilicate anions with Ht, and finally crystallization of saponite. Isomorphous substitution of Al³⁺ for Si⁴⁺ in silicate oligomers is the key for the above conversion, which generated the negative charge necessary for the condensation between the silicate oligomers and Ht surface and the formation of 2:1 saponite TOT layers. High pH value favored the condensation of silicate oligomers and led to crystallization of saponite. The new findings of this research have great significance for understanding the stability of Hydrotalcite, heterogeneous nucleation and growth of Hydrotalcite and silicate minerals, and the formation processes of the hydrothermal saponite deposits.

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A STUDY OF LITHIUM ISOTOPE ALTERATION IN METEORITIC ORGANICS

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Carbonaceous chondrite meteorites contain pristine, unaltered organic macromolecules which are similar to terrestrial kerogen in their compositions and structural characteristics. Lithium is found in trace amounts in organic materials such as kerogen (Williams et al., 2015). Li has been shown to be a particularly valuable trace element because of its tendency to become mobilized during surface weathering and under hydrothermal conditions (Pistiner and Henderson, 2003). The objectives of this study are to determine whether $\delta^7\text{Li}$ values of meteorite organic matter are altered by acid treatments which are designed to remove silicate material.

The matrix of CM-chondrite meteorites is made up of mostly fine-grained phyllosilicates intermixed with organic material. These clay minerals include Fe-Mg serpentinites, cronstedtite, and tochilinite (Howard et al., 2009). Pilot data measured on the Murchison carbonaceous chondrite suggested that Li is more highly concentrated in C-rich areas than in Si-rich areas. Therefore, we acquired insoluble organic matter (IOM) from Murchison, and analyzed for Li content and $\delta^7\text{Li}$ by Secondary Ion Mass Spectrometry. For isolation of IOM, inorganic constituents are removed by acid (HF-HCl) digestion, concentrating the organic constituents (Cronin et al., 1987). To test the effect of acid treatments on $\delta^7\text{Li}$ in these IOM samples, we compared the $\delta^7\text{Li}$ of a whole rock Murchison sample, to the Murchison IOM. The Center for Meteorite studies at Arizona State University, provided a fresh Murchison sample, which was cut and polished without water to avoid surface contamination. Results show that the whole rock Murchison sample has a mean matrix $\delta^7\text{Li}$ composition of $-4.5 \pm 0.8 \text{ ‰}$ ($n = 7$), whereas the Murchison IOM has a mean composition of $-17 \pm 2 \text{ ‰}$ ($n = 4$), suggesting significant loss of ^7Li during acid digestion. Additionally, the potential alteration of $\delta^7\text{Li}$ by hydrothermal processes was tested on IOM from Murchison, GRA(Graves Nunataks) and Bells meteorites, which were hydrothermally treated at 300°C , 100MPa, for one week. The hydrothermally treated IOM samples had $\delta^7\text{Li}$ values within error of the untreated IOM samples. In conclusion, these data indicate that δLi values of meteorite organic matter are altered by acid treatments to isolate IOM, but not by hydrothermal treatment post isolation. Future measurements of $\delta^7\text{Li}$ in meteorite organic matter will require NanoSIMS measurements with spatial resolution sufficient to resolve organic and silicate material and determine differences between meteorites.

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COMPARISON OF INFRARED AND RAMAN SPECTRA FOR STRUCTURAL CHARACTERIZATION OF MONTMORILLONITES

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The contribution demonstrates the potential and applicability of infrared and Raman spectroscopy in identification and structural characterization of montmorillonites. The vibrational spectra of montmorillonites (SAz-2, STx-1, SWy-2 and Kunipia-F), obtained by Fourier Transform infrared (FT-IR) spectroscopy in the near (NIR) infrared region (8000–4000 cm⁻¹) and in the middle (MIR) infrared region (4000–400 cm⁻¹) together with Fourier Transform Raman (FT-Raman) measurements in the region from 4000–50 cm⁻¹, will be presented. The aim of the experimental study was to compare the spectral data of both analytical techniques in terms of their sensitivity to chemical composition, isomorphic substitution of central atoms, and layer stacking order of the clay minerals. The results confirmed that FT-IR spectroscopy through MIR and NIR spectral regions provided the most comprehensive information about octahedral, tetrahedral and hydroxyl structure units of montmorillonites.

FATE AND TRANSPORT OF SOLUTES IN MICROPOROUS CHONDRITIC ASTEROIDAL AQUIFERS—AND CORES OF OCEAN WORLDS?

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Introduction: Some carbonaceous chondrites (C-chondrites) show evidence of mineral reactions with no-longer-present water. Aqueous alteration products of CM and CI chondrites include volumetrically abundant phyllosilicates, and amorphous silicates, carbonates, and sulfates. C-chondrite lithologies occur on many asteroids, including the targets of the Hayabusa2 and OSIRIS-Rex missions, and are inferred to occur as the cores of many icy ocean worlds, including moons of the outer planets.

Observations from mineral compositions, assemblages, and textures in CM chondrites: The composition of serpentine (srp) pseudomorphically replacing chondrule-hosted and isolated olivine (ol) and pyroxene (px) during alteration is much more uniform in any given CM2 chondrite than the wide range of olivines replaced. Also, means and ranges of serpentine compositions differ between CMs.

Implications for elemental mobility as solutes: The reaction describing isovolumetric pseudomorphic replacement of coarse chondrule-hosted and isolated olivine by serpentine ($5\text{ol} \rightarrow 2\text{srp}$) conforms to textural observations, quantitative modal-abundance data, and constraints from geochemical kinetics better than other serpentinization reactions. The $5\text{ol} \rightarrow 2\text{srp}$ (isovolumetric) reaction requires that (in addition to water) some dissolved (solute) species must have been added to or removed from the volume within which pseudomorphic / alteromorphic replacement of olivine by serpentine occurred. Solute redistribution between primary and secondary minerals resulted in control of secondary mineral compositions by the interplay between (1) primary-mineral reaction rates and depletion, and (2) the associated evolving solute compositions of the aqueous medium. Solvent and solute species diffused through the serpentine between the olivine-serpentine interface and the aqueous solution outside the pseudomorphs. Regardless of the olivine's composition, isovolumetric replacement of coarse olivine by serpentine always released more Mg and Si from the replaced volume than was required to form serpentine of the observed composition, and the excess Mg and Si were exported from the replaced volume and available to be incorporated into the last neofomed Mg-rich serpentine in surrounding, rim, matrix, and more distant pseudomorphs after other olivine crystals or grains.

Redox-sensitive elements had more complex import-export behaviors during serpentinization. To form serpentines of the observed compositions, Fe had to be exported from pseudomorphs after ferroan olivine but imported into pseudomorphs and meshwork after forsteritic olivine; thus, Fe must have been a mobile solute—Fe(II)—in these aqueous solutions.

IRON/CEMENTIOUS BENTONITIC MATERIAL/CLAYSTONE INTERACTION UNDER HYDROTHERMAL CONDITIONS

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Management of high level radioactive waste is a crucial socio-economic and environmental issue, requiring a long-term solution. The deep geological disposal is considered as one of the best containment option, and in France, the Callovo-Oxfordian claystone (COx) formation is studied to be the potential host rock.

It is expected that when galleries and disposal cells are drilled, the COx, and particularly the pyrite, is oxidized. Consequently, pH of the pore water decreases, carbonate minerals dissolve, CO₂ is released in the repository. After the closure of the repository, claystone rehydrates and CO₂, trapped in the disposal cells, dissolves. It induces transient acidic conditions that can increase the corrosion rate of the carbon steel components of the cells (i.e. lining and canister). The use of a cementitious bentonitic grout (MREA) injected between the oxidized COx and the steel lining is planned to neutralize the acidic transient and to preserve the carbon steel canisters. In order to optimize the buffer properties of this material, it is essential to understand its behavior in contact with COx and carbon steel under (P,T,X) characteristic conditions of the repository.

Batch experiments in instrumented stainless steel autoclave allowed us to measure variations of pressure, temperature and pH under conditions close to those of a geological disposal. Different mixtures of powders of COx, MREA, iron or carbon steel were introduced into the autoclave with a solution in excess, and were heated to 90°C for 3 months. Gas, experimental solutions and solid run-products were analyzed, and results were compared with those published about iron-clay interaction experiments (without MREA) in same conditions [1]. First conclusions indicate that the presence of MREA in the system reduces the oxidation of iron and that the carbon steel is less oxidized compared to iron.

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MONTMORILLONITE AS VEHICLE OF TUBERCULOSTATIC ISONIAZID

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Interest in the interaction of drug molecules with inorganic surfaces leading to hybrid drug-inorganic materials has greatly increased in recent years. Isoniazid (INH), a first-line tuberculostatic drug, was intercalated into this inorganic matrix and the equilibrium and thermodynamic aspects of the adsorption process were evaluated. Adsorption experiments were conducted at different times and temperatures in aqueous medium. The overall adsorption process was the result of two simple processes: drug adsorption on the activated sites of montmorillonite followed by a slight precipitation phase of drug molecules over the adsorbed monolayer. Formation of the nanohybrid was spontaneous, exothermic and exoentropic, obtaining an increase in the thermodynamic stability of the system. The hybrid material (MMT-INH) was successfully prepared with high drug loading. Solid state characterization of the pure materials and the resulting nanohybrid was carried out. Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TGA), differential scanning calorimetry (DSC), surface charge, X-ray powder diffraction (XRPD) and high resolution transmission electron microscopy (HRTEM) coupled with energy dispersive spectroscopy (XEDS) served to correctly resolve the structure of the nanohybrid and to assess the nature and degree of the drug-clay interactions. Effective loading and full study of the clay drug nanohybrid structure as well as the nature of the interactions involved provided positive features for future development of modified drug delivery systems based on the MMT-INH interaction.

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NOVEL ENVIRONMENT-FRIENDLY RED HYBRID PIGMENT FABRICATED FROM NATURAL NANOCLAY

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Iron oxide (α -Fe₂O₃), as a durable, nontoxic, low cost and safe inorganic pigment, has been potentially applied in various industrial areas [1]. However, the red colour of pure α -Fe₂O₃ is not vivid enough in contrast to the toxic pigment containing heavy metals, and its stability needs to be improved further [2]. In this work, we developed successfully a series of hybrid red pigments with vivid colour, low cost and excellent stability by one-step hydrothermal process using natural clay minerals, e.g., palygorskite (PAL), sepiolite (SEP) and halloysite (HAL), and FeCl₃ as starting materials. It was found that PAL, SEP and HAL was essential to induce the formation of vivid red hybrid pigments, because they can regulate effectively the crystallization process and dispersion of α -Fe₂O₃ crystals. The clay minerals induce the in-situ crystallization of α -Fe₂O₃ to form stable inorganic-inorganic hybrid structure. The hybrid pigment derived from PAL (PAL-IOR) showed the reddest colour with a* coordinate value of +36.3, which is obviously higher than commercial product. The color of the hybrid pigments can be easily tuned by altering the dosage of Fe(III) or reaction time to form products with different colors (i.e., light amber, orange red and bright red). In addition, the hybrid pigments have excellent resistance to acids and alkalis and organic solvents, and can be easily coated on different substrates, e.g., glass, wood, ceramic, cotton fabric, and paper.

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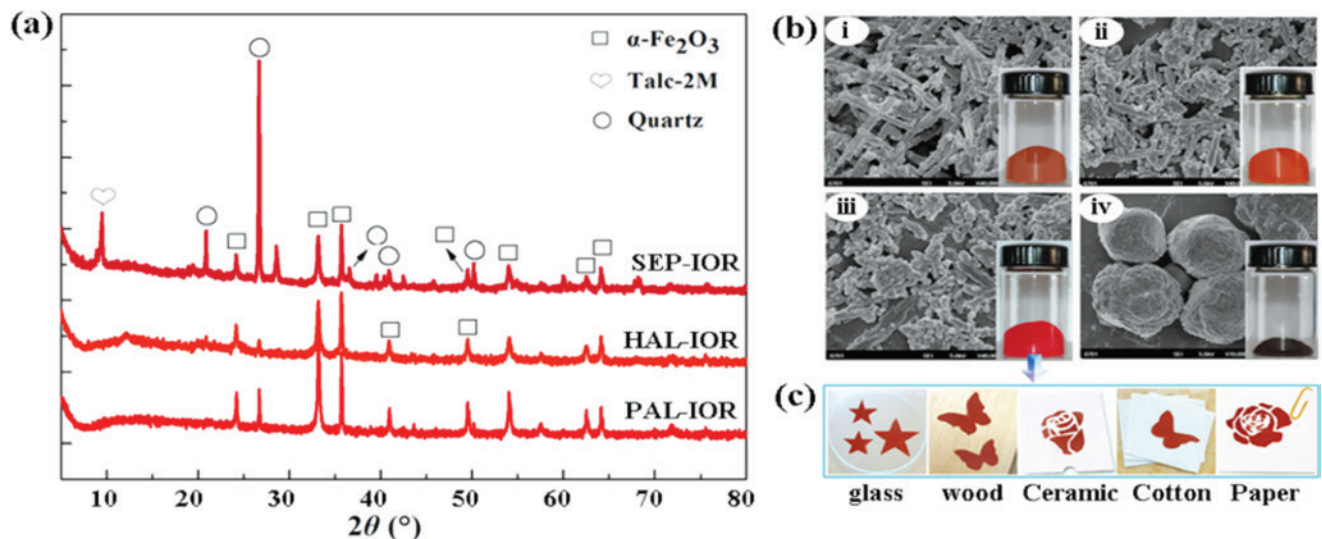


Fig. 1 XRD curves of the hybrid pigments (a); and SEM images of SEP-IOR (bi), HAL-IOR (bii), PAL-IOR (biii) and pure α -Fe₂O₃ (biv); Digital images of the PAL-IOR coating on different substrates (c).

SIMULTANEOUS TRANSFORMATION OF PALYGORSKITE AND ASSOCIATED MINERALS TO FABRICATE HIGHLY EFFICIENT MESOPOROUS SILICATE ADSORBENT

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Silicates, as the materials of “greening 21st century material world”, have found extensive applications in many industrial fields. Palygorskite (PAL) is a special one-dimensional nanorod-like silicate with a 2:1 ribbon-layer structure composed of two continuous tetrahedron sheets and one discontinuous octahedron sheet. The abundant resource, nanorod-like morphology, high stability and plentiful nanoporous feature of PAL endow it with inherent advantages to be developed as a variety of promising adsorbents for removing pollutants. However, natural PAL clay mineral is complicated due to the geological formation process. In addition to PAL, it also contains various associated minerals such as quartz, mica, and chlorite, and so its overall performance is poor, which restricts its application in the industrial field. as naturally available low-cost adsorbents.

In order to design new adsorbent with high adsorption capacity by simultaneously utilizing PAL and associated minerals, we successfully transformed low-grade PAL and associated minerals as new mesoporous silicate adsorbent by a one-step hydrothermal reaction in the presence of silicate and magnesium salts at 180 °C for 12h. It was found that at the Si/Mg dosage ratio of 2:1, the quartz in low-grade PAL could be transformed as magnesium silicate with better adsorption activity, and the silicate adsorbents show micro-sphere morphology (Fig. 1) and greater specific surface areas (482 m²/g). The adsorbent exhibits superior adsorption capacity for cationic dyes methylene blue (MB) and methyl violet (MV), with the maximum adsorption capacity of 325.78 mg/g for MB (97.2 mg/g for raw PAL) and 317.73 mg/g for MV (121.3 mg/g for raw PAL). The removal ratio reaches 99.6% for MB and 98.23% for MV at the initial dye concentration of 200 mg/L and the adsorbent dosage of 1 g/L, which is greatly higher than that of raw PAL. The electrostatic interaction, ion exchange and chemical association of -Si-O⁻ groups contribute to the enhanced adsorption. The adsorbent based low-grade PAL minerals could be regarded as a promising adsorbent for environmental applications..

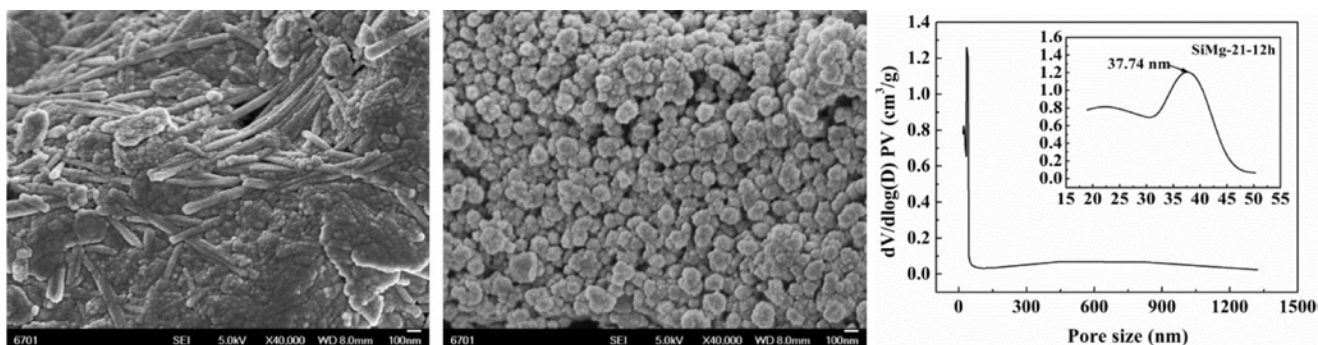


Fig. 1 SEM images of (left) Raw PAL and (mid) the composite adsorbent; (right) the pore-size distribution curves.

REDUCED IRON-CONTAINING CLAY MINERALS AS ANTIBACTERIAL AGENTS AND FACTORS THAT INFLUENCE ITS EFFICIENCY

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Previous work documented the general antibacterial mechanism of iron containing clays that involved hydroxyl radical ($\bullet\text{OH}$) production from soluble Fe^{2+} , and attack of cell membrane and intracellular proteins. Here we explore the role of clay structural Fe(II) in $\bullet\text{OH}$ production at near neutral pH and identify a lipid protein involved in the antibacterial process. Structural Fe(III) in nontronite rNAu-2 was chemically reduced (called rNAu-2) and *E. coli*, a model bacterium, was exposed to rNAu-2 in oxic suspension. The antibacterial activity of rNAu-2 was dependent on pH and Fe(II) concentration, where *E. coli* were completely killed at pH 6, but survived at pH 7 and 8. In the presence of a $\bullet\text{OH}$ scavenger or in an anaerobic atmosphere, *E. coli* survived better, suggesting that cell death may be caused by $\bullet\text{OH}$ generated from oxidation of structural Fe(II) in rNAu-2. In-situ imaging revealed damage of a membrane lipid, cardiolipin, in the polar region of *E. coli* cells, where reactive oxygen species and redox-active labile Fe were enriched. Our results advance the previous antibacterial model by demonstrating that the structural Fe(II) is the primary source of $\bullet\text{OH}$, which damages cardiolipin, triggers the influx of soluble Fe^{2+} into the cell, and ultimately leads to cell death.

In order to further improve the efficiency of the antibacterial activity, a direct contact of rNAu-2 with bacteria may be required. Our recent work focused on the bactericidal properties of chitosan-intercalated, positively-charged reduced nontronite (Chit-rNAu-2), which was proved to be a more efficient bactericidal agent with a higher lethality at a lower Fe(II) concentration. The slow oxidation of ferrous iron in Chit-rNAu-2 contributed to its long-lasting antibacterial effect. We also investigated how common cations (K, Na, Ca, Mg) influenced the bactericidal effect of rNAu-2. Our results showed that low concentrations of divalent cations (Ca, Mg) would dramatically inhibit the toxicity of rNAu-2 to *E. coli*. The toxicity of rNAu-2 to *E. coli* also decreased with increasing concentration of monovalent cations (Na, K). The protective role of these cations to *E. coli* may be explained by a biotic ligand model.

WHAT CAN WE LEARN FROM IRON-BENTONITE INTERFACES WITH REGARD TO SAFETY ASSESSMENT OF HIGH-LEVEL WASTE REPOSITORIES?

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Bentonite in contact with steel components is foreseen as backfilling material in many countries. The favorable sealing properties of this material may be offset by corroding iron species interacting with the clay, thus potentially leading to cementation and montmorillonite alteration. The latter process strongly depends on redox conditions in the repository which, in many cases, will be oxidizing initially and become reducing upon O₂ depletion. Such a setting has been simulated by a number of in-situ experiments at the Äspö Hard Rock Laboratory (S), the Grimsel Test Site (CH) and the Mont Terri rock Laboratory (CH). We have studied different bentonite materials exposed to corroding carbon steel at temperatures up to 140°C over time periods ranging from 2 to 18 years. The focus was on the characterization of the Fe-bentonite interface, i.e. the identification and quantification of the different iron species and of other elements at high spatial resolution. A suite of tools, including both highly spatially resolved (SEM/EDX, μ -Raman spectrometry), and bulk (XRD, XRF, Mössbauer spectrometry) techniques was applied.

Overall, a consistent picture arises from the different in-situ experiments implying that similar processes are governing the evolution of the interfaces regardless of the experimental setup, type of bentonite and exposure times. Accumulation of Fe(III) oxides (mainly goethite) has been systematically observed in the corrosion layer adjacent to the bentonite (Fig. 1). Fe(II) exhibits a second front further into clay. This observed behavior of iron species is explained by the variable redox conditions in the experiments, electron transfer in

the corrosion layer and the specific migration properties of Fe(II). The results indicate that the reducible pool of generated Fe(III) (oxyhydr)oxides during the oxic phase needs to be considered in the assessment of the stability of the bentonite barrier during the main anaerobic phase.

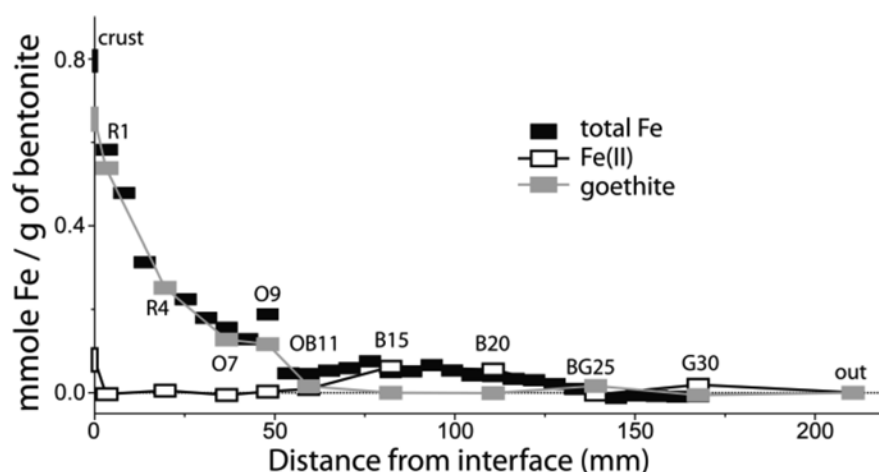


Fig. 1: Speciation of Fe (shown as excess iron relative to natural clay) as function of distance from steel contact determined from Mössbauer spectrometry and XRF. Sample from FEBEX experiment.

NANOSCALE CONTROLS ON CLAY-ORGANIC INTERACTIONS

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The behavior of organic molecules in the subsurface is recurrent theme in the fields of energy, water, and the environment. In particular, it plays central roles in soil carbon storage, the migration of hydrocarbons in sedimentary formations, geologic carbon sequestration, and the fate and transport of organic contaminants. A key factor that controls the behavior of organic compounds in the subsurface is their interaction with mineral surfaces, and in particular with clay mineral surfaces. These interactions are known to depend strongly on aqueous chemistry, the type of organic compound, and the clay mineral in question. Here, we review the existing evidence regarding the affinity of organic molecules for smectite clay mineral surfaces and we discuss our ongoing efforts to test and refine these theories using atomistic-level simulations.

LITHIUM ISOTOPE HETEROGENEITY IN COALS AND KEROGEN: AN UNRECOGNIZED LITHIUM CONTRIBUTION TO THE GLOBAL GEOCHEMICAL CYCLE

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Empirical studies of Li in black shales suggest that organic matter is a significant source of Li, but its role in global geochemical cycles has been largely overlooked. Previous studies of Li in coals used acids to extract silicates thus isolating the organic fraction of the rock. However, solid-state studies of Li using secondary ion mass spectrometry (SIMS) have shown that acid also removes organically-bound Li, therefore our understanding of the organic-Li contribution to the geochemical cycle is lacking. NanoSIMS measurements allow *in situ* examination of kerogen at a scale (<50 nm spatial resolution), which allows mapping of C-rich versus Si-rich areas of a kerogen rich source rock and therefore the heterogeneity of Li associated with organic or silicate matrices in coal or black shale can be directly evaluated. For example, NanoSIMS mapping of Li in kerogen from the Bakken shale (North Dakota, USA) showed that Li was associated with the organic matrix, not silicates. Argon-ion polished shales showed that kerogen-rich areas contain nanopores where Li is concentrated. These nanopores are the efflux channels for generated hydrocarbons, thus Li released with hydrocarbons, leaves a trail marking migration pathways, and its isotopic composition can be linked to the source region.

New SIMS measurements were made of Li in a low rank coal from the Jungar Coalfield, Inner Mongolia, China, where bulk Li measurements indicated concentrations >500 ppm. Vitrinite reflectance ($R_o = 0.56\%$) indicates a temperature $\sim 60^\circ\text{C}$. Previous studies of the coal petrology indicated that the Li was in silicates (Dai et al., 2012), which include: kaolinite, illite and cookeite. The coal also contains varying amounts of calcite, ankerite, siderite, boehmite and the phosphate mineral goyazite. This study examined whether Li might also be found in the organic matrix, and if so, if it was isotopically distinct from Li in the silicates or other phases. Results indicate that Li in this coal is highly variable in content and isotopic composition. The Si-rich matrix contains up to 630 ppm Li with an average $\delta^7\text{Li}$ of $-1.4 \pm 0.4\text{‰}$ ($n = 7$). The C-rich areas had lower Li concentrations (~ 10 ppm), with $\delta^7\text{Li}$ values from -10 to -36‰ in plant derived organic macerals. These results show that there is a distinctly light-Li component of coals that may be released with increasing thermal grade. Li released from organic components of the coal may be taken up by authigenic clays under diagenetic conditions.

Determining the mineral or organic host of Li in coals is important considering its potential use as an economic resource (Sun et al., 2012; Qin et al., 2015). The results of this research will contribute to our understanding of the global cycling of Li, develop its use as an isotopic tracer of organic-inorganic interactions, and could lead to new resources of Li for 'clean energy'.

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EXPERIMENTAL INVESTIGATIONS ON WATER CONDENSATION IN SHALES

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Condensation is an important mechanism influencing the flow and accumulation of water in shales, which is widely interested in many issues. Initial water saturation is a factor affecting fracturing fluid loss and gas flow to production well in shale reservoirs. Shale (or mud-rock) is currently considered as a feasible host rock for nuclear waste depository. In this context, the water in the capillary pores is important to prevent the gas, which is produced in the rock around the depository, from migrating to the ground-surface. This paper presents a laboratory study on the capillary condensation process of water in the nanoscale pores of shales.

Four borehole core samples of shale obtained from the Qaidam Basin were used to perform the experiment. We obtained the mineral composition of the shale by X-ray diffraction. Low-pressure nitrogen and carbon dioxide adsorption and high-pressure mercury intrusion were applied to obtain the distribution of the pores of the shales. The water condensation experiments were performed at various degrees of relative humidity ranging from 65% to 95%. During the experiment, the samples were kept in a constant temperature and humidity environment for about 8 days. Capillary water condensation happened spontaneously. The samples were weighed every three hours to determine the amount of condensed water.

The condensation experiments indicate that the amount of condensed water increases with relative humidity. Clay minerals and total organic carbon are the main factors affecting the amount of condensation and quartz has little effect on the formation of condensed water. At the beginning of water condensation, the formation rate of condensed water in shale increases first with the increase of relative humidity before a critical relative humidity and then decreases. It is suggested that the rapid condensation of water may clog the pores, and some of the gas may be trapped in the dead end pores. As a result, the decrease in water storage space leads to the decrease in the rate of water condensation. We found that the water condensation saturation shows a good linear correlation with relative humidity in the condition of high relative humidity (the relative humidity in this experiment is above 65%). We also found that, after modification, Kelvin equation could be used to describe the relationship between the relative humidity (RH) and water condensation saturation of shales.

FORMATION OF CONCRETIONS IN CONNECTICUT VALLEY VARVED CLAY

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This paper presents experimental studies of the mineral composition, the microfabric feature, and the mechanical behavior of the naturally formed small-size concretions found in the sediment of Connecticut Valley Varved Clay (CVVC) using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), and nanoindentation testing. The results show that carbonate binds the silt and clay particles as agglomerates, which provide insight of formation mechanism for CVVC concretions and knowledge of mechanical properties.

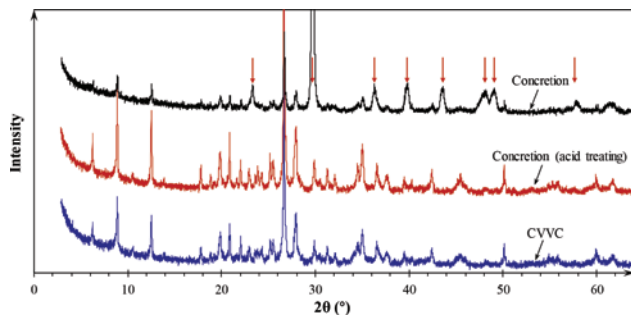


Fig. 1 Diffraction patterns of the random powders of both CVVC concretions and soil samples.

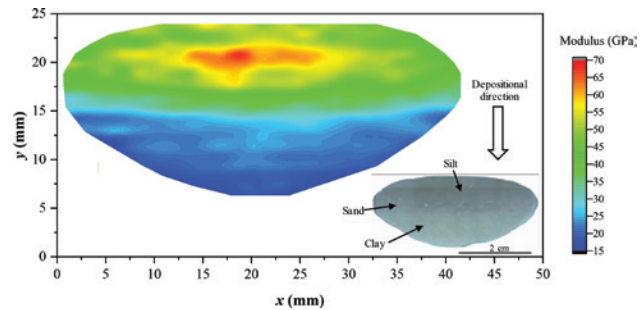


Fig. 2 Distribution of Young's modulus across the cross-section of a layered CVVC concretion

CLAY NANOPARTICLES AS EFFICIENT VACCINE ADJUVANTS FOR ANIMAL AND HUMAN HEALTH

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Pathogenic *Escherichia coli*, such as enterohemorrhagic *E. coli* (EHEC) and enteropathogenic *E. coli* (EPEC), are responsible for a series of human diseases worldwide, and vaccine offers a more efficient and feasible public intervention. As the key component of vaccine, adjuvant has been actively pursued, including various nanomaterials, to enhance the immunity against the bacteria. Recently, clay nanoparticles, i.e. layered double hydroxides (LDHs) and hectorite (HEC), appear as effective adjuvants with desirable physicochemical properties.

We investigated the vaccine formulations containing the essential infectious factor IB for EHEC and EPEC and clay nanoparticles. Both LDH and HEC nanoparticles are able to carry an appreciable amount of IB, and significantly facilitate the cellular internalization of IB. The medium size LDH (115 nm) and HEC (77 nm) both induced much stronger antibody and cell-mediated immune responses than those by commercial adjuvants, QuilA as well as Alum, and maintained much higher levels of specific antibody immune response for at least four months. Such immunization in mice showed a very strong immunity for the host cells against the target bacteria in the in vitro assays. We finally examined the possible mechanism for the immunity promotion using clay nanoparticles as the adjuvant, which has demonstrated that both clay nanoparticles with suitable size appear as very promising vaccine adjuvants for animal and human health.

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RAPID ADSORPTION AND REDUCTIVE DEGRADATION OF NAPHTHOL GREEN B FROM AQUEOUS SOLUTION BY POLYPYRROLE/ATTAPULGITE COMPOSITES SUPPORTED NANOSCALE ZERO-VALENT IRON

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Polypyrrole/Attapulgite-supported nanoscale zero-valent iron was successfully synthesized by chemical oxidative polymerization and liquid-phase reduction method. After 25min 99.59% of Naphthol Green B were removed by the composites. A removal mechanism based on the adsorption and degradation is proposed, including prompt adsorption and reduction. Additionally, the activity of nanoscale zero-valent iron is dramatically enhanced due to the introduction of Polypyrrole / Attapulgite composites.

SOLVING CRYSTAL STRUCTURES AND CONSTRUCTING SIZE-DEPENDENT PHASE MAPS FOR Fe(III)-OXIDE NANO-MINERALS

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Understanding interface structures, nano-precipitates, vacancies, impurities, and adsorbed heavy metals on mineral surfaces are important to elucidate formation mechanism and reactions of minerals in the earth environments. Modern technology allows us to detect, characterize, and understand the nature of nano-minerals. In the case of macroscopic minerals, X-ray diffraction is useful tool to study their structure from the Bragg peak positions and intensities. However, this is not realistic for nano-minerals, which show broad and continuous intensity distribution that is not amenable to a crystallographic structure solution. Especially, it is challenging to determine their structures when structures include the short-range ordering, defects, and local domain. Aberration-corrected Z-contrast imaging can provide chemical images with sub-Å resolution. Z-contrast images are HAADF images with atomic resolution. Multiple diffraction effects that appear in high-resolution transmission electron microscopic (HRTEM) images can be eliminated or minimized in Z-contrast images, because Z-contrast imaging uses non-coherent elastically scattered electrons at high scattering angle. We can obtain positions of atoms directly over a large range of thickness, with Z-contrast to help distinguish columns of different atoms and their occupancies along the beam direction. Interface structures and crystal structures of nano-minerals and nano-precipitates can be solved by combining the Z-contrast imaging and ab-initio calculation using density functional theory (DFT) methods. Vacancies, impurities, adsorbed heavy atoms can be also revealed directly. Vacancy ordering in Fe-bearing olivine and Fe-sulfides, adsorbed heavy metals (e.g., As, Au, U) on Fe-oxyhydroxide minerals are resolved clearly. Z-contrast imaging provides direct and local information about the nano-minerals. Z-contrast images of the Fe-oxyhydroxides show ordered FeOOH proto-goethite nano-domains intergrown with nanophase goethite. With determined structure topology, the structural details can be tuned by using pair distribution function (PDF) method using total X-ray and/or neutron scattering. Size dependent phase maps for FeOOH, Fe₂O₃, and TiO₂ systems based on experimental and theoretical calculation methods will be also be presented.

DEPTH SEQUENCE PHOSPHORUS DISTRIBUTION AND SPECIATION IN INTENSIVELY MANAGED CLAYEY AGRICULTURAL SOILS IN CENTRAL ILLINOIS

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Phosphorus loss has long been known to be transported primarily by sediment erosion through surface runoff. Many scientists downplayed tile drainage losses in the Midwestern agricultural systems. Concentrations of dissolved RP (DRP) and total P can range from just detectable to many tenths of a mg L^{-1} in tile lines. These concentrations and loads of DRP and total P are more than enough to lead to eutrophication and algal production in downstream water bodies. There is a great interest in understanding the subsurface distribution of P in intensively managed Midwest agricultural soils. It is virtually unknown the P level and the P speciation in subsoils that are in contact with tile line networks. In this case study, a soil that represents the Midwestern agricultural soils, Drummer Silty clay loam, was chosen. It generally contains about 25% of clay minerals (e.g., Illite and smectite) and most of them are in the upper layer of the soil mainly come from soil parent materials, and the Al and Fe contents are relatively low in the mollisol. At different depths of soil, P sorption capacity should vary due to the different content of clay minerals and metal oxides. Because of high OM in the upper horizon, P can be readily immobilized into organic P and inorganic P might be accumulated in subsoils. To test these hypotheses, inorganic P fractionation and P-31 NMR will be used to characterize P in soils (0-2m) collected from the Central IL agricultural soils.

RAPID TRANSFORMATION OF LAYERED TO TUNNELED MANGANESE OXIDES TRIGGERED BY TRIVALENT MANGANESE ADSORBED ON VACANCIES

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Tunneled Mn oxides (TMOs), common minerals in ferromanganese nodules of oceanic and lake sediments, host a considerable amount of transition and rare earth metals, thus mediating metal cycling and bearing potential economic interest for exploiting these metals. TMOs form through topotactic transformation of layered Mn oxides (LMOs), which is believed to be extremely slow at room temperature. Trivalent Mn (Mn(III)) in LMO structures is a critical player in the transformation. However, the specific role of Mn(III) in the transformation remains unknown.

In this study, δ -MnO₂, a hexagonal birnessite analogous to naturally occurring vernadite, was equilibrated with Mn(II) in 100 mM NaCl solution at pH 4 for 2 hours to prepare Mn(II)-adsorbed δ -MnO₂ (Mn(II)-bir). Mn(II)bir was rinsed with pH 4 water and then incubated in 100 mM NaCl solution at pH 6, 7 or 8 in an anaerobic chamber or in air. Reacted solids were collected at various pre-determined time intervals, and characterized using X-ray diffraction, atomic pair distribution function analysis, X-ray absorption spectroscopy, and high-resolution transmission electron microscopy.

Results show that Mn(II)-bir rapidly transformed to a 4 × 4 TMO under all conditions. The rapid transformation was triggered by vacancy-adsorbed Mn(III) produced by the comproportionation reaction between the vacancy-adsorbed Mn(II) and adjacent Mn(IV). The transformation was fastest at pH 7. An incubation at acidic or alkaline pH retarded the transformation due to an insufficient amount of Mn(III) (pH 6) or the formation of triclinic birnessite (pH 8) as an intermediate product. The presence of O₂ retarded the transformation at pH 8 whereas O₂ promoted it at pH 6. We proposed a novel transformation mechanism of LMOs to TMOs (Figure 1), highlighting the role of vacancy-adsorbed Mn(III) in the transformation.

This work changes our understanding of TMO formation kinetics and suggests TMOs can readily form in low-temperature redox-fluctuating environment, such as lake and oceanic sediments where Mn(II) often coexists with LMOs.

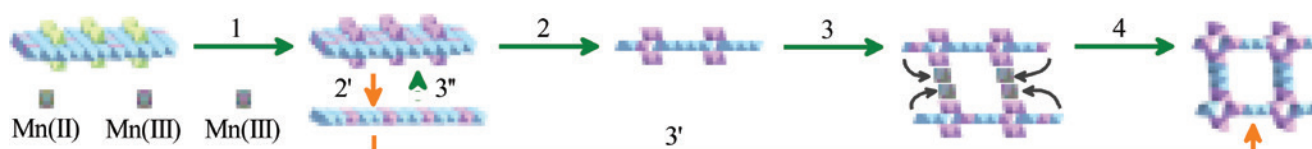


Figure 1. Proposed transformation pathways from Mn(II)adsorbed δ -MnO₂ (Mn(II)-bir) to a 4 × 4 TMO. Mn(II)-bir transforms into a 4 × 4 TMO through comproportionation between vacancy-adsorbed Mn(II) and structural Mn(IV) (Step 1), rearrangement of Mn(III) into vacancy-adsorbed Mn(III) segregated by four rows of structural MnO₆ octahedra (Step 2), dissolution of edge MnO₆ units (Step 3), and condensation of dissolved MnO₆ to form the second walls of 4 × 4 tunnels (Step 4) at acidic or neutral pH. At alkaline pH, Mn(III)adsorbed δ -MnO₂ may transform into triclinic birnessite (T-bir) through incorporation of Mn(III) into vacancies (Step 2'). Then, T-bir can slowly transform into a 4 × 4 TMO through folding of the MnO₆ sheets (Step 3').=

TOXICITY MECHANISM OF LAYERED DOUBLE HYDROXIDE NANOPARTICLE-INDUCED OXIDATIVE STRESS AND INFLAMMATION IN HUMAN LUNG EPITHELIAL CELLS

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Layered double hydroxide nanoparticles (LDH-NPs), also known as anionic clays, have attracted much attention as efficient delivery carriers for drugs or bioactive molecules. Although LDH-NPs are generally considered to have low toxicity, our previous research demonstrated induction of reactive oxygen species and pro-inflammation response by LDH-NPs. In this study, LDH-NPs-induced oxidative stress and inflammation response were further evaluated by analyzing antioxidant enzymes and released cytokines. The expression of mitogen-activated protein kinase (MAPK) cascades, including extracellular signal-regulated kinases (ERKs), the c-Jun-N-terminal kinases (JNKs), and p38, was also investigated to determine toxicity mechanism. Furthermore, Src family kinases (SFKs), nuclear factor kappa B (NF-kappa B), and nuclear factor-erythroid 2-related factor-2 (Nrf-2) were investigated as upstream and downstream events of MAPK. The results showed that the activity of antioxidant enzymes increased in LDH-exposed cells via SFK-JNK and p38-NF-kappa B signaling pathway, but cell proliferation was not affected. Moreover, the activation of these signaling pathways eventually induced proinflammatory cytokines, IL-6 and IL-8. These findings suggest that oxidative stress caused by LDH-NPs mediates the inflammation response in human lung epithelial cells.

CONTAMINANT OXIDATION WITH Fe(II)-BEARING CLAY MINERALS

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Clay minerals play an important role for the fate of organic and inorganic contaminants. In addition to contaminant sorption, clay minerals also contribute to contaminant transformation, for example of organic contaminants such as nitroaromatic compounds or halogenated hydrocarbons, in the presence of structural Fe(II) in clay minerals. Most studies so far have focussed on investigating contaminant reduction with Fe(II)-bearing clay minerals and it has only recently been demonstrated that organic contaminants can also be oxidized during the reaction of Fe(II)-containing clay minerals with oxygen, similar to what is known for dissolved Fe(II). However, Fe(II) in clay minerals is stably bound in a solid silicate matrix, which may alter the mechanism of reactive oxidizing species (ROS) production compared to aqueous Fe(II). To date, it is unknown how clay mineral properties affect the formation of ROS, and thus the oxidation of organic contaminants, from the oxygenation of Fe(II)-containing clay minerals.

To address this knowledge gap, we carried out a kinetic study using a range of model organic contaminants, including phenol, benzoic acid, and formic acid, to probe the oxidative reactivity in our clay mineral systems. We related contaminant oxidation with simultaneously measured Fe(II) consumption, which was used as a proxy for reactive oxidizing species formation, and determined the efficiency of the overall advanced oxidation process. To determine the effect of clay mineral properties on the oxidation efficiency, we used standard clay minerals differing in total clay mineral Fe content, the amount and location of excess charge, and the location of Fe binding. Additionally, we used selective scavengers and likely intermediate species formed during the Fe(II) oxygenation reaction to verify our hypothesized reaction mechanism. Finally, we integrated all results and developed a mathematical model describing the contaminant oxidation reaction.

SORPTION CHARACTERISTICS OF NATURAL AND ACID-TREATED BENTONITES FROM RUSSIAN DEPOSITS

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Bentonites are widely used in industrial waste management including radioactive waste disposal. The main bentonite component determining its properties is montmorillonite. Its characteristic feature is the ability for intracrystalline swelling due to the lability of the interlayer space and also large specific surface area and high cation exchange capacity. Acid modification of bentonites is a widespread technique aimed to the improvement of the sorption capacity. However, at several waste disposal sites in Russia, bentonites suffer various aggressive conditions including acid influence. It changes its properties dramatically and must be taken into account.

This work has been conducted on four samples from Russian and near abroad deposits: Taganskoye (Kazakhstan), Dashkovskoe (Moscow region, Russia), Zyryanskoe (Kurgan, Russia) and 10th Khutor (Rep. Khakassia, Russian Federation). Composition of the samples was studied by X-ray diffraction, IR spectroscopy, and X-ray fluorescence chemical analysis. Acid treatment was conducted with 13M HNO₃ at 90 °C for 1 and 5 hours.

To estimate the adsorption properties, the values of the cation exchange capacity (CEC) were determined by the methylene blue (MB) and Cu [(Trien)]²⁺ titration methods. Experiments on the adsorption of Cs⁺ and Sr²⁺ were carried out at static conditions. Thus a series of CsNO₃ and SrCl₂ solutions was prepared in the concentration range from 50 to 2700 mg/l and from 10 to 1500 mg/l. Solutions were poured into the flasks with bentonite samples at a solid:liquid ratio 1:100. After reaching equilibrium, supernatants were filtered. Determination of cation concentrations in equilibrium solutions was carried out by ICP-MS. Based on the obtained data, adsorption isotherms were plotted. Since the shape of the isotherms corresponds to the Langmuir theory it was possible to obtain adsorption constants from the linear form of the Langmuir adsorption equation.

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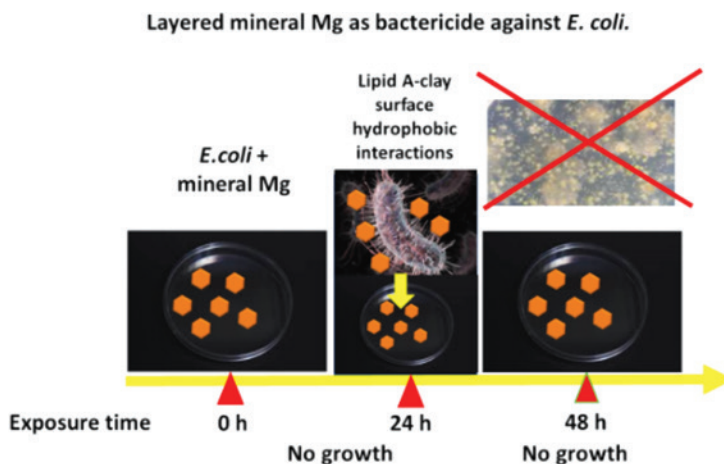
NATURALLY OCCURRING LAYERED-MINERAL MAGNESIUM AS A BACTERICIDAL AGAINST *ESCHERICHIA COLI*

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Escherichia coli (*E. coli*) is a versatile organism that can colonize and adapt in the environment, and an example of antibiotic resistant bacteria, persistent throughout the world because they have evolved to express various defense mechanisms to cope with antibiotics and the immune system, therein the need to find good strategies for their treatment, such as the application of industrial minerals. The application of layered-mineral Mg in concentrations as low as 20 $\mu\text{g mL}^{-1}$ sufficed to provoke irreversible alterations in the membrane of *E. coli* causing death. Arguably, structural factors, stacking over bioavailability of Mg, explained the bactericidal activity of brucite and talc but not sepiolite. Brucite induced LP. However, that was not the case for talc. Pre-treatment with EDTA showed labile and non-labile components in brucite were just as active, supporting the notion that transport over chemical processes were limiting. Yet, neither *in-vitro* cell viability nor *in vivo* LP induction determinations served as predictors for the bactericidal activity of layered mineral Mg against *E. coli*. Located in the outer section of the external membrane of gram negative bacteria is lipid A, which is responsible for its toxicity, and thought to interact specifically with layered mineral Mg and, by doing so, masks its toxic effects. This proposal agrees well with a related study reporting growth curves (log phase) for six antibiotic resistant bacteria [*E. coli*, *Pseudomonas aeruginosa*, *Salmonella*, and *Klebsiella pneumonia* (gram-negative) and *Listeria* and *Staphylococcus aureus* (gram-positive)], showing that saponite acted as bacteriostat *tantrum* if against gram-negative bacteria (Zarate-Reyes *et al.*, 2018, *Journal of Hazardous Materials*, **342**, 625-632). Thus, the composition of the bacterial membrane is critical for allowing clays (and clay minerals and clayey components) to act as antibacterial (bacteriostat or bactericide), while membrane charge played a lesser role. In particular for *E. coli*, critical are specific interactions between lipid A and surface of layered mineral Mg, or smectites (Zarate-Reyes *et al.*, 2017, *Applied Clay Science*, **149**, 87-96).



EFFECT OF LIGANDS ON THE OXIDANT PRODUCTION FROM OXYGENATION OF REDUCED NONTRONITE

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Oscillation of redox state of structural iron in clay minerals has profound influence on various environmental processes. Despite numerous studies exploring the “reducing behavior” (i.e. using them as reductants) of iron-containing clay minerals, their “oxidizing ability” has long been neglected. Recent studies demonstrated that some biologically or chemically reduced iron-containing clay minerals such as nontronite could activate oxygen to produce hydroxyl radicals ($\bullet\text{OH}$), one of the most powerful oxidizing species in nature, thus oxidatively degrading certain organic pollutants such as tetracycline, 1,4-dioxane, and trichloroethylene. However many questions remain unresolved with respect to their behaviors in natural environment.

In this work, four different ligands and iron-chelating agents, phosphate, tripolyphosphate (TPP), nitrilotriacetic acid (NTA) and ethylene diamine tetraacetic acid (EDTA) were selected to evaluate their potential effects on the yield and nature of oxidants (including $\bullet\text{OH}$ and/or hyper-valent iron such as Fe(IV)) from oxygenation of reduced nontronite. Results showed that all four ligands could significantly promote the oxidant yields and produce different types of oxidants. However, the specific effects and mechanisms varied with ligand types. NTA and EDTA addition resulted in considerable amounts of structural Fe dissolution. During oxygenation, fast electron transfer happened between structural Fe(II) and chelated aqueous Fe^{3+} . So aqueous Fe^{3+} , which was produced from homogenous Fenton reaction in the solution, was continuously reduced by structural Fe(II) . Thus, in the presence of these two ligands, homogeneous Fenton reaction in aqueous solution mainly contributed to the oxidant yields and the reduced nontronite served as an electron source. Phosphate was strongly adsorbed on the nontronite surface via a ligand exchange mechanism by substituting the hydroxyl group of the nontronite structure, thus affecting its surface catalytic properties and oxidant production. This sorption shifted the type of oxidant from weak Fe(IV) to strong $\bullet\text{OH}$. TPP played a double role by changing the surface catalytic properties of nontronite through surface sorption and by enhancing the homogeneous Fenton reaction through chelation with dissolved Fe. These results shed lights on how commonly present natural and synthetic ligands affect the oxidation process and oxidant production from reduced clay minerals, hence providing a theoretical basis for understanding the mechanisms of oxidant-promoted organic matter transformation and organic pollutant degradation.

MOLECULAR DYNAMICS SIMULATIONS OF HEAVY METALS ADSORPTION ON CLAY MINERALS

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Clay minerals attract special attention for their important roles in the transport and immobilization of toxic metals in soils and aquifers. Adsorption of heavy metals on clay surfaces has been studied extensively by experiments, but current experimental techniques usually cannot provide atomic-scale structural and thermodynamic information, which is directly pertinent to understanding of the geochemical cycle of metal elements and the relevant environmental problems. In this study, classical molecular dynamics simulations were carried out to investigate the sorption of Ni(II), Cd(II), and Pb(II) on basal surfaces of clay minerals. Both inner-sphere and out-sphere surface complexes were observed and the most probable sorption site were identified. Potential of mean force (PMF) calculations were then conducted to obtain site-specific adsorption free-energy profiles for the above metals ions as function of their distance from the surface. The results show that the energy barriers between outer-sphere and inner-sphere surface complexes are not very high for Cd(II) and Pb(II), while for Ni(II) this barrier is much higher, indicating that the formation of Ni(II) inner-sphere surface complexes is unfavorable. Our findings provide a physical basis for molecular scale understanding of the processes controlling the behavior of heavy metals at clay-water interface, which is essential for predicting their fate in subsurface environments.

SUPERHYDROPHOBIC AND SUPERAMPHIPHOBIC COATINGS BASED ON PALYGORSKITE

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Biomimetic superhydrophobic and superamphiphobic coatings are receiving extensive attention because of their unique self-cleaning properties.¹ The coatings are prepared by the combination of proper surface microstructures and materials of low surface tension. Most of the microstructures are based on synthetic nanomaterials, which are expensive and complicated. Also, preparation of the synthetic nanomaterials is often pollutive.

Here we report our recent progress about superhydrophobic and superamphiphobic coatings based on palygorskite, the natural nanomaterial (Figure 1).²⁻⁴ The coatings are prepared by modification of palygorskite with silanes followed by spray-coating onto substrates. The coatings showed excellent superhydrophobicity and superamphiphobicity as well as high stability. The influences on the microstructure of clay minerals on surface microstructure, wettability and stability of the coatings are discussed.

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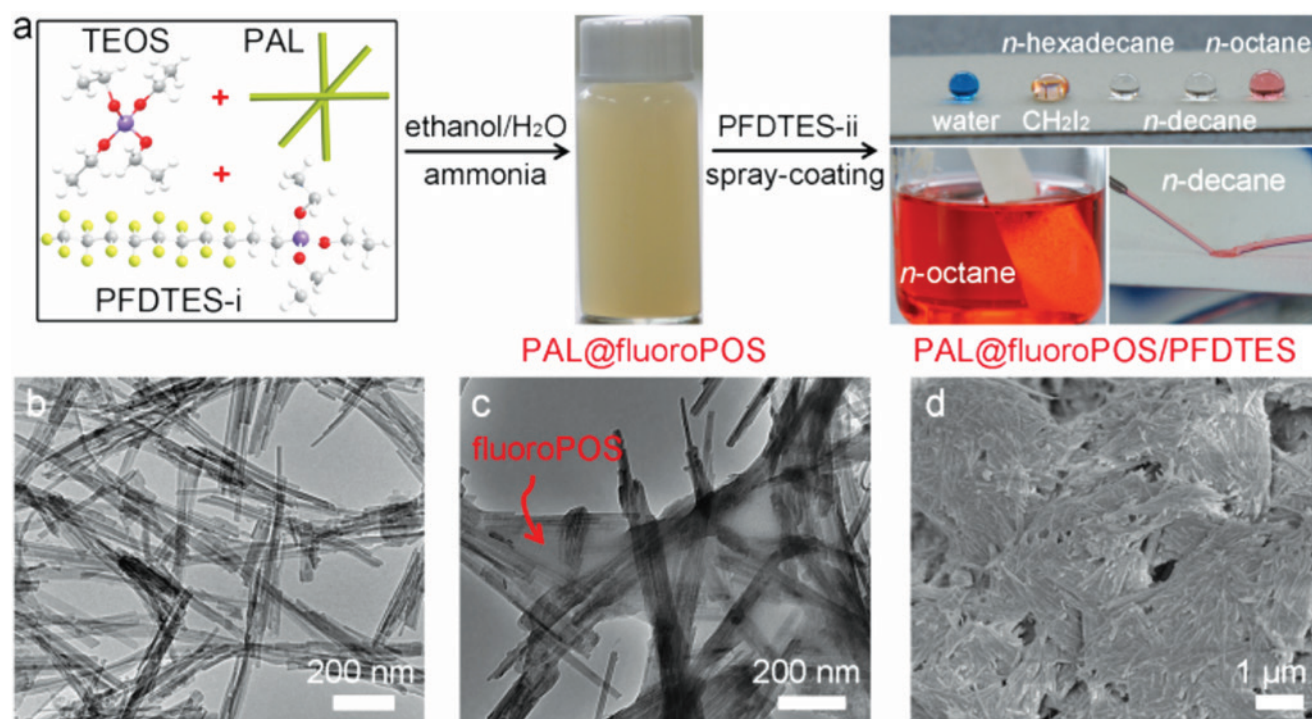


Figure 1. Superamphiphobic coatings with low sliding angles based on palygorskite.

FUNCTION OF THE OUTER-MEMBRANE CYTOCHROMES IN REDUCTION OF NONTRONITE BY *SHEWANELLA ONEIDENSIS* MR-1 AND COMPARISON BETWEEN DIFFERENT ELECTRON SHUTTLES

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Electrons can be transferred from the dissimilatory iron-reducing bacteria (DIRB), such as *Shewanella oneidensis* MR-1, to structural ferric iron in clay minerals. Electron shuttle such as AQDS facilitates the electron transfer and enhances the extent and rate of reduction. Recent studies have revealed the extracellular electron transfer pathway of *Shewanella oneidensis* MR-1, which is composed of six multihaem c-type cytochromes: CymA, Fcc₃, MtrA, MtrC, and OmcA. In this study, we use *Shewanella oneidensis* MR-1 wild-type, membrane protein deletion mutants deficient in CymA, MtrA, MtrB (an outer-membrane protein), MtrC, OmcA, and double deletion mutants deficient in both MtrC and OmcA to reduce ferric iron in nontronite (an iron-rich smectite variety). We also compare the electron shuttling ability of AQDS, magnetite, and flavin in the reduction process. Several conclusions could be drawn from our study: first, between the two c-type cytochromes located on the cell surface (e.g., OmcA and MtrC), the mutant deficient in OmcA has a similar reduction rate and extent as those by the wild type, while the mutant deficient in MtrC has a significantly lower reduction extent, suggesting that MtrC is more important than OmcA in the electron transfer chain. The mutant deficient in CymA has the lowest reduction extent among all the mutants, suggesting its essential role in the electron transfer process. Second, magnetite can work as an extracellular electron shuttle to facilitate the reduction process. Third, among three different electron shuttles, magnetite and flavin could only help shuttling electrons once they reach the surface, while AQDS has the ability to shuttle electrons from CymA across outer-membrane to extracellular nontronite.

LEARNING FROM ANCIENT MAYA: FACILE PREPARATION OF STABLE PLYGORSKITE/ASTROZON BRILLIANT RED 4G@SiO₂ MAYA-BLUE LIKE PIGMENT

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Maya Blue pigment has attracted considerable attention owing to their extraordinary stability. The growing interest in this field has largely expanded the study of Maya Blue-like pigments. Herein, a facile method for the preparation of stable palygorskite/Astrozon Brilliant Red 4G@SiO₂ (PAL/ABR@SiO₂) Maya Blue-like pigments was reported. The PAL/ABR@SiO₂ pigment with a purple-red hue was fabricated by adsorption of ABR onto PAL, then deposition of a layer of SiO₂ on the surface by hydrolysis and polycondensation of tetraethoxysilane (TEOS). The weight ratio of ABR onto PAL is up to 12%, which is higher than all the state-of-the-art Maya Blue-like pigments. The SiO₂ layer formed on the surface of PAL/ABR contributes greatly to the improved stability of the pigment due to shielding effect. The PAL/ABR@SiO₂ pigment shows excellent stability against chemical elution, thermal aging and intensive UV irradiation.

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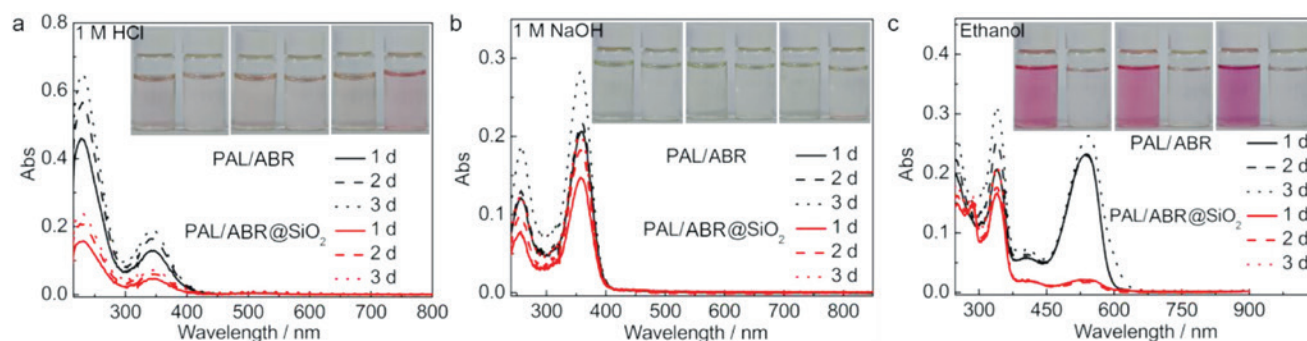


Fig.1 Variations of UV-Vis spectra and images of the supernatants of PAL/ABR and PAL/ABR@SiO₂ pigments after chemical attacks for 3 d using (a) 1 M HCl, (b) 1 M NaOH and (c) ethanol.

EFFECTS OF METAL IMPURITIES ON THE STRUCTURE AND REACTIVITY OF MN OXIDE NANOPARTICLES

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Manganese (Mn) oxides are a group of ubiquitous metal oxides with great environmental significance. Due to their small particle size, large surface area, and high sorptive and oxidative capacities, Mn oxides can participate in a wide range of sorption and redox reactions, and exert significant influences on the biogeochemical cycling of metals, nutrients, and organics. The majority of natural Mn oxides are thought to be formed from microbial activities and the predominant form of biogenic Mn oxides is a highly disordered nanocrystalline phase similar to hexagonal birnessite. This phase is highly reactive and can undergo abiotic ripening or transformations to form phases with higher structural order and less reactivity.

Numerous efforts have been dedicated to understand the structure and reactivity of pure Mn oxides, yet much still remain unknown regarding the formation, structure, and reactivity of the oxide phases formed biologically and under conditions representative of complex environmental systems. Due to the negative surface charge of Mn oxides across a wide range of pH, metal cations have strong tendency to interact with and affect the oxide surface and structure properties. In order to develop predictive biogeochemical models involving Mn oxides as an active component, it is critical to develop a systematic understanding of the impacts of metal cations on the structure-reactivity relationship of Mn oxides.

Our research systematically investigated the role of a common metal cation Zn on the formation, structure, and transformation pathways of biotic and abiotic Mn oxide phases. Zn almost exclusively existed as surface adsorbed species at vacancy sites due to its high structural incompatibility. Its presence significantly altered the morphological and structural properties of the oxides, which resulted in altered sorptive and oxidative reactivities, as well as Mn(II)-induced transformation kinetics and pathways. Such effects were also phase specific, i.e. different oxide phases show different degrees of alteration. Taken together, our study demonstrated the importance of understanding the structure-reactivity relationship of Mn oxides under environmentally relevant conditions.

THE EFFECT OF ORGANIC LIGANDS ON BIOTIC OXIDATION OF STRUCTURAL Fe(II) IN REDUCED NONTRONITE BY *PSEUDOGULBENKIANIA* SP. STRAIN 2002

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Nitrate-dependent Fe(II) oxidation (NDFO) is important for multiple environmental processes including nitrate remediation, heavy metal mobility and transport, and nuclear waste disposal. Past Research has focused on microbial oxidation of either aqueous or structural Fe(II) in minerals, however, the effects of organic ligands on this process is not yet well understood, though organic ligands are common in natural environments. The aim of this research was to study nitrate-dependent microbial oxidation of structural Fe(II) in reduced nontronite (NAu-2) by lithoautotrophic *Pseudogulbenkiania* sp. Strain 2002 in the presence nitrilotriacetic acid (NTA) and oxalate under bicarbonate buffered neutral pH condition. Our results showed that Fe(II) oxidation extent was enhanced when NTA and oxalate were present, with observed Fe(II) oxidation extent being 84%, 82% and 47% for NTA, oxalate, and without ligand, respectively. Dissolved Fe^{2+} contributed approximately 16.4 % and 15.5 % to total amount of Fe(II) oxidation in NTA and oxalate group, but no soluble Fe^{2+} was observed in no-ligand control group. The chelation of NTA and oxalate to Fe(II) in the nontronite structure and subsequent liberation of Fe(II) from the structure to aqueous solution probably provided increased amounts of bioavailable Fe(II) for microbial oxidation. X-ray powder diffraction (XRD) show similar (001) diffraction patterns of ethylene glycolated NAu-2 before and after bio-oxidation, with or without organic ligands, indicating that NAu-2 did not turn amorphous under the effect of organic ligands. In all treatment, nitrate was reduced to N_2 gas while a negligible amount of nitrite was detected. The ratio of oxidized Fe(II) to reduced nitrate was not stoichiometrically 5:1, probably because of heterotrophic nitrate reduction by cell debris such as glycine or due to microbial nitrate assimilation. These findings have important implications for iron and nitrogen biogeochemical cycles in natural environments.

POLYVINYLDENE FLUORIDE ULTRAFILTRATION MEMBRANE BY INCORPORATION OF THERMO-RESPONSIVE Palygorskite Nanofibers with Enhanced Flux and Antifouling Properties

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Herein, the surfaces of Palygorskite (PGS) nanofibers were grafted with thermo-responsive poly (N-isopropylacrylamide) (PNIPAAm) brushes, and then incorporated into poly (vinylidene fluoride) to fabricate PVDF hybrid membranes via a combined nonsolvent-induced phase separation and thermally induced phase separation process. The PGS-g-PNIPAAm nanofibers were uniformly dispersed in the PVDF matrix, acted as nucleation seeds and expedited the crystallization process. The nanofibers improved tensile strength, elongation, thermal stability, hydrophilicity and permeability of the membranes without sacrificing average pore size and porosity. With increasing PGS-g-PNIPAAm nanofibers dose, water contact angle decreased from 82.2° to 52.7°, and pure water flux increased from 122 L·m⁻²·h⁻¹ to 246 L·m⁻²·h⁻¹ at 20°C. More importantly, the hybrid membranes exhibited superior BSA-fouling resistant and easy-cleaning properties, that is, low flux decay, high flux (more than twice that of PVDF membrane) and flux recovery (about 91%), compared to the pure PVDF membrane. The outstanding performance of the membrane highlights its potential for practical applications.

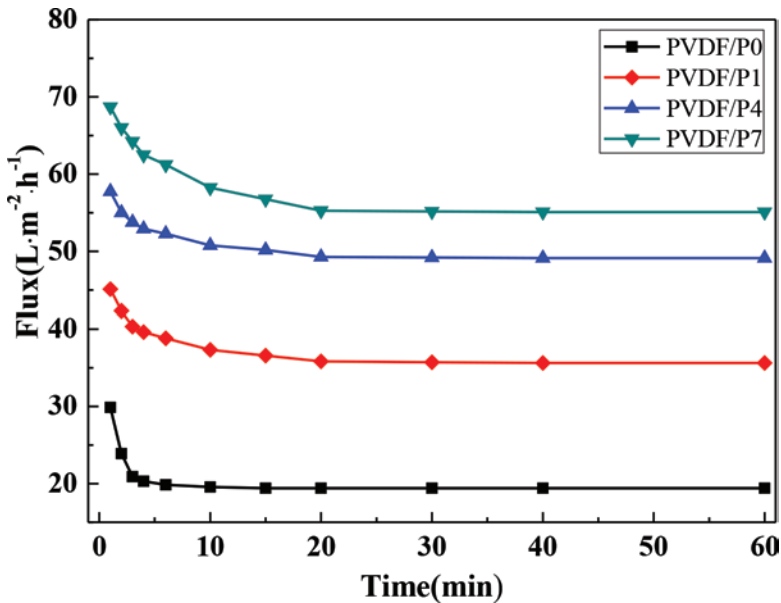


Fig.1 Time course of BSA permeation flux during filtration for membranes

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DYNAMIC STRUCTURAL AND COMPOSITIONAL CHANGES OF BIRNESSITE DURING REDUCTIVE DISSOLUTION

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Birnessite is the most common manganese (Mn) oxide and mediates elemental cycling in nature. The structure of birnessite consists of stacked layers of edgesharing MnO_6 . The Mn site in MnO_6 layers is dominated by Mn(IV) with minor Mn(III) and Mn vacancies. Both Mn(II) and Mn(III) can adsorb on vacancies. The relative proportions of the three Mn oxidation states strongly affect birnessite adsorption and oxidation reactivity and its transformation to other Mn oxide phases. Natural organic matter (NOM) can reduce birnessite and change its structure and Mn oxidation state composition. However, it remains unclear how pH and co-existing cations affect the process.

In this study, $\delta\text{-MnO}_2$, a nanoparticulate birnessite with hexagonal layer symmetry was partially reduced by fulvic acid (FA) at pH 4–8 in the presence or absence of Ca^{2+} or Zn^{2+} under anoxic conditions. The reacted solids were collected at different reaction times and characterized using an array of synchrotron X-ray techniques. Results indicate that Mn(III) substantially accumulated with little Mn(II) in the structure of $\delta\text{-MnO}_2$ at pH 8 but substantial amounts of Mn(II) with little Mn(III) at pH 4 and 6 during oxidizing FA. The Mn(III) resided either in MnO_6 layers or over vacancies of δMnO_2 . The Mn(III) accumulation at pH 8 was stronger at higher FA/solid mass ratios. At FA/solid ratio ≥ 1 , minor hausmannite and MnOOH phases formed due to high ratios of produced Mn(II) to $\delta\text{-MnO}_2$. Ca^{2+} favored but Zn^{2+} disfavored the Mn(III) formation in layers and on vacancies during oxidizing FA at pH 8. The presence of the divalent cations resulted in less Mn(II) adsorbed on vacancies. In addition, minor MnOOH and hausmannite formed in the presence of the divalent cations. The formation of Mn(III) in the reacted $\delta\text{-MnO}_2$ was ascribed to disproportionation between Mn(IV) and adsorbed Mn(II) on vacancies or at edge sites. The coexisting divalent cations imposed the impacts via competing with Mn(II) for surface sites. Compared to anoxic conditions, oxic conditions led to a higher Mn(III) concentration in δMnO_2 structure at pH 8 but not at pH 5 during its reduction by FA. The altered δMnO_2 displayed a much higher FA adsorption capacity than the initial oxide. These findings have important implications for understanding structure, composition and reactivity of birnessite coexisting with NOM in natural environment.

IDENTIFICATION AND QUANTIFICATION OF SILICATE, PHOSPHATE AND SULFATE SPECIES ON IRON OXIDE SURFACES USING SPECTROSCOPIC AND ATOMIC PAIR DISTRIBUTION FUNCTION ANALYSES

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Phosphate, sulfate and silicate are common oxyanions in soils. They are either critical nutrients to plants and/or important ions actively involved in many soil biogeochemical processes. Sorption of these oxyanions on mineral surfaces strongly controls their mobility and availability in soils, and in turn affects mineral stability and surface reactivity. However, the sorption mechanisms of these oxyanions on mineral surfaces have been contentious. Thanks to the recent advancement in X-ray absorption spectroscopy (XAS) of sulfur, phosphorus and silicon and X-ray atomic pair distribution function (PDF) analysis, more insights have been gained into the speciation of the oxyanions sorbed on iron (Fe) oxide surfaces. In a series of studies, we used PDF, XAS and FTIR analyses and batch sorption experiments to revisit sorption of these oxyanions on ferrihydrite and hematite surfaces. We convincingly showed that phosphate formed bidentate-binuclear complexes and amorphous Fe phosphate on ferrihydrite surfaces, and that phosphate promoted ferrihydrite dissolution. Sulfate formed both outersphere complexes and bidentate-binuclear inner-sphere complexes on ferrihydrite or hematite surfaces; and the relative proportions of these two types of complexes were determined and showed expected dependence on ionic strength and pH. The respective adsorption loadings of the two types of complexes were further modeled using a surface complexation model. As to silicate, it formed monodentate-mononuclear complexes on ferrihydrite at low Si loadings; with increasing silicate loading, silicate started to form oligomers that adsorbed on ferrihydrite surfaces via the bidentate-binuclear mode. These findings clarify the sorption mechanisms of these oxyanions at mineral-water interfaces and improve our understanding on how secondary minerals, such as iron oxides, regulate mobility and availability of these oxyanions in the soil environment.

EFFECT OF SURFACTANT PACKING DENSITY ON THE SORPTION OF HYDROPHOBIC ORGANIC CONTAMINANTS ON ORGANOCLAYS

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Organoclays are synthesized by exchanging the interlayer inorganic cations using cationic surfactants (e.g. cetyltrimethylammonium, CTMA), to effectively and efficiently uptake hydrophobic organic contaminants (HOCs) from aqueous media. However, the sorption mechanisms underlying the uptake process have not been unambiguously clarified yet. Early studies indicated that the sorption of HOCs was primarily a partition process, i.e., partition of OCs between bulk water and the organic phases formed by surfactant aggregates in organoclays. However, the K_{oc} for a given HOC on different organoclays, which have been synthesized even with the same surfactant, can vary over a wide range (more than one order of magnitude).

We applied the FTIR technique to study the conformation of surfactant (CTMA) on a variety of organoclays, and then tried to correlate the surfactant packing density with the sorption capacity of HOC (i.e., K_{oc}) on these organoclays. The studied organoclays were CTMA intercalated montmorillonite (OMt) and hydrobiotite (Oht), with different CTMA loading level. Generally, the packing density of CTMA is related to the conformation of its alkyl chains (indicated by the wavenumber of $\nu_{as}(\text{CH}_2)$), and higher packing density of CTMA results in higher ratio of *all trans* to *gauche* conformation. In this work, we found that with rising CTMA loading level, the packing density of CTMA on OMt was shown to increase accordingly, while on Oht it remained relatively constant. Because of the higher charge density of hydrobiotite, CTMA showed higher packing density on Oht than on OMt. Interestingly, with rising the packing density of CTMA, the K_{oc} value of the tested HOC (naphthalene) was shown to first increase and then decrease, on all of the studied organoclays (Fig. 1). CTMA had much higher packing density on Oht, and accordingly Oht showed much weaker sorption capacity. We propose that the packing density of surfactant can significantly affect the sorption capacity of organoclays toward HOCs, and a proper packing density can be beneficial for optimizing the sorption capacity of organoclays.

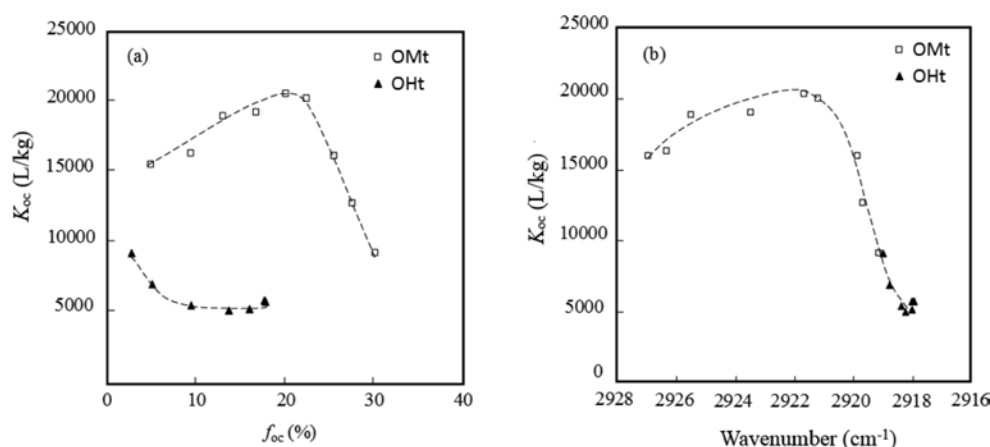


Fig.1 Plot of K_{oc} of naphthalene on OMt and Oht against f_{oc} (a) and $\nu_{as}(\text{CH}_2)$ (b)

HIGH-PRESSURE METHANE ADSORPTION ON MONTMORILLONITE: EXPERIMENTS AND MONTE CARLO SIMULATIONS

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Clay minerals are abundant in environments where methane (CH_4) occurs under high pressure and they provide adsorption sites for CH_4 . It is, however, still unknown whether the interlayer space of expandable clays is available for CH_4 or the gas is adsorbed only on external surfaces of crystallites. High-pressure experiments do not provide sufficient information about the total amount of adsorbate present as the adsorbed phase (absolute adsorption). The conversion of measurable excess isotherm to absolute adsorption requires knowing either volume or density of adsorbed phase, which are not readily available from an experiment.

In the present study CH_4 adsorption experiments were performed on Cs-, Li-, Mg-, Ca-, and Tetramethylammonium (TMA)-exchanged montmorillonite (Mtm) SAz-1 (Cheto) dried at temperatures: 60, 110 and 210 °C. A series of Monte Carlo (MC) simulations were used to calculate the density profiles of CH_4 in smectite d-spacing in range of 11.3 to 57 Å.

The measured TMA-Mtm's isotherms were three times higher than those of Cs-Mtm. Cs- and Li-Mtm's isotherms reached similar maximum and did not change much with pre-drying temperature, whereas CH_4 adsorption on Mg- and Ca-Mtm decreased significantly after drying at 110 °C (Fig.) in respect to that at 60 °C. Mg- and Ca-Mtm showed a hysteresis loop that did not close even under vacuum. Variability in the isotherms' behaviour among different interlayer cations suggests different adsorption sites availability and/or affinity for CH_4 , which may change during drying. The calculated absolute adsorption varied greatly, depending on the MC-based density profile applied, and was used to compute the enthalpy of CH_4 adsorption. The calculated enthalpy of adsorption also varied among samples, from 37 (TMA-Mtm), 26 (Cs-Mtm) to 22 kJ/mol (Mg-Mtm), and the values reached up to 20% relative difference, depending on the density profiles used.

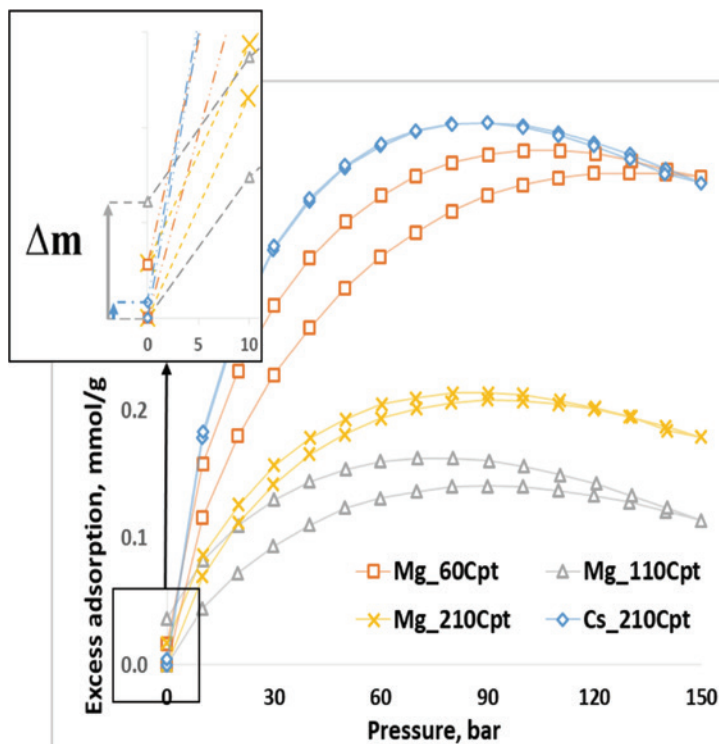


Fig. CH_4 adsorption isotherms of Mg- and Cs-exchanged sample of montmorillonite

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FTIR SPECTROSCOPY TO STUDY FORMATION AND FUNCTIONALISATION OF POROUS CLAY HETEROSTRUCTURES DERIVED FROM LAPONITE

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Formation of hybrid structures merging the properties of crystalline clay mineral and amorphous mesoporous silica in porous clay heterostructured composite (PCH) and its further functionalization proved to be a very promising approach in design of unique nanoscale structures with catalytic application. Present work introduces the potential of FTIR techniques in the middle MIR, near NIR and far FIR regions to investigate the evolution of the Laponite[®] derived PCH composite during its synthesis and post-synthetic functionalization by heteroatoms doping. Surface composition and structural changes occurring in the composite during subsequent synthesis steps were evaluated. IR spectra are significantly altered throughout synthesis stages and the spectrum of final product reflects structural integration of two main composites components: two-dimensional clay mineral and three-dimensional silica. As a result MIR spectrum shows a broad intensive complex band assigned to the stretching $\nu_{\text{Si-O}}$ vibrations of different origin. While the stretching $\nu_{\text{asSi-O}}$ vibration of tetrahedral sheets of Laponite[®] occurs at 1008 cm^{-1} in PCH attributed band is shifted to 1030 cm^{-1} and accompanied by 1084 cm^{-1} component assigned to amorphous silica phase. The creation of two-dimensional Si-O-Si linkages between tetrahedral sheets of Laponite[®] and silica network is confirmed by appearance the new $\nu_{\text{asSi-O}}$ band at 1054 cm^{-1} . Presence of the stretching and bending modes of structural OH groups of Laponite confirmed that layered structure of clay mineral withstand the thermal treatment during removal of the templates. Doping of PCH by Fe^{3+} cations with the use of wet, post-synthesis impregnation method slightly affects the structure of composite decreasing the intensity of the band at 1084 cm^{-1} . This change confirms that Si-O bonds in amorphous component of composite are broken due to partial incorporation of Fe into the silica network in PCH. For samples to which hydrothermal treatment was applied, intensity of amorphous $\nu_{\text{Si-O}}$ bands increased relatively to the band at 1030 cm^{-1} indicating the enlarged amorphous component contribution, despite the higher efficiency of Fe embedding into PCH confirmed ⁵⁷Fe Mössbauer spectroscopy. Simultaneous diminution of intensities of structural OH ($\delta\text{Mg}_3\text{OH}$) and Mg-O_{ap} groups at 668 cm^{-1} and 535 cm^{-1} points to slight violations of octahedral sheets in Laponite. This finding suggests that the high pressure treatment forces the migration of trivalent heterocations along the composite network, resulting in the further development of amorphous, Laponite derived silica upon octahedral sheets impairment. Removal of Mg cations from the octahedral sheets (indirect indicated by FTIR) and subsequent surface enrichment with Mg species was also confirmed by XPS study. The insight into characterization of surface nanostructures was provided by FIR spectra in 400–100 cm^{-1} region giving the complementary results to those obtained from ⁵⁷Fe Mössbauer spectroscopy, capable to distinguish between $\delta\text{-Fe}_2\text{O}_3$ and Fe_3O_4 oxide phases in the spectra of Fe doped PCH samples. NIR spectra showed decrease in the intensity of $2\nu_{\text{SiO-H}}$ band due to silanol interaction and creation of Si-O-Fe linkages in sub-surface areas upon functionalization of PCH composite with iron species. Acknowledgments: This work was supported by the Polish-Norwegian RP PC No Pol-Nor/210445/53/2013

MICROMECHANICAL PROPERTIES OF CLAY POLYMER NANOCOMPOSITE COATINGS

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The role of polymer composites among constructional, protective and decorative materials is constantly increasing due to low specific gravity, chemical resistance, electrical insulation, ease of forming as well as a satisfactory specific strength and good tribological properties. The use of some reinforcing nanoparticles derived from natural chemical compounds that can be functionalized in the intended manner opens up a new perspective in the formation of composites with controlled properties. Nowadays the strategy to combine good functional properties and excellent mechanical properties in creation of wear resistance or outdoor protective coatings is desirable. Highly ordered, layered structure of the clay polymer nanocomposite can exceed the mechanical properties of classical nanocomposite materials. Therefore nanocomposites with clay fillers are used e.g. in the production of car engine parts or in the aerospace industry.

This work focused on the hardness and elastic modulus study of hybrid inorganic–organic nanomaterials based on layered silicates from smectite group (Mt) and cationic polymer polydiallyldimethylammonium chloride (PDDACl). The tribological behaviour of the selected nanocomposites was also investigated. Clay polymer nanocomposite (CPN) samples were prepared by delamination of the natural smectites (Jelšovský Potok or Kopernica) and synthetic Kunipia differ in the composition and the dimension of the single plate-like particles and subsequent intercalation of the organic cationic polymer species. As a result the polymer chains were sandwiched between the layers of smectites. The samples with Mt:PDDACl ratio equal to 1:0.05; 1:0.25 and 1:3 were synthesised. The physico-chemical properties of the obtained composites were studied with the use of XRD, SEM, TEM microscopy and FTIR spectroscopy in MIR and NIR region. The amount of PDDACl influenced the interlayer spaces of the clays. XRD analysis showed an increase of the d_{001} basal spacing in organo-clays (1.45–1.8 nm) compared to the natural clay mineral (1.25 nm), indicating intercalation of polycations between the layers of smectite with parallel two-dimensional orientation along the a, b crystallographic directions of pristine clay, the more dense packed the higher Mt:PDDACl ratio was applied.

The micromechanical properties of the synthesized nanocomposites deposited on glass and metal substrates in a form of coatings were evaluated. The hardness and elastic modulus were assessed using micro-indentation technique. In the first step the scratch tests were done for determination coating's adhesion to the substrate. Results of the scratch tests indicated the sufficient adhesion of the coatings to the substrates. Finally the wear resistance of these coatings in tribological tests was determined. The influence of coating structures, particularly the dimension of the single plate-like particles in the CPN, on their hardness and elastic modulus was examined. Acknowledgments: Thanks to AGH University of Science and Technology, No. 11.11.130.174 and mobility support within Polish-Slovak joint project 2016-2018 under the PAS-SAS agreement.

AGING OF BIOCHAR/ATTAPULGITE COMPOSITES AND ITS APPLICATION FOR Pb(II) REMOVAL

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Biochar/clay mineral composites, as novel adsorbents, have recently received considerable attention for their potential applications on soil fertility and remediation in recent years^{1,2}. While geochemical weathering process has caused many concerns about negative effect of biochar for its properties changed with aging³.

Laboratory experiments were conducted to assess how the addition of biochar (BC), biochar/attapulgite (BA) and aged biochar/attapulgite (ABA) to an agricultural soil affected the sorption and leaching of soil residues of. Laboratory experiments showed that the sorption of Pb^{2+} ranked as follows: unamended soil < BC-amended soil < BA-amended soil < ABA-amended soil (Figure 1). Our results show that addition of amendments with high sorptive capacities can be beneficial in reducing bio-availability of Pb(II) from soil, and for BA both biochar and attapulgite contributed to the texture and structure, which provided varied surface and various adsorptive sites. while with aging processing, BA would increase adsorption efficiency because over time, biochar gets more functional groups⁴, so this will increasing its ability to form heavy metal and BA interactions.

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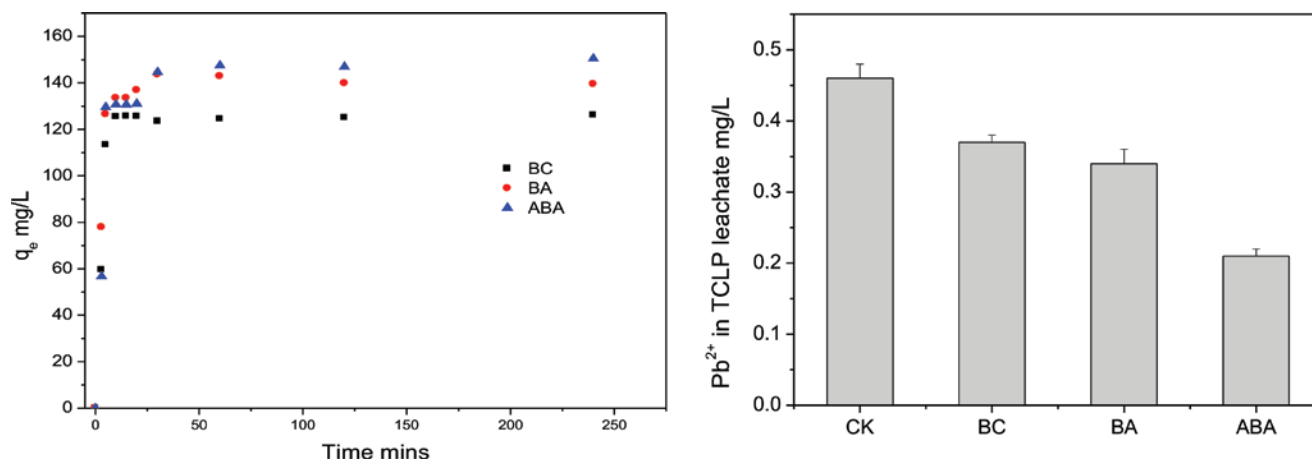


Figure 1. Sorptive capacities of BC, BA and ABA and soil remediation efficiency

HIGH CATALYTIC PERFORMANCE OF FE-NI/PALYGORSKITE IN THE STEAM REFORMING OF TOLUENE FOR HYDROGEN PRODUCTION

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The inexpensive and abundant material, palygorskite (PG), was used as a promising catalyst support to prepare the Fe₃Ni₈/PG catalyst. This catalyst with high dispersion exhibited outstanding catalytic performance for steam reforming of toluene. Higher than 97% toluene conversion, 63% H₂ yield, and 60% CO yield were achieved under 700 °C and S/C=1.0. The H₂/CO molar ratio stabilized at 1.55 during the stability evaluation, and the reusability result indicated that its catalytic activity could be recovered by re-injecting steam into the system.

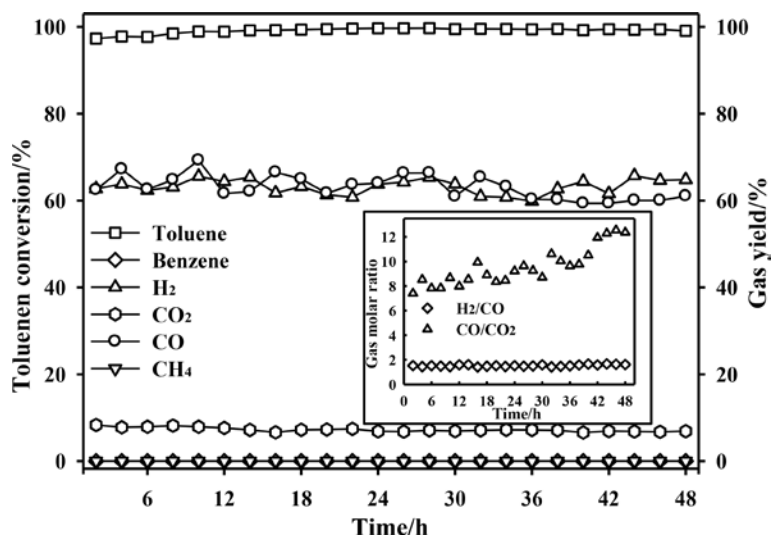


Fig. 1. Stability and lifetime evaluation of the Fe₃Ni₈/PG catalyst for steam reforming of toluene.

EFFECTS OF MICROBIAL ACTIVITIES ON ORGANIC MATTER-CLAY MINERAL ASSOCIATIONS

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Previous studies have focused on associations of soil organic matter (SOM) with either bulk soil or metal oxides, and the role of clay minerals on SOM transformation has not been well studied, despite their ubiquity in soils and sediments. Nontronite (NAu-2), a well-studied Fe-rich clay mineral, was used to synthesize SOM-clay mineral association. Suwannee River humic acid (HA) and fulvic acid (FA) were used as representative SOM and sorbed onto the surface of NAu-2 (0.29% and 0.14% by weight, respectively). The effect of Fe(III) bioreduction on transformation of HA- and FA-sorbed NAu-2 was examined by performing experiments of Fe(III) bioreduction by *Shewanella putrefaciens* in a bicarbonate-buffered system with H₂ and lactate as electron donors. Bioreduced NAu-2 samples were analyzed with Mössbauer spectroscopy, transmission electron microscopy (TEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS).

With H₂ as electron donor, both HA-coated and FA-coated NAu-2 samples showed faster rates but lower extents of Fe(III) bioreduction relative to the un-coated NAu-2, suggesting that HA and FA served as electron shuttle to accelerate the rate of bioreduction, but their sorption to NAu-2 surface may have partially blocked the electron transfer pathway, thus resulting in a lower extent of bioreduction. In contrast, with lactate as electron donor, HA/FA-coated NAu-2 exhibited higher reduction rate and extent than uncoated NAu-2, suggesting lactate may have alleviated the blocking effect. Mössbauer-modelled amounts of Fe(II) in the NAu-2 samples were consistent with chemically determined Fe(II) contents. TEM observations revealed neo-formation of mica and zeolite. Molecular compositions on the NAu-2 surface after OM coating and Fe(III) bioreduction were compared by spectral analysis with ToF-SIMS. Spectral PCA based on negative ions revealed significant separation of native NAu-2 from others along PC2 axis (Fig. 1A). Increasing PC2 value of HA- and FA-coated NAu-2 samples suggests that inorganic species (e.g., Cl, Si, Na-related clusters) greatly decreases, while organic signals (e.g., CN⁻ and CH₂O⁻) increase after OM coating, especially by HA (Fig. 1C), indicating strong adsorption of OM. Bio-reduced and un-reduced NAu-2 samples are separated mainly on PC1 axis, showing that microbial activity increased organic/nutrient ions (e.g., CNO, PO clusters) but decreased inorganic compounds (e.g., Si, O) (Fig. 1B). Thus, microbial activity either provided some new OM onto NAu-2 or modified the existed HA/FA coated on NAu-2. Furthermore, the separation between HA- and FA-coated NAu-2 along PC2 increased after Fe(III) bioreduction, suggesting higher resistance of HA (on the positive PC2) than FA (on the negative PC2) against bio-reduction.

DISTINGUISHING FEATURES AND IDENTIFICATION CRITERIA FOR K-DIOCTAHEDRAL MICAS (ILLITE-ALUMINOCELADONITE AND ILLITE-GLAUCONITE-CELADONITE SERIES) FROM MIDDLE-INFRARED SPECTROSCOPY DATA

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K-dioctahedral 1M micas form two intersecting isomorphous series: (a) Fe-poor varieties range in composition from (Mg, Fe)-poor illite to aluminoceladonite through Mg-rich illite, and (b) Fe-bearing varieties, from illite to celadonite through Fe-illite, Al-glaucconite and glauconite. The high degree of crystal-chemical heterogeneity, as well as the ambiguity in conventional nomenclature, complicate the identification of these mica varieties.

The approach suggested for the interpretation of the FTIR spectroscopy data involves relationships between band positions and cation composition and provides distinguishing features that include the band positions and profile in the regions of Si-O bending, Si-O stretching, and OH-stretching vibrations.

In series (a), FTIR data allow unambiguous identification of illite and aluminoceladonite, which are often confused based on superficial interpretation of XRD data. Specifically, a sharp maximum from the AlOHMg stretching vibration at $\sim 3600\text{ cm}^{-1}$, the presence of a MgOHMg stretching vibration at $3583\text{--}3585\text{ cm}^{-1}$, as well as characteristic band positions in the Si-O bending ($435\text{--}439$, $468\text{--}472$, and $509\text{--}520\text{ cm}^{-1}$) and stretching regions ($985\text{--}1012$ and $1090\text{--}1112\text{ cm}^{-1}$) are typical of aluminoceladonite. Distinguishing between Mg-poor and Mg-rich illites based solely on FTIR data appears problematic, but the position of the Si-O bending modes and the maximum absorption in the region of OH-stretching vibrations may serve as additional criteria. Regression equations relating the band positions in the Si-O bending region with the contents of tetrahedral Al, octahedral Al and octahedral Mg allow evaluation of the contents of corresponding cations in illites and aluminoceladonites with *esd*'s of 0.06, 0.075 and 0.05 cations per half formula unit (*phfu*). According to FTIR characteristics, the series (b) micas are divided into 5 groups differing in the value of $K_{Al} = \text{Al}/(\text{Al} + {}^{\text{VI}}\text{Fe}^{3+})$, where Al and ${}^{\text{VI}}\text{Fe}^{3+}$ are the amounts of Al and Fe^{3+} octahedral cations *phfu*: Fe-bearing Mg-rich illites ($K_{Al} \sim 0.9$); Fe-illites ($0.65 \leq K_{Al} \leq 0.75$) and Al-glaucconites ($0.5 < K_{Al} \leq 0.6$); Al-glaucconites ($K_{Al} \sim 0.5$); glauconites ($K_{Al} < 0.5$); celadonites ($K_{Al} < 0.2$). FTIR data allow not only unambiguous identification of Fe-bearing Mg-rich illites and celadonites but also distinction between Fe-illites and illites proper, as well as between Al-glaucconites and glauconites. On the other hand, Fe-illites and Al-glaucconites have similar FTIR features but differ in cation composition and unit-cell parameters variation ranges.

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