Program & Abstracts

Expanding Clay Science
Over the Pacific and Beyond

61st Annual Meeting of
The Clay Minerals Society and
5th Asian Clay Conference

3–7 June 2024 • University of Hawaii at Manoa

clayconferences.org

The Clay Minerals Society

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Abstracts A1

Expanding Clay Science
Over the Pacific and Beyond

61st Annual Meeting of The Clay Minerals Society and 5th Asian Clay Conference

Held jointly on the Campus of the University of Hawai'i at Manoa

June 3–7, 2024

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THE CLAY MINERALS SOCIETY

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1952–1956	Ralph E. Grim
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Presidents

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2013–2014	Michael A. Velbel
2014–2015	W. Crawford Elliott
2015–2016	Prakash B. Malla
2016–2017	Jan Środoń
2017–2018	Douglas K. McCarty
2019–2020	Lynda B. Williams
2020–2021	Bruno Lanson
2021–2022	Jeffrey A. Greathouse
2022–2023	Stephen Hillier
2023–2024	Sabine Petit

Marilyn and Sturges W. Bailey Distinguished Member Awardees

1968: Ralph E. Grim
1969: Clarence S. Ross
1970: Paul F. Kerr
1971: Walter D. Keller
1972: George W. Brindley
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1975: William F. Bradley
1975: José J. Fripiat
1977: Marion L. Jackson
1979: Toshio Sudo
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1984: C. Edmund Marshall
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1988: Max M. Mortland
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1990: Joe L. White
1990: John Hower
1991: Joe B. Dixon
1992: Philip F. Low
1993: Thomas J. Pinnavaia
1995: William D. Johns
1996: Victor A. Drits
1997: Udo Schwertmann
1998: Brij L. Sawhney
2000: Boris Zvyagin
2001: Keith Norrish
2002: Gerhard Lagaly
2004: Benny K. G. Theng
2005: M. Jeff Wilson
2006: Frederick J. Wicks
2008: Norbert Clauer
2009: Joseph W. Stucki
2010: José M. Serratosa
2011: Sridhar Komarneni
2012: Akahiko Yamagishi
2013: Stephen Guggenheim
2015: R. James Kirkpatrick
2016: Lisa Heller-Kallai
2018: G. Jock Churchman
2019: Dennis “Denny” Eberl
2020: Eduardo Ruiz-Hitzky
2021: David L. Bish
2022: Jin-Ho Choy
2023: Randal T. Cygan
2024: Jan Środoń

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

2014: Will P. Gates
2015: Balwant Singh
2016: Janice L. Bishop
2018: Stephen J. Hillier
2019: Colleen M. Hansel
2020: Eric E. Roden
2021: Hongping He
2022: Young Shin Jun
2023: Christophe ‘tournassat
2024: Eric Ferrage

George W. Brindley Lecture Awardees

1984: Walter D. Keller
1985: José J. Fripiat
1986: Ralph E. Grim
1987: Sturges W. Bailey
1988: Marion L. Jackson
1989: William D. Johns
1990: Alain Baronnet
1991: Thomas J. Pinnavaia
1992: Philip F. Low
1993: Dennis D. Eberl
1994: Robert C. Reynolds, Jr.
1995: Gerhard Lagaly
1996: Samuel M. Savin
1997: Paul H. Nadeau
1998: Bruce Velde
1999: Richard Eggleton
2000: Duane M. Moore
2001: Robert Schoonheydt
2002: David L. Bish
2003: Alain Manceau
2005: Maria F. Brigatti
2008: Robert J. Gilkes
2009: Michael F. Hochella, Jr.
2010: Randall T. Cygan
2013: Andrey G. Kalinichev
2017: Sridhar Komarneni
2018: Cliff T. Johnston
2019: Bruno Lanson
2020: No Award Made
2021: No Award Made
2022: Lynda B. Williams
2023: No Award Made
2024: Prakash B. Malla

Pioneer in Clay Science Awardees

1987: Marion L. Jackson
1988: R. M. Barrer
1989: H. van Olphen
1990: John W. Jordan
1991: Charles E. Weaver
1992: Udo Schwertmann
1993: Linus Pauling
1994: Joe L. White
1995: Rustum Roy
1996: Max M. Mortland
1997: Koji Wada
1998: Robert C. Reynolds
1999: V. Colin Farmer
2000: William F. Moll
2001: Don Scafe
2002: Victor Drits
2003: Vernon J. Hurst
2004: Hideomi Kodama
2005: Jillian Banfield
2006: Jean-Maurice Cases
2007: Spencer G. Lucas
2008: Emilio Galan

2009: Haydn H. Murray
2011: Glenn A. Waychunas
2013: Thomas J. Pinnavaia
2014: Douglas W. Ming
2015: Reinhard Kleeberg
2016: Donald L. Sparks
2017: Fred J. Longstaffe
2018: Jan Środoń
2019: Laurent J. Michot
2020: James D. Kubicki
2021: No Award Made
2022: Michael Hochella
2023: Susant Brantly
2024: Toshihiro Kogure

Citation of Special Recognition

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

Editors of *Clays and Clay Minerals*

1952: J. A. Pash and M. D. Turner
1953: Ada Swineford and Norman Plummer
1954: W. O. Milligan
1955–1961: Ada Swineford
1962–1964: William F. Bradley
1964–1969: Sturges W. Bailey
1970–1972: Max M. Mortland
1973–1974: William T. Granquist
1975–1978: Richards A. Rowland
1979–1990: Frederick A. Mumpton
1990–1991: Kenneth M. Towe
1991–1995: Ray E. Ferrell, Jr.
1995–1998: Wayne H. Hudnall
1999–2000: Stephen Guggenheim
2000–2007: Derek C. Bain
2008–2014: Joseph W. Stucki
2014–2015: Michael Velbel
2016–Present: Joseph W. Stucki

THE ASIAN CLAY GROUPS

1st Asian Clay Conference at Nagoya, Japan in 2010 (Chairperson: Dr. Hirohisa Yamada)

2nd Asian Clay Conference at Seoul, South Korea in 2012 (Chairperson: Prof. Jin-Ho Choy)

3rd Asian Clay Conference at Guangzhou, China in 2016 (Chairperson: Prof. Hongping He)

4th Aian Clay Conference at Pattaya, Thailand in 2000 (Chairperson: Prof. Makoto Ogawa)

Program

JUNE 3

COURTYARD

8:00	REGISTRATION AND WELCOME RECEPTION

BALLROOM

10:00	OPENING CEREMONIES
	PLENARY
11:00	INTRODUCTION OF JAN ŚRODOŃ, RECIPIENT OF THE MARILYN AND STURGES W. BAILEY DISTINGUISHED MEMBER AWARD **Sabine Petit**
11:05	ROLE OF ILLITE IN THE GLOBAL CYCLING OF ELEMENTS **Jan Środoń**
12:00	LUNCH
13:30	INTRODUCTION OF PRAKASH B. MALLA, RECIPIENT OF THE GEORGE W. BRINDLEY LECTURE AWARD **Joseph W. Stucki**
13:35	TRANSITION FROM EXPANDABLE TO NON-EXPANDABLE CLAYS VIA NANOPOROUS MATERIALS **Prakash B. Malla**
14:30	INTRODUCTION OF AKIRA ONO, REPRESENTING THE CLAY SCIENCE SOCIETY OF JAPAN **Takeo Ebina**
14:35	STANDARDIZATION OF CLAY NANOPLATE MATERIALS FOR QUALITY ASSESSMENT AND CERTIFICATION **Akira Ono**, Takeo Ebina, Hajime Yoshida, and Tetsuji Itoh
15:30	BREAK

	Monday June 3			Tuesday June 4										
Time/ Room		Ballroom 1&2	Ballroom 3		Ballroom 1&2	Ballroom 3	CC 307	CC 308	CC 309	CC 310	Exec Din		Ballroom 1&2	Ball
8:00	Registration—Courtyard		Welcome Mixer in Courtyard	Registration— Ballroom Foyer	Coffee & Danish							Registration— Ballroom Foyer	Coffee & Danish	
8:30														
9:00						Kogure Plenary								Fer Ple
9:20														
9:40														
10:00			Opening Ceremony			Session 13	Session 18	Session 5	Session 8	Session 14				Ses 1
10:20														
10:40					Break								Break	
11:00			Srodon Plenary		Coffee & Danish	Session 13	Session 18	Session 5	Session 8	Session 14			Coffee & Danish	Ses 1
11:20														
11:40														
12:00		Lunch 12:00-1:30												
12:20													Hawaiian Buffet Lunch 12:20-2:00	
12:40					Box Lunch 12:40-2:00						PP & Sustainers 12:40-2:00			
13:00														
13:30			Malla Plenary											
13:50														
14:10							Sess. 18	Session 5	Session 8	Session 14				Ses 1
14:30			Ono Plenary			Session 13	Session 23							
14:50										Session 10				
15:10									Session 2					
15:30		Coffee & Danish	Poster Session											
15:50					Break								Break	
16:10					Coffee & Danish	Session 13	Session 23	Session 5	Session 2	Session 10			Coffee & Danish	Ses 1
16:30														
16:50														
17:10														
17:30														
17:40		Asian Clay Groups Council—CC-203E	CMS Council Meeting—Exec Din								CCM Editorial Board Meeting			
18:00														
18:20														
18:40														
19:00														
19:20														
19:40														
20:00														

Wednesday June 5					**Thursday June 6**							**Friday June 7**	
room 3	CC 307	CC 308	CC 309	CC 310		Ballroom 1&2	Ballroom 3	CC 307	CC 308	CC 309	CC 310		Time/ Room
					Registration— Ballroom Foyer	Coffee & Danish							8:00
												FIELD TRIP Sherman Laboratory, 1910 East-West Rd	8:30
rage nary							**CMS Business Meeting**						9:00
													9:20
													9:40
sion 17	**Session 15**	**Session 21**	**Session 16**	**Session 3**			**Session 17**	**Session 4**	**Session 11**	**Session 12**	**Session 6**		10:00
													10:20
						Break							10:40
sion 17	**Session 15**	**Sess. 21**	**Session 16**	**Session 3**		Coffee & Danish	**Session 17**	**Session 4**	**Session 11**	**Session 12**	**Session 6**		11:00
													11:20
		Session 20											11:40
													12:00
							Sess. 19	**Sess. 9**					12:20
						Hot Buffet Lunch 12:40-2:00							12:40
													13:00
													13:30
													13:50
sion 17	**Session 7**	**Session 20**	**Session 16**	**Session 1**			**Session 19**	**Session 9**	**Session 11**	**Session 12**	**Session 6**		14:10
													14:30
													14:50
		Session 22											15:10
													15:30
						Break							15:50
sion 17	**Session 7**	**Session 22**		**Sess. 1**		Coffee & Danish	**Session 19**	**Session 9**					16:10
													16:30
							Closing Ceremony						16:50
													17:10
													17:30
													17:40
													18:00
													18:20
													18:40
													19:00
													19:20
													19:40
													20:00

Session key on next page

Session Titles

1 Role of clays in contaminant fate and transport

2 Sediment transport mechanics, morphologic expressions, depositional patterns, and climate impacts of clay-rich dispersal systems

3 Natural hazards and clays: how determining/understanding their physicochemical properties can aid in modeling and mitigation efforts

4 New insights into the mechanisms of microbe-mineral interactions in geological processes

5 Mineral-organic matter interactions and their regulation of organic carbon stabilization in terrestrial and aquatic environments

6 Biogeochemical evolution of Fe and Mn (oxyhydr)oxide and their environmental impacts

7 Geochemical behaviors and mineralization of rare earth elements in near surface settings

8 Iron redox processes in clays and clay minerals

9 Honoring Dr. Goro Uehara and his work in variable charge clay systems in Hawai'i & beyond

10 Functional soft materials from clays and related compounds topics: colloids, nanocomposite gels and plastics, self-assembly, soft materials

11 Clay as nanomaterials: modification, functionalization, and application

12 Synthetic and natural clays for nanomedicine and nanocosmetics

13 Nanosized or nanostructured tubular and fibrous clay minerals for versatile functionalization and application.

14 Clay-related low dimensional nanoarchitectonics for enhanced electronical and optical properties

15 Clay minerals in building materials

16 Clays and clay minerals for carbon dioxide removal in negative emission technologies

17 Scientific and engineering aspects of clays in nuclear waste disposal

18 Electron microscopy on clay sciences—featuring a special session honoring Dr. Toshihiro Kogure

19 Molecular simulation of clay minerals and related phases

20 Investigation of phyllosilicates on mars through remote sensing, rover instruments, and analog studies

21 Characterization of phyllosilicates and their mineral assemblages in asteroids and meteorites

22 Remote identification of phyllosilicates for critical metals exploration and resource characterisation

23 General session

POSTER SESSION—AUTHORS PRESENT IN GATHER.TOWN

SESSION 1

15:30-17:30 LATERITIC ENVIRONMENTAL DUSTS CHARACTERIZATION AND QUANTIFICATION: IS MINING EXPLOITATION PROMOTING TRACE METAL-RICH DUST DISPERSION IN THE ENVIRONMENT? A CASE STUDY FROM EASTERN NEW CALEDONIA.

France Pattier, **Maximilien Mathian**, Peggy Gunkel-Grillon, Sylvie Russet, Kapeliele Gututauava, Mark Patrick Taylor, and Estelle Roth

15:30-17:30 REMOVAL OF EMERGING METALS USING CLAY/IRON-BIOCHAR COMPOSITES

Ming-Chih Huang and **Kai-Yue Chen**

15:30-17:30 CHROMIUM OXIDATION ON FERRIHYDRITE UNDER ATMOSPHERIC CONDITIONS WITH UV IRRADIATION: TRENDS AND MECHANISMS

Li-Pang Lin, Yu-Yu Kung, Yu-Ting Liu, and **Liang-Ching Hsu**

SESSION 2

15:30-17:30 RELATIONSHIP BETWEEN PARTICLE SIZE AND CHARACTERISTICS IN THE SEDIMENT COLLECTED FROM LAKE OKUTAMA, JAPAN

Toru Takahashi, Masanobu Shimizu, Hibiki Shirata, Taiga Kaseda, and Yuya Koike

15:30-17:30 CAN STRONTIUM AND NEODYMIUM ISOTOPES OF THE CLAY MINERAL-RICH COLD-SEEP CARBONATES BE A TRACE TO RECORD THE SOURCE OF THE COLD-SEEP FLUIDS?

J.Y. Cao, S.X. Yang, and J.X. Feng

SESSION 6

15:30-17:30 MOBILITY OF METALS IN TYPICAL ROCKS FROM ULTRAMAFIC SUBSTRATES IN NEW CALEDONIA

Chloé Dubernet, Aurélie Barats, Christophe Renac, Peggy Gunkel-Grillon, **Maximilien Mathian**, France Pattier, and Kapeliele Gututauava

SESSION 8

15:30-17:30 IRON REDOX PROCESSES IN CLAYS AND CLAY MINERALS

Hamida Diab

15:30-17:30 ADVANCING UNDERSTANDING OF BIOTITE WEATHERING REACTIONS: XAFS AND AB INITIO SIMULATION INSIGHTS

Akiko Yamaguchi, Yoshio Takahashi, and Masahiko Okumura

SESSION 9

15:30-17:30 EVALUATING ORIENTATION OF CLAY MINERALS BY POWDER X-RAY DIFFRACTOMETRY

Hibiki Shirata, Atsushi Ohbuchi, and Yuya Koike

SESSION 10

15:30-17:30 PARTICLE SIZE EVALUATION OF CLAY-DYE COLLOID BY MEANS OF TWO-PHOTON FLUORESCENCE CORRELATION SPECTROSCOPY

Katsuhiro Ishii, Yuya Minami, Yasutaka Suzuki, and Jun Kawamata

SESSION 11

15:30-17:30 ADHESION AND MICROMECHANICAL PROPERTIES OF NANOSTRUCTURAL LAYERED DOUBLE HYDROXIDE COATINGS DEVELOPED ON ZN ALLOY FOR SMART CORROSION PROTECTION

Sławomir Zimowski, Małgorzata Zimowska, Dzmitry Kharytonau, and Konrad Skowron

15:30-17:30 ESTABLISHMENT OF PEDOTRANSFER FUNCTIONS FOR SOIL ORGANIC CARBON SATURATION

C.H. Syu and **S.H. Jien**

15:30-17:30 INTERACTIONS OF AFLATOXIN B1 WITH BENTONITE—ADSORPTION AND CATALYTIC TRANSFORMATION

Yu-Min Tzou and Sheng-Yi Chen

15:30-17:30 STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATION OF MONTMORILLONITE MODIFIED WITH POLY(2-N-ALKYL-2-OXAZOLINE)S

Marek Pribus, **Luboš Jankovič**, Valéria Kureková, Martin Barlog, and Jana Madejová

15:30-17:30 STABLE DISPERSION METHOD OF K-TYPE MONTMORILLONITE

Shoji Morodome

SESSION 12

15:30-17:30 NANO-SPECIFIC AFFINITIES: SELECTIVE ADSORPTOIN OF DEOXYRIBONULEIC ACID STRANDS ON LAYERED DOUBLE HYDROXIDE NANOMATERIALS THROUGH DIMENSIONAL SIMILARITY

Xie Jing, Kyoung-Min Kim, Tae-il Kim, and Jae-Min Oh

15:30-17:30 ANTIBACTERIAL CAPACITIES OF REDUCED SMECTITE-ILLITE CLAY MINERALS

Dongyi Guo, Qiang Zeng, and Hailing Dong

15:30-17:30 INTRODUCTION OF DEFECT SITE IN LAYERED DOUBLE HYDROXIDE AND ITS MODIFIED MAGNETIC PROPERTY

Taeho Kim, Jing Xie, and **Jae-Min Oh**

15:30-17:30 FACTORS INFLUENCING THE GROWTH OF LAYERED DOUBLE HYDROXIDE LAYERS ON ZN ALLOY FOR SMART CORROSION PROTECTION

Małgorzata Zimowska, Dzmitry Kharytonau, Konrad Skowron, Grzegorz Mordarski, Sławomir Zimowski

15:30-17:30 HIGHLY ENHANCED BIOCOMPATIBILITY OF DEXAMETHASONE WITH CLAY-BASED DRUG DELIVERY SYSTEM

Sieun Park, Goeun Choi, and Jin-Ho Choy

15:30-17:30 HYDROTALCITE-NICLOSAMIDE NANOHYBRIDS AS AN ORAL FORMULATION FOR SARS-COV-2: A NOVEL THERAPEUTIC APPROACH

Sieun Park, N. Sanoj Rejinold, Seungjin Yu, Goeun Choi, and Jin-Ho Choy

15:30-17:30 PH-RESPONSIVE NICOTINIC ACID-LAYERED DOUBLE HYDROXIDE FOR CONTROLLED DRUG DELIVERY

Seungjin Yu, N. Sanoj Rejinold, Goeun Choi, and Jin-Ho Choy

15:30-17:30 NONIONIC POLYMER-COATED NICLOSAMIDE-MONTMORILLONITE HYBRIDS: A STRATEGY FOR ENHANCED BIOAVAILABILITY IN COVID-19 TREATMENT

Seungjin Yu, N. Sanoj Rejinold, Goeun Choi, and Jin-Ho Choy

SESSION 13

15:30-17:30 RESEARCH ON THE APPLICATION OF HALLOYSITE IN LOW CARBON-FOOTPRINT BUILDING MATERIALS: GEOPOLYMER AND LIMESTONE CALCINED CLAY CEMENT

Peng Yuan, Baifa Zhang, and Ting Yu

15:30-17:30 ENGINEERING DRUG-LOADED HALLOYSITE NANOTUBE AND ITS DRAWBACKS IN THE INTRACENOUS ADMINISTRATION ROUTE

Yi Zhang, Zongwang Huang, and Guangjian Tian

SESSION 14

15:30-17:30 EMISSION FROM HIGHER EXCITED STATE OF MONO-CATIONIC DYE ADSORBED ON SURFACE OF SAPONITE NANOSHEET

Takuya Fujimura, Masashi Sugahara, and Ryo Sasai

SESSION 16

15:30-17:30 EFFECTS OF BASALT APPLICATION AND THE MINERAL COMPOSITION ON SUGAR BEET GROWTH

Ayaka Wakao, Hiroshi Uchibayashi, Hayato Maruyama, Toshihiro Watanabe, Tsutomu Sato, **Atsushi Nakao**, and Takuro Shinano

SESSION 17

15:30-17:30 STABILIZING EFFECT OF RADIOACTIVE CESIUM IN INCINERATED FLY ASH AND SOIL MIXED GEOPOLYMER BY CLAY MINERALS

Rina Sekino, Atsushi Ohbuchi, and Yuya Koike

15:30-17:30 LARGE-SCALE MOLECULAR DYNAMICS SIMULATIONS OF CESIUM DIFFUSION IN SYSTEMS WITH CLAY PARTICLES AND WATER MOLECULES

Atsuki Hiraguchi, Xiaojin Zheng, Thomas R. Underwood, Keita Kobayashi, Akiko Yamaguchi, Mitsuhiro Itakura, Masahiko Machida, Ian C. Bourg, and Masahiko Okumura

15:30-17:30 THE INFLUENCE OF MINERALOGY AND ORGANIC MATTER CONTENT ON ACTINIDE SORPTION IN A CARBONATE DOMINATED REPOSITORY ENVIRONMENT

Keith D. Morrison, Gauthier Deblonde, Zachary Murphy, Harris Mason, Annie B. Kersting, Enrica Balboni, Ofra Klein-BenDavid, and Mavrik Zavarin

15:30-17:30 COMPREHENSIVE SIMULATION AND ASSESSMENT OF SWELLING BEHAVIOR IN KOREAN BENTONITE BUFFER BLOCKS ACROSS DIVERSE INITIAL DRY DENSITY CONDITIONS

Gyuhyun Go

SESSION 19

15:30-17:30 MACHINE LEARNING MOLECULAR DYNAMICS STUDY OF HYDRATED KAOLINITE UNDER HIGH PRESSURE

Keita Kobayashi, Akiko Yamaguchi, and Masahiko Okumura

15:30-17:30 MOLECULAR DYNAMICS STUDY OF STABILITY OF CS IN INTERLAYER SPACE

Marek Szczerba, Michał Skiba, and Mariola Kowalik-Hyla

15:30-17:30 MOLECULAR DYNAMICS STUDY OF ICE IN/ON KAOLINITE UNDER EXTREME CONDITIONS

Masahiko Okumura and Keita Kobayashi

SESSION 20

15:30-17:30 STRUCTURE DETERMINATION OF SMECTITE

Qi Tao, Chaogang Xing, Seungyeol Lee, Long Yang, Tianqi Zhang, Qingjin Zeng, Shangying Li, Guanglie Lv, Hongping He, and Sridhar Komarneni

15:30-17:30 LAVA-BAKED CHEMICAL WEATHERING OF PYROCLASTICS DEPOSITS IN TENGCHONG VOLCANIC FIELD, SOUTHWEST CHINA – IMPLICATIONS TO MARS EXPLORATION

Binlong Ye, Chang Huang, Qi Tao, and Joseph, R Michalski

SESSION 21

15:30-17:30 MICRO-FT-IR HYPERSPECTRAL SURFACE CHARACTERIZATION OF INDIVIDUAL RYUGU GRAINS: MATRIX COMPOSITION AND SPACE-WEATHERING EFFECTS

Stefano Rubino et al.

15:30-17:30 SPECTRAL VARIABILITY IN CM CHONDRITE MATRICES

William M. Lawrence and Bethany L. Ehlmann

15:30-17:30 MULTI-ANALYTICAL INVESTIGATIONS OF TWO RYUGU PARTICLES

M. Ferrari et al.

SESSION 23

15:30-17:30 CATALYTIC MECHANISM OF COBALT-CONTAINING LAYERED DOUBLE HYDROXIDES FOR CARBON NANOTUBE SYNTHESIS

Chida Chika, Kei Yokoyama, Kumagai Riku, Aisawa Sumio, Sang Jing, Hirahara Hidetoshi, Kimura Hiroe, and Don N. Futaba

15:30-17:30 INTERACTIONS OF SMECTITES WITH BITUMEN: RELEVANCE TO NON-AQUEOUS SOLVENT BITUMEN EXTRACTION

Marek Osacký, Yuqing Bai, Peter Uhlík, Martin Brček, and Pavol Hudec

15:30-17:30 THE ION-EXCHANGE MECHANISM OF HYDROBIOTITE AND THE BEHAVIOR OF IT'S INTERNAL WATER MOLECULES

Noriko Suzuki and Ayami Suzuki

15:30-17:30 LAYERED DOUBLE HYDROXIDES (LDH) PREPARED BY COPRECIPITATION METHOD WITH MICRO FLOW RATES OF RAW SOLUTIONS

Yoshikazu Kameshima, Itaru Ishihara, Yuya Sato, and Shunsuke Nishimoto

15:30-17:30 CHEMICAL COMPOSITION ANALYSIS OF WHITE AND CELADON CLAYS USING PORTABLE X-RAY FLUORESCENCE ANALYSIS: A COMPARATIVE STUDY OF CERAMICS EXCAVATED FROM HIRAIZUMI AND CHINA

Sumio Aisawa, Jing Sang, Hidetoshi Hirahara, and Daisuke Tokudome

15:30-17:30 CHARACTERIZATION OF KAOLINITE SOURCE CLAYS; COMPARISON OF JCSS-1101 (KANPAKU KAOLIN) WITH KGA-1B (GEORGIA KAOLIN)

Toshihiro Kogure and Kazuya Morimoto

15:30-17:30 REMOVAL PERFORMANCE OF ARSENATE AND ARSENITE ANIONS OF LAYERED DOUBLE HYDROXIDE

Ryo Sasai, Tomohiro Yoshisue, Kazuya Ujiie, Takashi Kojima, and Takuya Fujimura

15:30-17:30 EFFECTS OF PCO2 ON HYDROXYAPATITE FORMATION AND ITS SOLUBILITY

Yuji Arai, Shravani Kalita, and Ai Chen

15:30-17:30 FLUVIO-LACUSTRINE FORMATION OF NEW CALEDONIA: POST-DEPOSIT PROCESSES AND DYNAMICS OF TRACE METALLIC ELEMENTS

Jean-Baptiste Parmentier, **Maximilien Mathian**, France Pattier, Virginie Gaullier, Pierre Maurizot, Nicolas Tribovillard, Alain Zanella Cyril Marchand, and Peggy Gunkel-Grillon

ROOM CC-203E

17:40-20:00 ASIAN CLAY GROUPS COUNCIL MEETING

EXECUTIVE DINING ROOM

17:40-20:00 CMS COUNCIL MEETING

JUNE 4

8:00-12:00 COFFEE & DANISH—BALLROOM 1&2

PLENARY—BALLROOM 3

9:00 INTRODUCTION OF TOSHIHIRO KOGURE, REPICIENT OF THE PIONEER IN CLAY SCIENCE AWARD

Jinwook Kim

9:05 LAYER-STACKING VARIETY IN KAOLIN GROUP MINERALS OF SEVERAL ORIGINS

Toshihiro Kogure

SESSION 13 BREAKOUT—BALLROOM 3

Nanosized or nanostructured tubular and fibrous clay minerals for versatile functionalization and application

Peng Yuan, Pilar Aranda, Giuseppe Lazzara, Antoine Thill, Lala Setti Belaroui, Wei Yanfu, and Pooria Pasbakhsh

10:00 INVITED: DIAMETER AND CHIRALITY OF NATURAL AND SYNTHETIC IMOGOLITES

Pierre Picot, Frédéric Gobeaux, Thibault Charpentier, Luc Belloni, Atsushi Takahara, Shin-Ichiro Wada, and **Antoine Thill** **ORAL IN PERSON**

10:20 SEPIOLITE: A POWERFUL CLAY FILLER FOR THE ADVANCED MATERIALS

Barbara Di Credico, Massimiliano D'Arienzo, Silvia Mostoni, and Roberto Scotti **ORAL IN PERSON**

10:40 BREAK—BALLROOM 1&2

11:00 COMPOSITE MATERIALS BASED ON HALLOYSITE CLAY NANOTUBES: FROM MARINE WASTE TO ADVANCED FILMS AND GEOPOLYMERS

Martina Maria Calvino, Giuseppe Cavallaro, Stefana Milioto, Giuseppe Lazzara **ORAL REMOTE**

11:20 CLAY MINERALS MEET NATURAL PLANTS: VALUE CREATION FOR NATURAL RESOURCE UTILIZATION AND SUSTAINABLE DEVELOPMENT

Fangfang Yang, Yusheng Lu, Bin Mu, and Aiqin Wang **ORAL IN PERSON**

11:40 PALYGORSKITE-INDIGO INTERACTION OF MAYA BLUE PIGMENT

Guanzheng Zhuang, Li Li, Peng Yuan **ORAL IN PERSON**

12:00 INVITED: THE STABILITY, LOCAL BONDING AND ELECTRONIC PROPERTIES OF SINGLE-WALLED HNTS WITH THEIR INNER DIAMETER UPTO 20 NM

Liangjie Fu, Tianyu Liu, Beibei Shi, and Huaming Yang **ORAL IN PERSON**

12:20 INFLUENCE OF INDIGO-HYDROXYL INTERACTIONS ON THE PROPERTIES OF SEPIOLITE-BASED MAYA BLUE PIGMENT

Li Li, Guanzheng Zhuang, and Peng Yuan **ORAL REMOTE**

12:40 LUNCH—BALLROOM 1&2

12:40 PAST PRESIDENTS & SUSTAINERS LUNCHEON (BY INVITATION)—EXECUTIVE DINING ROOM

14:00 INVITED: HALLOYSITE CLAY NANOTUBES AS A MULTIFACETED MATERIAL FOR BIOLOGICALLY SELF-HEALING CONCRETE

Mohammad Fahimizadeh, Pooria Pasbakhsh, Joash B.L. Tan, Raman K.R. Singh, and Peng Yuan **ORAL REMOTE**

14:20 GEOPOLYMERIZATION OF ION-ADSORPTION TYPE RARE EARTH TAILINGS FOR HEAVY METALS IMMOBILIZATION AND ITS MECHANISM

Baifa Zhang, **Peng Yuan**, and Ting Yu **ORAL REMOTE**

14:40 INVITED: LIGNIN-SEPIOLITE BIONANOCOMPOSITE FOAMS: PREPARATION AND USE IN REMOVAL OF POLLUTANTS IN WATER

Brenda Azharel Jiménez-López, Raquel Martin-Sampedro, Roberto Leyva-Ramos, Margarita Darder, and **Pilar Aranda** **ORAL IN PERSON**

15:00 HALLOYSITE-BASED ADSORPTION MATERIAL WITH ULTRAHIGH LEAD ION ADSORPTION CAPACITY AND STABILITY

Liangjie Fu, Dikang Fan, Jie Zhang, Yuying Qu, Peiwen Ouyang, and Huaming Yang **ORAL REMOTE**

15:20 INVITED: ACTIVATION OF NANOSIZED CLAY MINERAL VIA CO-CALCINATION AND MAGNETITE VIA SUBSTITUTION FOR EFFICIENT PHOSPHATE ADSORPTION AND RECYCLING

Yanfu Wei, Peng Yuan, Zheng Li, and Honghai Wu **ORAL REMOTE**

15:40 BREAK—BALLROOM 1&2

16:00 PALYGORSKITE-SUPPORTED RUTHENIUM CATALYSTS FOR THE SELECTIVE OXIDATION OF 5-HYDROXYMETHYLFURFURAL TO 2, 5-DIFORMYLFURAN

Xuemin Zhong, Peng Yuan, Samahe Sadjadi, Dong Liu, and Yanfu Wei **ORAL REMOTE**

16:20 HALLOYSITE-BASED CATALYSTS: COMPUTATIONAL AND EXPERIMENTAL INVESTIGATIONS INTO BIOMASS CONVERSION

Ludovico Guercio, Marco Bertini, Francesco Ferrante, Lorenzo Lisuzzo, and Dario Duca **ORAL REMOTE**

16:40 INFLUENCE OF HALLOYSITE FROM DIFFERENT DEPOSITS ON ORGANIC MOLECULES DEGRADATION

C. Ferlito, L. Lisuzzo, G. Lazzara, Palumbo A. Piccionello, and S. Milioto **ORAL REMOTE**

17:00 CHARACTERIZATION OF SYNTHETIC IMOGOLITE AND GERMANIUM SUBSTITUTED IMOGOLITE BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Masashi Ookawa, Takuya Noaki, Hiroki Sugisawa, and Moe Yoshikawa **ORAL IN PERSON**

17:20 ION PAIRING OF CA2+, ZN2+, AND LA3+ TO ACETATE IN SILICA NANOPORE

Bidemi T. Fashina and Anastasia G. Ilgen **ORAL IN PERSON**

BREAKOUT SESSION 18—ROOM CC-307

Electron Microscopy on Clay Sciences – Featuring a Special Session Honoring Dr. Toshihiro Kogure

Ryosuke Kikuchi and Yuji Arai

10:00 CRYSTAL CHEMISTRY DURING SAPONITE GROWTH: A STUDY BASED ON FTIR AND HAADF-STEM ANALYSIS

Chaoqun Zhang, Alain Decarreau, Fabien Baron, Brian Gregoire, Jianxi Zhu, Hongping He, and Sabine Petit **ORAL IN PERSON**

10:20 ATOMIC RESOLUSION OBSERVATIONS FOR BEAM-SENSITIVE MINERAL SAMPLES USING LOW-DOSE SCANNING TRANSMISSION ELECTRON MICROSCOPY

Ichiro Ohnishi **ORAL IN PERSON**

10:40 BREAK—BALLROOM 1&2

11:00 TRANSMISSION ELECTRON MICROSCOPY STUDY OF SMECTITE-TO-ILLITE REACTION

Jinwook Kim **ORAL IN PERSON**

11:20 QUANTITATIVE ANALYSIS OF PETROGRAPHIC TEXTURES OF BENTONITE ORES BY IMAGE PROCESSING

Tobimaru Ishiwata, Ryosuke Kikuchi, Tsubasa Otake, and Tsutomu Sato **ORAL IN PERSON**

11:40 FORMATION MECHANISM OF FE-RICH CHLORITE FROM HYDROTHERMAL DEPOSIT IN JAPAN REVEALED BY HIGH RESOLUTION SCANNING TRANSMISSION ELECTRON MICROSCOPY

Sayako Inoué **ORAL IN PERSON**

12:00 NI-BEARING SMECTITE-SERPENTINE FROM THE TAGAUNG TAUNG NI-LATERITE DEPOSIT (MYANMAR): MINERALOGY AND NANOTEXTURES BY FIB-TEM

Ryosuke Kikuchi, Takahiro Daimon, Tsubasa Otake, and Tsutomu Sato **ORAL IN PERSON**

12:20 CHARACTERIZATION OF SUBMICRON-THICK LAYERED STRUCTURE IN HYDROGENETIC FERROMANGANESE NODULE

Junming Zhou, Toshihiro Kogure, Peng Yuan, and Shengxiong Yang **ORAL IN PERSON**

12:40 LUNCH—BALLROOM 1&2

12:40 PAST PRESIDENTS & SUSTAINERS LUNCHEON (BY INVITATION)—EXECUTIVE DINING ROOM

14:00 ABERRATION CORRECTED SCANNING TRANSMISSION ELECTRON MICROSCOPY AND THE NATURE OF NANOPARTICLE SURFACES

Kenneth JT Livi **ORAL REMOTE**

BREAKOUT SESSION 23—ROOM CC-307

General session

Yuji Arai and Joseph W. Stucki

14:20 THE PHYLLOSILICATE STRUCTURE: THE OCTAHEDRAL SHEET DIMENSION

Sabine Petit, Alain Decarreau, Brian Grégoire, and Eric Ferrage **ORAL-IN-PERSON**

14:40 SLOVAK BENTONITE DEPOSITS – A BRIEF OVERVIEW

Peter Uhlík, Jaroslav Lexa, Adrián Biroň, Faisal A. Gread, Jana Brčeková, Marek Osacký, and Peter Koděra **ORAL IN PERSON**

15:00 MEASURING ELECTRIC FIELD AND ELECTROSTATIC FORCES OF CLAY MINERALS: THE PRINCIPLES, METHODS, AND APPLICATIONS

Qinyi Li, Hang Li, and Xinmin Liu **ORAL IN PERSON**

15:20 STANDARDIZATION OF CLAY NANOPLATE PRODUCTS FOR BARRIER FILM APPLICATIONS

Takeo Ebina, Akira Ono, Hajime Yoshida, and Tetsuji Itoh **ORAL IN PERSON**

15:40 BREAK—BALLROOM 1&2

16:00 RANDOM FORESTS FOR PHASE SELECTION IN X-RAY POWDER DIFFRACTION ANALYSIS OF MINERAL MIXTURES

Barry R. Bickmore, Rachel E. Drapeau, and Emily J. Evans **ORAL IN PERSON**

16:20 ASSOCIATION RULES FOR IMPROVED QUANTITATIVE PHASE ANALYSIS

Emily J. Evans and Barry R. Bickmore **ORAL IN PERSON**

16:40 ATR-FTIR SPECTROSCOPY AS A COMPANION TECHNIQUE TO RANDOM-MOUNT XRPD FOR DETERMINING CLAY MINERAL IDENTITIES AND PROPERTIES

Aaron J. Chipman, Barry R. Bickmore, and Joshua LeMonte **ORAL IN PERSON**

17:00 STUDY OF TRANSMISSION ELECTRON MICROSCOPY OF ILLITE FROM YEONGDONG COUNTY, SOUTH KOREA: CANDIDATE FOR NEW ILLITE SOURCE CLAYS

Namgu Lee, Hanbeom Park, **Tae-hee Koo**, Kyungsoon Jung, Wansu Son, Hwa Jin Kim, Toshihiro Kogure, and Jinwook Kim **ORAL IN PERSON**

BREAKOUT SESSION 5—ROOM CC-308

Mineral-organic matter interactions and their regulation of organic carbon stabilization in terrestrial and aquatic environments

Mengqiang Zhu, Chunmei Chen, Hailiang Dong, Yuanzhi Tang, and Balwant Singh

10:00	STABILIZATION OF ORGANIC CARBON IN TOP- AND SUBSOIL BY BIOCHAR APPLICATION INTO CALCAREOUS FARMLAND **Yang Wang** and Jianying Shang **ORAL REMOTE**
10:20	THE ROLE OF EXTRACTABLE MINERALS ON MINERAL ASSOCIATED SOIL ORGANIC CARBON **Bright E. Amenkhienan** and Balwant Singh **ORAL IN PERSON**
10:40	BREAK—BALLROOM 1&2
11:00	ADSORPTION-DESORPTION OF DISSOLVED ORGANIC MATTER FROM DIFFERENT PLANT RESIDUES WITH DIFFERENT CLAY MINERALS **Zongtang Yang**, Feike A. Dijkstra, Georg Guggenberger, and Balwant Singh **ORAL IN PERSON**
11:20	MINERAL CATIONS MEDIATE FOREST SOC STORAGE IN RESPONSE TO N ADDITION THROUGH PLANT-ORGANO-MINERAL INTERACTIONS **Xu Xia**, Xu Chonghua, A. Zhejiang, and F. University **ORAL REMOTE**
11:40	MINERAL-OM INTERACTIONS AT THE MOLECULAR LEVEL: SELECTED KNOWLEDGE GAPS **Markus Kleber** **ORAL IN PERSON**
12:00	THE ORIENTATION OF GLYCEROL INTERCALATED IN SMECTITE AS A FUNCTION OF HUMIDITY **Stanislav Jelavić**, Bruno Lanson, and Marek Szczerba **ORAL IN PERSON**
12:20	APPARENT SATURATION OF SOIL MINERAL-ASSOCIATED ORGANIC CARBON IN THE UNITED STATES Ryan E. Champiny, Katerina Georgiou, and **Yang Lin** **ORAL IN PERSON**
12:40	LUNCH—BALLROOM 1&2
12:40	PAST PRESIDENTS & SUSTAINERS LUNCHEON (BY INVITATION)—EXECUTIVE DINING ROOM
14:00	MINERALOGICAL CONTROLS ON CLIMATE AND OXYGENATION **Caroline L. Peacock**, Lisa Curti, Oliver W. Moore, Ke-Qing Xiao, Peyman Babakhani, Mingyu Zhao, and Clare Woulds **ORAL REMOTE**
14:20	SUBSTANTIAL AMOUNTS OF REACTIVE FE AND FE-ASSOCIATED ORGANIC CARBON IN COASTAL WETLAND SOILS AT GLOBAL SCALES **Chunmei Chen** and Hua Ma **ORAL REMOTE**
14:40	CONTROLS OF MINERAL SOLUBILITY ON ADSORPTION-INDUCED MOLECULAR FRACTIONATION OF DISSOLVED ORGANIC MATTER REVEALED BY 21 T FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY **Zhen Hu**, Amy M. McKenna, K. Wen, Bingjun Zhang, Hairuo Mao, Lamia Goual, Xionghan Feng, and Mengqiang Zhu **ORAL REMOTE**

15:00 NANO- AND SUB-NANO SCALE INVESTIGATION ON ORGANIC CARBON DISTRIBUTION IN SOIL MINERALS

Zhenqing Shi **ORAL REMOTE**

15:20 MINERAL-ORGANIC ASSOCIATIONS INFLUENCE THE CAPACITY AND VULNERABILITY OF SOIL CARBON STORAGE

Katerina Georgiou **ORAL REMOTE**

15:40 BREAK—BALLROOM 1&2

16:00 INCREASE OF HUMIC ACID BIOAVAILABILITY BY HYDROXYL RADICALS PRODUCED UPON OXYGENATION OF FE(II) IN REDUCED NONTRONITE

Qiang Zeng and Hailiang Dong **ORAL REMOTE**

16:20 IMPORTANCE OF INNER-SPHERE P-O-FE BONDS IN MINERAL-ORGANIC ASSOCIATIONS OF A CREEK SEDIMENT

Karin Eusterhues, Jürgen Thieme, Andreas Haidl, Heinrich Tost, Lars Lühl, Philipp Hönicke, Thomas Wilhein, Birgit Kanngießer, and Kai Uwe Totsche **ORAL REMOTE**

16:40 ASSESSING THE EFFECT OF MINERALS ON THE OXIDATION OF ORGANIC MATTER BY FENTON CHEMISTRY

Aleksandar I. Goranov, Susan J. Carter, Ann Pearson, and Patrick G. Hatcher **ORAL REMOTE**

17:00 INTERACTION BETWEEN PHENOLIC CONTAMINANTS AND DISSOLVED ORGANIC MATTER DURING OXIDATION BY MANGANESE OXIDES

Matthew Ginder-Vogel, Christina K. Remucal, and Jenna T. Swenson **ORAL REMOTE**

17:20 PHOTOCHEMICAL ALTERATIONS OF FE-ORGANIC MATTER COPRECIPITATES PROMOTED THE ORGANIC MATTER PRESERVATION OR DEGRADATION: ROLE OF ORGANIC MATTER FUNCTIONAL GROUPS

Dawei Cai, **Yandi Hu**, and Suona Zhang **ORAL IN PERSON**

BREAKOUT SESSION 8—ROOM CC-309

Iron Redox Processes in Clays and Clay Minerals

Joseph W. Stucki and Anke Neumann

10:00 REDOX PROCESSES OF CLAY MINERAL-BOUND IRON

Anke Neumann **ORAL REMOTE**

10:20 INVITED: MULTI-SCALE ELECTRON TRANSFER PROCESSES ASSOCIATED WITH FE-BEARING CLAY MINERALS

Songhu Yuan, Ao Qian, Wenjuan Liao, Xixiang Liu, and Yanting Zhang **ORAL IN PERSON**

10:40 BREAK—BALLROOM 1&2

11:00 INVITED: MOLECULAR H2 GENERATION VIA OXIDATIVE DEHYDROGENATION IN FE(II)-PHYLLOSILICATES AND THEIR H ISOTOPE SIGNATURE

Arkadiusz Derkowski **ORAL IN PERSON**

11:20 THE CRITICAL ROLE OF MINERAL FE(IV) FORMATION IN LOW HYDROXYL RADICAL YIELDS DURING FE(II)-BEARING CLAY MINERAL OXYGENATION

Chenglong Yu, Wenwen Ji, and Shengyan Pu **ORAL IN PERSON**

11:40 FORMATION OF FE- AND MG-RICH 1:1 PHYLLOSILICATES: INFLUENCE OF PH

Alexandra Jourdain, Patrick Dutournié, Laure Michelin, Jean-Marc Le Meins, Amira Doggaz, Sayako Inoué, Mustapha Abdelmoula, Jocelyne Brendlé, Nicolas Michau, Christelle Martin, and **Liva Dzene** **ORAL IN PERSON**

12:00 MICROBE AND MINERAL INTERACTION DURING FREEZE-THAW CYCLES

Jinwook Kim, Young Kyu Park, Tae-hee Koo, Jaewoo Jung, Hanbeom Park, Kitae Kim, Kyu-Cheul Yoo, Brad E. Rosenheim, and Tim M. Conway **ORAL IN PERSON**

12:20 MICROBIAL REDUCTION OF FE(III) IN NONTRONITE: ROLE OF BIOCHAR AS A REDOX MEDIATOR

Hailiang Dong, Ethan S. Coffin, and Yizhi Sheng **ORAL IN PERSON**

12:40 LUNCH—BALLROOM 1&2

12:40 PAST PRESIDENTS & SUSTAINERS LUNCHEON (BY INVITATION)—EXECUTIVE DINING ROOM

14:00 FORMATION OF MIXED STRUCTURES OF 2:1 TYPE PHYLLOSILICATES AND LEPIDOCROCITE (Γ-FEOOH) IN PADDY SOIL

Toshihiro Kogure, Satoh Sakura, Yoshio Takahashi, Yoko Masuda, and Keishi Senoo **ORAL IN PERSON**

14:20 FE(II)-PILLARED MONTMORILLONITE

Joseph W. Stucki, Martin P. Pentrak, and Linda A. Pentrak **ORAL IN PERSON**

BREAKOUT SESSION 2—ROOM CC-309

Sediment transport mechanics, morphologic expressions, depositional patterns, and climate impacts of clay-rich dispersal systems

Judy Yang, Hongbo Ma, and Ian Bourg

15:00 QUANTITATIVE X-RAY DIFFRACTION ANALYSIS OF CLAY MINERALS IN MINING APPLICATIONS

Rong Fan, Mark D. Raven, Nathan A.S Webster, Nicholas D. Owen, Peter G Self, Rodrigo Gomez-Camacho, and Shu Huang **ORAL IN PERSON**

15:20 PEDOGENIC-WEATHERING EVOLUTION AND SOIL DISCRIMINATION BY SENSOR FUSION COMBINED WITH MACHINE-LEARNING-BASED SPECTRAL MODELING

Lulu Zhao, Hanlie Hong, and Qian Fang **ORAL IN PERSON**

15:40 BREAK—BALLROOM 1&2

16:00 IMPACT OF SALINITY ON THE EROSION THRESHOLD, YIELD STRESS, AND GELATINOUS STATE OF A COHESIVE CLAY

Jorge San Juan, Guanju Wei, and **Judy Yang** **ORAL IN PERSON**

16:20 DIFFERENCES IN TRANSPORT REGIMES BETWEEN SILT-RICH BEDDED AND SAND-BEDDED RIVER SYSTEMS

Hongbo Ma **ORAL IN PERSON**

16:40 DO MICROBES SHAPE LANDSCAPES? BIOPOLYMERS, CLAYS, AND CRUSTS IN MARS ANALOG ENVIRONMENTS

Natalie A. Jones, Kayla P. Blair, Embrey G. Saville, Keven S. Griffin, Elizabeth B. Rampe, Lauren A. Edgar, Kristen A. Bennett, Christopher S. Edwards, and Alicia M. Rutledge **ORAL IN PERSON**

17:00 MICROPLASTIC PARTICLES IN CLAY-SAND SEDIMENT MIXTURES: UNVEILING THEIR CONTRIBUTION TO EROSION

M. Ponce, S. Wieprecht, and S. Haun **ORAL IN PERSON**

BREAKOUT SESSION 14—ROOM CC-310

Clay-related low dimensional nanoarchitectonics for enhanced electronical and optical properties

Yusuke Ide, Miharu Eguchi, and Yusuke Yamauchi

10:00 END-TO-END PIERCED CARBON NANOSHEETS WITH MESO-HOLES DERIVED FROM MONTMORILLONITE CLAY

Minjun Kim, Miharu Eguchi, and Yusuke Yamauchi **ORAL IN PERSON**

10:20 SAPONITE CLAY NANOSHEETS FOR PROTEIN ADSORPTION

Yusuf Valentino Kaneti, Ping Cheng, Yusuke Yamauchi, and Miharu Eguchi **ORAL REMOTE**

10:40 BREAK—BALLROOM 1&2

11:00 CORRELATION BETWEEN SYNTHETIC TEMPERATURE AND CATION-EXCHANGE PROPERTY OF A LAYERED LITHIUM POTASSIUM TITANATE

Kanji Saito, Shuhei Yamagauchi, Makoto Ogawa, Masataka Ogasawara, and Sumio Kato **ORAL REMOTE**

11:20 FORMATION OF MOTH-EYE-LIKE STRUCTURES ON SILICON THROUGH IN SITU CRYSTALLIZATION OF HECTORITE-LIKE LAYERED SILICATE

Nakauchi Yuki and **Tomohiko Okada** **ORAL IN PERSON**

11:40 2D-TO-1D CONVERSION OF LAYERED TITANATES

Esraa Moustafa, Mohamed Esmat, Rafat Tahawy, and **Yusuke Ide** **ORAL IN PERSON**

12:00 LAYERED INORGANIC–ORGANIC COVALENLY BONDED HYBRID/RU-BASED METALLO-SUPRAMOLECULAR POLYMER COMPOSITE FOR IMPROVED ELECTROCHROMIC PROPERTIES

Kazuko Fujii, Dines C. Santra, Manas K. Bera, Takatsugu Wakahara, Ritsuko Nagahata, and Masayoshi Higuchi **ORAL IN PERSON**

12:20 MXENES VS. CLAY MINERALS: 2D SOLIDS FOR THE DEVELOPMENT OF HYBRID MATERIALS AND NANOCOMPOSITES

Eduardo Ruiz-Hitzky, Cristina Ruiz-García, and Xiaoying Wang **ORAL IN PERSON**

12:40 LUNCH—BALLROOM 1&2

12:40 PAST PRESIDENTS & SUSTAINERS LUNCHEON (BY INVITATION)—EXECUTIVE DINING ROOM

14:00 CATALYST DESIGN USING LAYERED SILICATES HUSs

Tsunoji Nao and Sadakane Masahiro **ORAL REMOTE**

14:20 STABILIZATION OF IRON OXO OLIGOMERS IN SMECTITE CLAY-DERIVED SILICA GELS

Hamza El-Hosainy and Yusuke Ide **ORAL REMOTE**

BREAKOUT SESSION 10—ROOM CC-310

Functional soft materials from clays and related compounds Topics: Colloids, Nanocomposite gels and plastics, Self-assembly, Soft materials

Nobuyoshi Miyamoto, Yasutaka Suzuki, and Fengxia Geng

14:40 CONTROL OF ADSORPTION REACTION OF AN ORGANIC COMPOUND TO SMECTITE BY OPTICAL MANIPULATION TECHNIQUE

Yasutaka Suzuki, Takumi Harada, Masahiro Yahara, Seiji Tani, and Jun Kawamata **ORAL IN PERSON**

15:00 INVITED: OPTICAL MANIPULATION AND MICROSCOPE OBSERVATION OF DELAMINATED CLAY LAYERS DISPERSED IN WATER

Jun Kawamata, Takumi Harada, Mahito Shintaku, Toshiaki Iwai, and Yasutaka Suzuki **ORAL IN PERSON**

15:20 DYNAMIC SELF-ASSEMBLY OF MONODISPERSE NANOSHEETS

Nobuyoshi Miyamoto, Naoya Nonaka, Hiroyuki Iwano, Matsuo Takumi, Yasushi Okumura, and Hirotsugu Kikuchi **ORAL IN PERSON**

15:40 BREAK—BALLROOM 1&2

16:00 SPECTROSCOPIC BEHAVIOR OF AN ANIONIC PORPHYRIN INFLUENCED BY COLLOIDAL CLAY PARTICLES

Teruyuki Nakato, Rio Sonoyama, and Emiko Mouri **ORAL IN PERSON**

16:20 INVITED: UV PROTECTIVE CLAY FILM WITH TUNABLE GAS/MOISTURE TRANSPARENCY CONSISTING OF LIGNIN, A PLANT AROMATIC POLYMER

Kazuhiro Shikinaka and Yuichiro Otsuka **ORAL REMOTE**

16:40 IONIC CONDUCTIVITY OF ION DEFECT INTRODUCED LAYERED DOUBLE HYDROXIDE

Noriyuki Sonoyama, Hirohito Kasuya, Syunsuke Uchimura, and Genki Yamaguchi **ORAL REMOTE**

17:40 CCM EDITORIAL BOARD MEETING—EXECUTIVE DINING ROOM

JUNE 5

8:00-12:00 COFFEE & DANISH—BALLROOM 1&2

PLENARY— BALLROOM 3

9:00 INTRODUCTION OF ERIC FERRAGE, RECIPIENT OF THE MARION L. AND CHRYSTIE M. JACKSON MID-CAREER CLAY SCIENTIST AWARD

Sabine Petit

9:05 WATER AT CLAY INTERFACES: STRUCTURE, DYNAMICS, AND UPSCALING STRATEGIES

Eric Ferrage

BREAKOUT SESSION 17—BALLROOM 3

Scientific and engineering aspects of clays in nuclear waste disposal

Jeffery Greathouse, Patricia Fox, Tsutomu Sato, Satoru Suzuki, and Cristophe Tournassat

10:00 MICROSTRUCTURAL EVOLUTION OF BINARY BENTONITE BARRIERS DURING SATURATION

M. Victoria Villar, Rubén J. Iglesias, Carlos Gutiérrez-Álvarez, Elena Real, and Luis Gutiérrez-Nebot **ORAL REMOTE**

10:20 PHYSICAL DEFORMATION OF ROCHESTER SHALE AND OPALINUS CLAY—IMPACTS ON ISOTOPIC SIGNATURES OF CLAY MINERALS

Horst Zwingmann, Alfons Berger, Andrew Todd, Niwa Masakazu, and Meinert Rahn **ORAL IN PERSON**

10:40 BREAK—BALLROOM 1&2

11:00 PHYSICAL ADSORPTION OF OH- IONS CAUSES CHARGING AT MINERAL-WATER INTERFACE

Xiandong Liu **ORAL REMOTE**

11:20 EXPERIMENTAL DETERMINATION OF PR(III) SORPTION ONTO SAPONITE AND CA-RICH MONTMORILLONITE TO 70°C

Yongliang Xiong, Yifeng Wang, and Vanessa Mercado **ORAL IN PERSON**

11:40 EFFECT OF CS+ ON TRANSFORMATION OF SMECTITE TO ILLITE (ILLITIZATION)

Amanda C. Sanchez, Melissa M. Mills, Lydia Boisvert, Clay B. Payne, Tuan A. Ho, and Yifeng Wang **ORAL IN PERSON**

12:00 ADSORPTION OF IODINE ANIONS BY CHRYSOTILE AND HALLOYSITE: THE EFFECT OF NANOPORE STRUCTURE

Wenbin Yu, Quan Wan, and Zonghua Qin **ORAL IN PERSON**

12:20 CONFERENCE BANQUET LUNCH—BALLROOM 1&2

14:00 IRON/BENTONITE INTERACTION—WHAT CAN WE LEARN FROM EUDIOMETER TESTS?

Stephan Kaufhold **ORAL IN PERSON**

14:20 RESEARCH STATUS ON DEVELOPMENT OF HIGH-PERFORMANCE BENTONITE BUFFER MATERIALS

Seok Yoon, Gi-Jun Lee, Deuk-Hwan Lee, Min-Hyung Lee, and Seeun Chang **ORAL IN PERSON**

14:40 BENCH-SCALE COLUMN TESTS ON BENTONITE BUFFER AND COUPLED THMC PROCESSES FOR GEOLOGIC DISPOSAL OF HIGH-LEVEL RADIOACTIVE WASTE

Chun Chang, Sharon Borglin, Chunwei Chou, Liange Zheng, Yuxin Wu, Timothy J. Kneafsey, Seiji Nakagawa, Toshiyuki Bandai, and Jens T Birkholzer **ORAL IN PERSON**

15:00 EVALUATION OF NOVEL MATERIALS FOR ANIONIC SORPTION

Jessica Kruichak-Duhigg, Nelson Bell, Jeffery Greathouse, Philippe Weck, Ben Juba, Mark Rodriguez, Edward Matteo, and Yifeng Wang **ORAL IN PERSON**

15:40 BREAK—BALLROOM 1&2

16:00 CHEMICAL AND HYDRATION TIME CONTROLS ON MICROSTRUCTURE AND SWELLING PRESSURE OF COMPACTED MONTMORILLONITE

Wenming Dong, Carl I. Steefel, Christophe Tournassat, Ayumi Koishi, Michael Whittaker, Benjamin Gilbert, Chenhui Zhu, Yunfei Wang, Stéphane Gaboreau, and Liange Zheng **ORAL IN PERSON**

16:20 SWELLING PRESSURE BEHAVIOR OF COMPACTED BENTONITE UPON WETTING WITH VARIOUS SALINE SOLUTIONS

Marcelo Sanchez, Roa'a Al-Masri, Camilo Sanchez, Jeffery Greathouse, Youjun Deng, and Leonardo Guimaraes **ORAL IN PERSON**

16:40 EFFECT OF PORE FLUIDS, EXCHANGEABLE CATION, AND TEMPERATURE ON THE SWELLING PROPERTIES OF BENTONITE

Camilo Sanchez-Avellaneda, Roa'a Al-Masri Jeffery Greathouse, Edward Matteo, Youjun Deng, and Marcelo Sanchez **ORAL IN PERSON**

17:00 FULL PORE SIZE DISTRIBUTION OF SHALE BY COMBINATION OF INNOVATIVE GAS ADSORPTION ISOTHERMS, MERCURY INTRUSION POROSIMETRY AND LABORATORY NANO-X RAY TOMOGRAPHY

D. Pret, Evarist S. Rogers, A. Mazurier, M. Faivre, and R. Giot **ORAL IN PERSON**

17:20 STUDY THE EVOLUTION OF BENTONITE BUFFER UNDER HIGH TEMPERATURE HEATING USING LARGE SCALE FIELD TEST AND THE CORRESPONDING MODELING

Liange Zheng and Radhavi A. Samarakoon **ORAL REMOTE**

BREAKOUT SESSION 15—ROOM CC-307

Clay minerals in building materials

Ana Guerrero, Yunfei Xi, and Pilar Aranda

10:00 STRENGTH IMPROVEMENT OF STEEL-SLAG DREDGED SOIL MIXTURES BY SOIL ORGANIC MATTER REMOVAL WITH CALCINATION

Kanako Toda, Takumi Saito, Yuzo Akashi, and Tsutomu Sato **ORAL IN PERSON**

10:20 EXPLORING THE USE OF MICA IN TRIBOELECTRIC NANOGENERATORS FOR BUILDING APPLICATIONS

David Jiménez-Merino, Maxim Ivanov, Harvey Amorín, Bernd Wicklein, and **Pilar Aranda**
ORAL IN PERSON

10:40 BREAK—BALLROOM 1&2

11:00 LIGHTWEIGHT GYPSUM BOARD WITH CLAY MINERAL AND GLASS FIBRE ADDITION TO ENHANCE FIRE RESISTANCE

Sen Wang, Mahen Mahendran, and Yunfei Xi **ORAL REMOTE**

11:20 CRITICAL EFFECTS OF KAOLINITE/ILLITE ON COMPRESSIVE STRENGTH OF FIRED BRICKS

Sen Wang, Lloyd Gainey, and **Yunfei Xi** **ORAL IN PERSON**

11:40 LOW EMBODIED CARBON CEMENT BLENDS FROM AUSTRALIAN CLAY MINERAL RESOURCES

Will P. Gates, Prateek Sharma, Rehman Munib Ul, Oluwatosin Babatola, Alastair J.N. MacLeod, Chathuranga Gallage, Laurie P. Aldridge, and Frank Collins **ORAL REMOTE**

12:20 CONFERENCE BANQUET LUNCH—BALLROOM 1&2

BREAKOUT SESSION 7—ROOM CC-307

Geochemical behaviors and mineralization of rare earth elements in near surface settings

Hongping He, W. Crawford Elliott, Yoshio Takahashi, Yuanzhi Tang, and Xiaoliang Liang

14:00 ENRICHMENT AND FRACTIONATION OF RARE EARTH ELEMENTS (REES) IN ION-ADSORPTION-TYPE REE DEPOSITS: CONSTRAINTS OF AN IRON (HYDR) OXIDE-CLAY MINERAL COMPOSITE

Puqiu Wu and **Xiaoliang Liang** **ORAL IN PERSON**

14:20 EVALUATION OF CLAYS AND CLAY-RICH SEDIMENTS IN THE SOUTHEASTERN UNITED STATES AS POTENTIAL RARE EARTH ELEMENT LITHIUM FEEDSTOCK MATERIALS

Ibrahim G. Okunlola and Rona J. Donahoe **ORAL IN PERSON**

14:40 ADSORPTION OF RARE EARTH ELEMENTS ON DISTINCT PLANES OF KAOLINITE

Gaofeng Wang, Lingyu Ran, Xiaoliang Liang, Jianxi Zhu, and Hongping He **ORAL IN PERSON**

15:00 REE DISTRIBUTION IN GNEISSIC REGOLITHS OF THE SOUTH CAROLINA PIEDMONT: EVIDENCE FOR CERIUM AND EUROPIUM REDOX MOBILITY IN THE CRITICAL ZONE

Paul A. Schroeder **ORAL IN PERSON**

15:20 RARE EARTH ELEMENTS IN THE GEORGIA KAOLIN DEPOSITS

W. Crawford Elliott, Yuanzhi Tang, Joell Ashcraft, Prakash Malla, and Ed Riley **ORAL IN PERSON**

15:40 BREAK—BALLROOM 1&2

16:00 EFFECTS OF PHOSPHATE ON RARE EARTH ELEMENT (REE) UPTAKE BY KAOLINITE

Hang Xu, Johannes Leisen, Alicia Robang, Anant Paravastu, Yinghao Wen, and **Yuanzhi Tang**
ORAL IN PERSON

16:20 CRITICAL MINERALS IN COLD-CLIMATE CLAYS: REGOLITH-HOSTED RARE EARTH ELEMENTS IN POLAR DESERT BASINS (DRY VALLEYS, ANTARCTICA)

Zachary F. M. Burton, Janice L. Bishop, Christian Koeberl, Peter A.J. Englert, Andrew B. Foerder, and Everett K. Gibson **ORAL REMOTE**

BREAKOUT SESSION 21—ROOM CC-308

Characterization of Phyllosilicates and Their Mineral Assemblages in Asteroids and Meteorites

Marco Ferrari, Toru Yada, Damien Loizeau, Slavka Andrejkovicová, and Janice Bishop

10:00 IMPORTANCE OF INFRARED SPECTROSCOPY ON SAMPLES RETURNED FROM EXTRATERRESTRIAL BODIES AS THEIR INITIAL DESCRIPTIONS

T. Yada et al. **ORAL IN PERSON**

10:20 MULTI-TECHNIQUE STUDY OF THE COEVOLUTION OF PHYLLOSILICATE, CARBON, SULFIDE, AND APATITE IN RYUGU'S PARENT BODY

Gerardo Dominguez et al. **ORAL IN PERSON**

10:40 BREAK—BALLROOM 1&2

11:00 CHARACTERIZATION OF NH4+-SMECTITES TO SUPPORT THEIR DETECTION ON CERES AND OTHER BODIES

Janice L. Bishop, Slavka Andrejkovičová, Alessandro Maturilli, Kierra Wilk, Helena Pálková, and Fernando Rocha **ORAL IN PERSON**

BREAKOUT SESSION 20—ROOM CC-308

Investigation of Phyllosilicates on Mars through Remote Sensing, Rover Instruments, and Analog Studies.

Janice Bishop and Joseph Michalski

11:40 HYDROLYSIS PRODUCTS OF FE(III)-SI SYSTEMS WITH DIFFERENT SI/(SI+FE) MOLAR RATIOS: IMPLICATIONS TO DETECTION OF FERRIHYDRITE ON MARS

Peixin Du, Xinyi Xiang, Binlong Ye, Hongling Bu, Dong Liu, Jiacheng Liu, Jian Hua, and Xiaolong Guo **ORAL IN PERSON**

12:00 SEARCH FOR POSSIBLE AMMONIUM-SMECTITES, IMPLICATIONS FROM CURIOSITY ROVER ON MARS

Slavka Andrejkovičová, Amy McAdam, Jennifer Stern, Christine Knudson, Maëva Millan, Fernando Rocha, and Paul Mahaffy **ORAL IN PERSON**

12:20 CONFERENCE BANQUET LUNCH—BALLROOM 1&2

14:00 ALTERATION OF SUBAERIAL VOLCANICLASTICS COMPRISING BASALTIC LITHICS AND DACITIC ASH IN SUBAQUEOUS ENVIRONMENTS IN THE SOUTHERN WASHINGTON STATE

Rui-Lin Cheng, Joseph R. Michalski, and Martin Jutzeler **ORAL IN PERSON**

14:20 MARS LABORATORY ANALOG SEDIMENT FLOWS: INVESTIGATING THE EFFECTS OF PRESSURE AND WATER-ROCK RATIO

Sharissa Y. Thompson, Frances Rivera-Hernández, Jacob B. Adler, Matthew E. Sylvest, Petr Brož, and Manish Patel **ORAL IN PERSON**

14:40 COMPLEX PHYLLOSILICATE - SULFATE ASSEMBLAGES AT MAWRTH VALLIS AS INDICATORS OF THE ANCIENT CLIMATE ON MARS

Janice L. Bishop, Mario Parente, Arun M. Saranathan, Christoph Gross, Yuki Itoh, and Megan E. Elwood Madden **ORAL IN PERSON**

BREAKOUT SESSION 22—ROOM CC-308

Remote Identification of Phyllosilicates for Critical Metals Exploration and Resource Characterization.

Carsten Laukamp, Ian Lau, Rui Wang, and Janice Bishop

15:00 PRELIMINARY RESULTS OF USING NEAR-INFRARED SPECTROSCOPY FOR SMECTITE QUANTIFICATION IN NATURAL MIXTURE

Faisal A. Gread, Peter Uhlík, and Ángel Santamaría-López **ORAL IN PERSON**

15:20 GEOSCIENCE FEATURE-GUIDED BAND MATH APPROACH FOR EMIT AND ENMAP HYPERSPECTRAL SATELLITE IMAGERY

A. Jo Miles, Carsten Laukamp, Heta Lampinen, and Ian Lau **ORAL IN PERSON**

15:40 BREAK—BALLROOM 1&2

16:00 USING AIRBORNE AND ORBITAL IMAGING SPECTROSCOPY TO DIFFERENTIATE LITHIUM BEARING HECTORITE FROM SPECTRALLY SIMILAR PHYLLOSILICATES AND CARBONATES

John M. Meyer, Gregg A. Swayze, Raymond F. Kokaly, Lisa L. Stillings, Todd M. Hoefen, and Evan Cox **ORAL IN PERSON**

16:20 REGIONAL-SCALE MAPPING OF PHYLLOSILICATES USING THE NEW GENERATION OF VNIR-SWIR HYPERSPECTRAL SATELLITE SENSORS

Carsten Laukamp, Ian C. Lau, Heta M. Lampinen, M. Williams, and Fang Huang **ORAL IN PERSON**

16:40 DISCUSSION

BREAKOUT SESSION 16—ROOM CC-309

Clays and clay minerals for carbon dioxide removal in negative emission technologies

Tsutomu Sato, Takao Nakagaki, Yuji Arai, and Corey Myers

10:00 NANO-CONFINEMENT EFFECT ON H2 AND CO2 CLUSTER FORMATION

Tuan A. Ho and Aditya Choudhary **ORAL IN PERSON**

10:20 EFFICIENCY AND FACTORS AFFECTING BASE PROPERTIES OF SMECTITE-DERIVED POROUS COMPOSITES

Małgorzata Zimowska, Michał Śliwa, Helena Pálková, Jacek Gurgul, Robert P. Socha, Piotr Niemiec, and Eva Scholtzova **ORAL IN PERSON**

10:40 BREAK—BALLROOM 1&2

11:00 THE VITAL ROLE OF CLAYS DURING GEOLOGIC CARBON SEQUESTRATION IN BASALT RESERVOIRS

Nabajit Lahiri, Quin R.S. Miller, Emily T. Nienhuis, and H. Todd Schaef **ORAL IN PERSON**

11:20 CLAY-MEDIATED RAPID CARBON MINERALIZATION DYNAMICS IN BASALTS: INSIGHTS FROM WALLULA PILOT PROJECT

Tianxiao Shen, Shaina A. Kelly, Quin R.S. Miller, Nabajit Lahiri, Olivia Terry, and H. Todd Schaef **ORAL IN PERSON**

11:40 CONSTRAINING THE ROLE OF AUTHIGENIC MAGNESIUM RICH CLAYS ON CARBONATE PRECIPITATION IN ALKALINE LACUSTRINE ENVIRONMENTS

Maria L. Arizaleta, Maija J. Raudsepp, Nina Zeyen, Janice Kenney, and Sasha Wilson **ORAL IN PERSON**

12:00 MG CARBONATE HYDRATE FORMATION IN ENHANCED WEATHERING EXPERIMENTS USING MGO

Yuto Nishiki, Masao Sorai, and Naoki Nishiyama **ORAL IN PERSON**

12:20 CONFERENCE BANQUET LUNCH—BALLROOM 1&2

14:00 PREDICTION METHOD FOR QUANTIFICATION OF CO2 MINERALIZATION BY GAS-SOLID CONTACTOR USED AS INDUSTRIAL ENHANCED ROCK WEATHERING

Takao Nakagaki and Yudai Takase **ORAL REMOTE**

14:20 APPLICATION OF ENHANCED ROCK WEATHERING IN ACID MINE DRAINAGE WITH ITS PASSIVE TREATMENT

Htut San Hkaung, Nono Kimotsuki, Naito Yamashita, Fugo Nakamura, Frances Chikanda, Ryosuke Kikuchi, Yoko Ohtomo, Tsubasa Otake, and Tsutomu Sato **ORAL REMOTE**

14:40 APPLICABILITY OF STEELMAKING SLAGS IN CARBON DIOXIDE REMOVAL FROM ATMOSPHERE BY THEIR ENHANCED WEATHERING

Nono Kimotsuki, Naito Yamashita, Htut San Hkaung, Ryosuke Kikuchi, Yoko Ohtomo, Tsubasa Otake, and Tsutomo Sato **ORAL IN PERSON**

15:00 THE IMPACT OF ONE YEAR BASALT POWDER APPLICATION ON SOYBEAN GROWTH AND SOIL CARBON IN A FIELD IN HOKKAIDO, JAPAN

Hiroshi Uchibayashi, Ayaka Wakao, Yilin Yang, Gen Kosaka, Yan Zhu, Mona Hironaka, Yo Toma, Shoichiro Hamamoto, Tsutomu Sato, Atsushi Nakao, Hayato Maruyama, Toshihiro Watanabe, and Takuro Shinano **ORAL IN PERSON**

15:20 BASIC STUDY ON ANION EXCHANGE PROPERTIES AND ALGAE GROWTH OF POROUS CONCRETE CONTAINING LAYERED DOUBLE HYDROXIDES IN SEAWATER

Satoko Tezuka, Rinako Shimada, and Minami Aikyo **ORAL IN PERSON**

BREAKOUT SESSION 3—ROOM CC-310

Natural Hazards and Clays: How determining/understanding their physicochemical properties can aid in modeling and mitigation efforts

Hiroshi Sakuma and Diane Moore

10:00 INVITED: ROLES OF CLAY MINERALS IN SEISMOGENESIS IN SHALLOW SUBDUCTION ZONES INVESTIGATED BY LABORATORY FRICTION EXPERIMENTS

Hanaya Okuda **ORAL IN PERSON**

10:20 INVITED: NATURAL AND EXPERIMENTAL SEISMIC SLIP ON CLAY GOUGE: IN THE CASE OF THE TAIWAN CHELUNGPU FAULT DRILLING PROJECT

Li-Wei Kuo, Thi Trinh Nguyen, Szu-Ting Kuo, Wen-Jie Wu, and Hsiu-Ching Hsiao **ORAL IN PERSON**

10:40 BREAK—BALLROOM 1&2

11:00 TEMPERATURE DEPENDENT FRICTIONAL PROPERTIES OF SINGLE-CRYSTAL MUSCOVITE

Hiroshi Sakuma, Diane Moore, David Lockner, and Toshihiro Kogure **ORAL IN PERSON**

11:20 MINERALOGY AND PHYSICAL PROPERTIES OF CORE FROM SERPENTINITE MUD VOLCANOES, NORTHERN MARIANA SUBDUCTION ZONE

Diane E. Moore, Carolyn A. Morrow, David A. Lockner, and Barbara A. Bekins **ORAL IN PERSON**

12:20 CONFERENCE BANQUET LUNCH—BALLROOM 1&2

BREAKOUT SESSION 1—ROOM CC-310

Role of Clays in Contaminant Fate and Transport

Marcus Flury, Jianying Shang, Maximilien Mathian, and Yingxue Yu

14:00 IMPACT OF COUPLED PHYSICAL AND CHEMICAL HETEROGENEITY ON COLLOIDAL TRANSPORT IN UNSATURATED POROUS MEDIA

Jianying Shang and Kang Zhao **ORAL REMOTE**

14:20 A MODEL TO PREDICT THE INFLUENCE OF PHYSICOCHEMICAL CONDITIONS ON COLLOID TRANSPORT AND RETENTION IN POROUS MEDIA

Scott A. Bradford **ORAL IN PERSON**

14:40 THE ROLE OF THE AIR-WATER INTERFACE ON COLLOID TRANSPORT IN THE VADOSE ZONE

Markus Flury **ORAL IN PERSON**

15:00 AGGREGATION KINETICS AND STABILITY OF BIODEGRADABLE NANOPLASTICS: EFFECTS OF WEATHERING AND PROTEINS

Yingxue Yu and Markus Flury **ORAL IN PERSON**

15:20 THE ROLES OF •OH AND MINERAL FE(IV) FOR PHENOL DEGRADATION DURING FE(II)-BEARING CLAY MINERAL OXYGENATION

Shengyan Pu, Chenglong Yu, and Wenwen Ji **ORAL IN PERSON**

15:40 BREAK—BALLROOM 1&2

16:00 FATE AND TRANSPORT OF VIRAL PATHOGENS THROUGH CLAYS
Himanshu Yadav, Deepa Mehta, **Tadikonda Venkata Bharat**, and Sachin Kumar **ORAL IN PERSON**

JUNE 6

8:00-9:00 COFFEE & DANISH—BALLROOM 1&2

BALLROOM 3

9:00 CMS BUSINESS MEETING

BREAKOUT SESSION 17—BALLROOM 3

Scientific and engineering aspects of clays in nuclear waste disposal

Jeffery Greathouse, Patricia Fox, Tsutomu Sato, Satoru Suzuki, and Cristophe Tournassat

10:00 SWELLING CLAYS AND THE NUCLEAR 137-CS THREAT
Michal Skiba, Sylwester Smoleń, Katarzyna Maj-Szeliga, Marek Szczerba, and Ryosuke Kikuchi **ORAL IN PERSON**

10:20 TEMPERATURE EFFECTS ON URANIUM ADSORPTION TO MONTMORILLONITE
Jasmine K. Rattanpal, Ben Urick, Christophe Tournassat, and Ruth M. Tinnacher **ORAL IN PERSON**

10:40 BREAK—BALLROOM 1&2

11:00 THE ROLE OF MINERAL IMPURITIES FOR THE ADSORPTION OF URANIUM(VI) ONTO BENTONITE
Ruth M. Tinnacher, LaQuynh Diem, Kanishka Fnu, Patricia M. Fox, Edward Pizzini, Marlena Rock, Kirsten Sauer, Florie Caporuscio, and Christoph Tournassat **ORAL IN PERSON**

11:20 STUDY OF MICROBIAL VIABILITY IN KUNIGEL V1Å BENTONITE AND IMPACT ON THE METAL CORROSION
Satoru Suzuki, Takahiro Goto, Toru Nagaoka, Shin-ichi Hirano, and Yoshito Kitagawa **ORAL IN PERSON**

11:40 TRACKING SUBTLE MINERALOGICAL CHANGES IN THE BUFFER MATERIALS TO MODEL THEIR LONG-TERM ALTERATIONS IN NUCLEAR WASTE REPOSITORIES
Arkadiusz Derkowski and The ClayLab Team **ORAL IN PERSON**

12:00 THERMO-HYDRO-MECHANICAL BEHAVIOR OF A CLAY-PELLETS MIXTURE INTENDED FOR BARRIER SYSTEMS
Abdulvahi Sahin and **Marcel Sanchez** **ORAL IN PERSON**

BREAKOUT SESSION 19—BALLROOM 3

Molecular Simulation of Clay Minerals and Related Phases

Ian C. Bourg, Kideok D. Kwon, and Christophe Tournassat

12:20	DISJOINING PRESSURE IN ADSORBED WATER FILMS ON SMECTITE CLAY PARTICLES Xiaochan Li and **Ian C. Bourg** **ORAL IN PERSON**
12:40	LUNCH—BALLROOM 1&2
14:00	QUANTIFYING THERMO-OSMOTIC FLOW MECHANISMS IN NA-MONTMORILLONITE NANOPORES USING MOLECULAR DYNAMICS SIMULATIONS **Jackson C. Stewart** **ORAL IN PERSON**
14:20	INTERLAYER WATER STRUCTURES AND FRICTIONAL PROPERTIES OF SUPER-HYDRATED KAOLINITE AND TALC **Juhyeok Kim** and Kideok D, Kwon **ORAL IN PERSON**
14:40	EFFECT OF LAYER BENDING ON MONTMORILLONITE HYDRATION AND STRUCTURE FROM MOLECULAR SIMULATION **Jeffery A. Greathouse**, Tuan A. Ho, and Carlos F. Jové-Colón **ORAL IN PERSON**
15:00	CHARGING THE MINERAL/WATER INTERFACE: MOLECULAR DYNAMICS SIMULATIONS OF THE ELECTRIC DOUBLE LAYER UNDER APPLIED ELECTRIC FIELDS **Thomas R. Underwood**, Sebastien N. Kerisit, and Kevin M. Rosso **ORAL IN PERSON**
15:20	ANGLING FOR A NEW (CLAY-)MINERAL FORCEFIELD **Michael Holmboe** **ORAL IN PERSON**
15:40	BREAK—BALLROOM 1&2
16:00	MOLECULAR DYNAMICS STUDY ON NANOCRYSTALLINE VERNADITE STRUCTURE **Gerica Joie P. Castro** and Kideok D. Kwon **ORAL REMOTE**
16:20	FACET-DEPENDENT DISPERSION AND AGGREGATION OF AQUEOUS HEMATITE NANOPARTICLES Jianbin Zhou, Duo Song, Sebastian T. Mergelsberg, Yining Wang, Narendra M. Adhikari, Nabajit Lahiri, Yatong Zhao, Ping Chen, Zheming Wang, Xin Zhang, **Kevin M. Rosso** **ORAL IN PERSON**

16:40-18:00 CLOSING CEREMONY

BREAKOUT SESSION 4—ROOM CC-307

New insights into the mechanisms of microbe-mineral interactions in geological processes

Jinwook Kim, Eric Roden, Juan Liu, and Tae-hee Koo

10:00 MANGANESE NANOCLUSTERS IN ROCK VARNISH ANALOGOUS TO PHOTOSYNTHETIC OXYGEN-EVOLVING COMPLEXES

Qian Fang, Yan Li, Anhuai Lu **ORAL IN PERSON**

10:20 MICROBIAL COMMUNITY STRUCTURE AND FUNCTIONAL POTENTIALS IN THE QUATERNARY AS-BEARING CLAY LAYERS AT JIANGHAN PLAIN, CHINA

Zhou Jiang, Dandan Song, and **Liang Shi** **ORAL IN PERSON**

10:40 BREAK—BALLROOM 1&2

11:00 MICROBIAL FE-REDUCTION IN NONTRONITE AT 4 °C: EVIDENCE OF PSYCHROPHILIC REDUCTIVE DISSOLUTION OF FE

Tae-hee Koo and Jinwook Kim **ORAL IN PERSON**

11:20 INVESTIGATION OF MICROBIALLY MEDIATED TRANSFORMATION OF FE-RICH SMECTITE TO ILLITE

Jessica Kruichak-Duhigg, Amanda Sanchez, Carlos Lopez, George Bachand, and Yifeng Wang **ORAL IN PERSON**

11:40 SYNERGY OF SEMICONDUCTING MINERALS AND ELECTROACTIVE BACTERIA IN ELEMENT CYCLING AND ENERGY CONVERSION

Juan Liu, Chao Zhong, and Yongheng Jiang **ORAL REMOTE**

12:00 EFFECT OF FE(III)-CONTAINING CLAY MINERALS ON THE METABOLIC ACTIVITY OF METHANOGENS

Shanshan Yang and Deng Liu **ORAL REMOTE**

BREAKOUT SESSION 9—ROOM CC-307

Honoring Dr. Goro Uehara and his work in variable charge clay systems in Hawai'i & beyond

Jonathan L. Deenik, Susan E. Crow, Tai McClellan Maaz, Luiz F. Pires, , and Kristy I. Lam

12:20 DR. GORO UEHARA: FROM CLAY MINERALS TO GLOBAL SOLUTIONS

Jonathan L. Deenik **ORAL IN PERSON**

12:40 LUNCH—BALLROOM 1&2

14:00 X-RAY COMPUTED TOMOGRAPHY FOR SOIL PORE CHARACTERIZATION

Luiz F. Pires, Fabio A.M. Cássaro, A.M. Brinatti, Sergio C. Saab **ORAL REMOTE**

14:20 MINERALOGICAL AND MANAGEMENT EFFECTS ON SOIL PORE SIZE DISTRIBUTION OF AN ALLOPHANIC ANDISOL AND HALLOYSITIC MOLLISOL

Kristy I. Lam, Luiz F. Pires, Jonathan L. Deenik, Sayed Bateni, and Yinphan Tsang **ORAL IN PERSON**

14:40 SOIL MINERAL AND CHEMICAL GRADIENTS STRUCTURE MICROBIAL COMMUNITIES IN AN HAWAIIAN VOLCANIC ASH SOIL ACROSS DEPTH AND SPACE

Tai McClellan Maaz, Casey McGrath, Christian Fullmer, Caitlin Pries Hicks, Susan Crow, and Nhu Nguyen **ORAL IN PERSON**

15:00 FROM VOLCANIC ASH TO ABUNDANT EARTH: UNDERSTANDING ANDISOL ORGANIC MATTER DYNAMICS AND SOIL HEALTH IN TWO MINERALOGICALLY DISTINCT MOISTURE REGIMES ON HAWAI'I ISLAND

Tanner B. Beckstrom, Tai M. Maaz, Jonathan L. Deenik, Hayley Peter-Contesse, Amy Koch, Christine Tallamy Glazer, Johanie Rivera-Zayas, and Susan E. Crow **ORAL IN PERSON**

15:20 MODELING PEDOGENIC THRESHOLD OCCURRENCE IN HAWAIIAN VOLCANIC SOILS ACROSS A CHRONOSEQUENCE FROM ~5 KY TO ~4 MY OLD

Thomas P. Haensel and Noa K. Lincoln **ORAL IN PERSON**

15:40 BREAK—BALLROOM 1&2

16:00 WHAT IS ISOTIC ANYWAY? A SOIL TAXONOMY MINERALOGY CLASS REVISITED

Ryan C. Hodges, Dylan E. Beaudette, and Joey N. Shaw **ORAL REMOTE**

16:20 DIGGING DEEP: AGGREGATE STABILITY ACROSS SOIL DEPTHS IN A FERRIHYDRITIC ANDISOL

Christian Fullmer, Susan E. Crow, Jonathan Deenik, Tai Maaz, and Nhu H. Nguyen **ORAL IN PERSON**

BREAKOUT SESSION 11—ROOM CC-308

Clay as nanomaterials: modification, functionalization, and application

Chunhui Zhou, Runliang Zhu, Xiaofeng Guo, Yu-Ting Liu, and Hongping He

10:00 REVERSE EXCHANGE OF FELDSPATHOIDS FORMED IN CARBONATE-RICH ALKALINE SOLUTION

Chiawei Lin, Markus Graefe, Julie A. Howe, and Youjun Deng **ORAL IN PERSON**

10:20 CHARACTERIZATION OF SMECTITE-CLAY POLYMER HYBRIDS BY DENSITY FUNCTIONAL THEORY METHOD

Sanam Bashir, Daniel Tunega, and **Eva Scholtzová** **ORAL IN PERSON**

10:40 BREAK—BALLROOM 1&2

11:00 EFFECT OF ORGANIC ACID LEACHING ON THE STRUCTURE OF MIXED-DIMENSIONAL ATTAPULGITE CLAY

Yushen Lu, Bin Mu,Yuru Kang, Qin Wang, and Aiqin Wang **ORAL IN PERSON**

11:20 EFFECTIVENESS OF NANOMATERIALS AND THEIR COUNTERPARTS IN IMPROVING RICE GROWTH AND YIELD UNDER ARSENIC CONTAMINATION

Fugen Dou, Xiufen Li, Xiaoxuan Wang, Xingmao Ma, Wenjie Sun, and Kun Chen **ORAL IN PERSON**

11:40 ENHANCING PHOSPHORUS FERTILIZATION EFFICIENCY AND SOIL ORGANIC CARBON SEQUESTRATION WITH MG-FE LAYERED DOUBLE HYDROXIDES

Yu-Ting Liu, Wen-Hui Li, Liang-Ching Hsu, and Han-Yu Chen **ORAL IN PERSON**

12:00 HYBRID LDHS ADVANCING FOOD SECURITY AND CLIMATE ACTION THROUGH SLOW-RELEASE FERTILIZATION AND CARBON CAPTURE

Wen-Hui Li **ORAL IN PERSON**

12:20 HYBRID MATERIALS PREPARED BY INTERCALATION OF ALKYL-AMMONIUM AND -PHOSPHONIUM SURFACTANTS INTO MONTMORILLONITE

Jana Madejová, Martin Barlog, Michal Slaný, Helena Pálková, and Ľuboš Jankovič **ORAL IN PERSON**

12:40 LUNCH—BALLROOM 1&2

14:00 INFRARED SPECTROSCOPIC DETECTION OF LUMINOPHORE COMPONENTS IN ORGANOCLAY PIGMENTS

Helena Pálková, Martin Barlog, and Juraj Bujdák **ORAL IN PERSON**

14:20 NANOSILICON DERIVED FROM CLAY MINERALS AS HIGH PERFORMANCE LITHIUM-ION BATTERY ANODE

Runliang Zhu, Qingze Chen, Jing Du, Jieyang Xie, and Hongping He **ORAL IN PERSON**

14:40 UPTAKE BEHAVIOR OF TWO HEAVY METALS AND AN DIMETHYLATED POLYCYCLIC AROMATIC HYDROCARBON ON RAW AND ALUMINUM PILLARED QUICK CLAYS

Alexandre Coulombe, Youssouf Djibril Soubaneh, Émilien Pelletier, Zhe Lu, and Jean-Sébastien L'Heureux **ORAL IN PERSON**

BREAKOUT SESSION 12—ROOM CC-309

Synthetic and Natural Clays for Nanomedicine and Nanocosmetics

Jae-Min Oh, Goeun Choi, Keith Morrison, and Youjun Deng

10:00 NATURAL TO SYNTHETIC: HOW ANTIBACTERIAL CLAYS CAN HELP FIGHT ANTIBIOTIC RESISTANCE

Keith D. Morrison, Meghan B. Reiss, Tanya D. Tanner, and Travis R. Gollott **ORAL IN PERSON**

10:20 STRUCTURAL FACTORS IN DETERMINING THE EFFICIENCY OF NATURAL AND SYNTHETIC CLAYS IN BINDING BIOLOGICAL TOXINS

Youjun Deng **ORAL IN PERSON**

10:40 BREAK—BALLROOM 1&2

11:00 CLAYS FOR COMBINED PELOTHERAPY AND ELECTROTHERAPY

Fernando Rocha and Carla Bastos **ORAL IN PERSON**

11:20 CLAYS AND ZEOLITES AS ROBUST FRAMEWORK FOR PHOTODYNAMIC REACTION: BIOLOGICAL APPLICATIONS OF LIGHT SENSITIZING MATERIALS

Jae-Min Oh and **Kang-Kyun Wang** **ORAL IN PERSON**

11:40 BORON NEUTRON CAPTURE THERAPY ASSISTED BY CLAY-BASED DRUG DELIVERY SYSTEM

Goeun Choi **ORAL IN PERSON**

12:00 CONTROLLED MOLECULAR ARRANGEMENT OF CINNAMIC ACID IN LAYERED DOUBLE HYDROXIDE THROUGH PI-PI INTERACTION FOR CONTROLLED RELEASE

Taeho Kim, Jaeseong Kim, Kang-Kyun Wang, and **Jae-Min Oh** **ORAL IN PERSON**

12:20 THERANOSTIC ANIONIC CLAYS THROUGH TOPOTACTIC LATTICE ENGINEERING AND DRUG INTERCALATION

Jae-Min Oh **ORAL IN PERSON**

12:40 LUNCH—BALLROOM 1&2

14:00 CONCENTRATED COLLOIDAL NANOCRYSTALS OF METAL HYDROXIDES FOR BIOMEDICAL CONTRASTING AGENTS

Yasuaki Tokudome, Yosuke Ando, Katsuki Yoneda, Hidenobu Murata, and Atsushi Nakahira **ORAL IN PERSON**

14:20 INSIGHTS INTO THE BONDING MECHANISMS OF PYOCYANIN AND MONTMORILLONITE

Bidemi T. Fashina and Youjun Deng **ORAL IN PERSON**

14:40 EFFECT OF MONO-AND POLYSACCHARIDE ON PYOCYANIN ADSORPTION BY SMECTITE AND SEPIOLITE

Wasek Foysal and Youjun Deng **ORAL IN PERSON**

BREAKOUT SESSION 6—ROOM CC-310

Biogeochemical evolution of Fe and Mn (oxyhydr)oxide and their environmental impacts

Tongxu Liu, Xionghan Feng, Zimeng Wang, and Wei Li

10:00 ADSORPTION MECHANISMS OF GLYPHOSATE ON FERRIHYDRITE: EFFECTS OF AL SUBSTITUTION AND AGGREGATION STATE

Xiaoming Wang, Xuewen Li, Xionghan Feng, and Wenfeng Tan **ORAL REMOTE**

10:20 EVALUATION THE REMOVAL OF GLYPHOSATE BY TWO DIFFERENT COLLOIDAL MNO2

Caixiang Zhang, Ruihan Xiong, Shuxin Huang, and Bin Liu **ORAL IN PERSON**

10:40 BREAK—BALLROOM 1&2

11:00 MINERAL SURFACE-CATALYZED FORMATION OF MN OXIDES ON MARS

Ke Wen and Mengqiang Zhu **ORAL IN PERSON**

11:20 AUTHIGENIC TITANIA ALTERED FROM VOLCANIC GLASSES IN MODERN DEEP OCEAN: IMPLICATION FOR TI MIGRATION DURING DIAGENETIC PROCESSES

Jing Liu and Junming Zhou **ORAL IN PERSON**

11:40 A NOVEL USE OF ZINC ISOTOPE AS AN ATOMIC TRACER TO REVEAL MOLECULAR-LEVEL INSIGHT INTO ZINC SORPTION MECHANISM ON CALCITE

Yiren Duan, Hongtao He, and Wei Li **ORAL REMOTE**

12:00 HEMATITE-MEDIATED MN(II) ABIOTIC OXIDATION UNDER OXIC CONDITIONS: EFFECTS OF PH AND MODEL QUINONE COMPOUND

Shiwen Hu, Tongxu Liu, and Chongxuan Liu **ORAL IN PERSON**

12:20 INVITED: COPRECIPITATION OF CR(III)/FE(III) HYDROXIDE IN SOLUTION AND ON MINERAL/ORGANIC SURFACES

Yandi Hu ORAL IN PERSON

12:40 LUNCH—BALLROOM 1&2

14:00 POST-OBDUCTION HISTORY OF NEW CALEDONIA: NEW TEMPORAL CONSTRAINTS FROM GOETHITE (U-TH)/HE DATING OF DURICRUSTS IN REWORKED LATERITES

Maximilien Mathian, Martin Danišík, France Pattier, Pierre Maurizot, Jean-Baptiste Parmentier, Ludovic Delbes, Dominique Cluzel, Rosella Pina-Jamme, Willy Foulcher, Benoit Baptiste, Frédérique Haurine, Cécile Gautheron ORAL IN PERSON

14:20 INVESTIGATING NATURAL MINERAL TRANSFORMATION PROCESS USING ELECTROCHEMICAL METHODS AND IN SITU CHARACTERIZATIONS

Haesung Jung, Martial Taillefert, Lufeng Yang, **Hailong Chen**, and Tang Yuanzhi ORAL IN PERSON

14:40 CARBONATE-ENHANCED TRANSFORMATION OF FERRIHYDRITE TO HEMATITE IN ALKALINE MEDIA

Ying Li and Arai Yuji ORAL IN PERSON

15:00 THE EFFECT OF CRITIC ACID ON THE CATALYTIC OXIDATION OF MN(II) ON FERRIHYDRITE

Xionghan Feng, Feng Zhang, Yanting Pan, Xiaoming Wang, Hui Yin, Zimeng Wang, and Wenfeng Tan ORAL REMOTE

15:20 MOLECULAR COMPOSITION OF OGRANIC MATTER IN AN OXISOL DOES ALTER WITH LAND USE CHANGE

Balwant Singh, **Zongtang Yang**, and Tsutomu Ohno ORAL IN PERSON

BALLROOM 3

16:40-18:00 CLOSING CEREMONY

JUNE 7

8:30 DEPART FOR FIELD TRIP—SHERMAN LABORATORY
(1910 EAST-WEST RD, HONOLULU, HI 96822)

16:30 RETURN FROM FIELD TRIP—SHERMAN LABORATORY
(1910 EAST-WEST RD, HONOLULU, HI 96822)

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Abstracts

Plenary Sessions

WATER AT CLAY INTERFACES: STRUCTURE, DYNAMICS, AND UPSCALING STRATEGIES

Eric Ferrage

Institut de Chimie des Milieux et Matériaux de Poitiers, IC2MP-Hydrasa, UMR 7285 CNRS, France

The interaction of water with clay interfaces is a topic of permanent interest in the field of environmental sciences, given its influence on a multitude of processes, including the water cycle, swelling and shrinkage of soils, and the migration of pollutants. Among the various types of clay minerals, those that exhibit swelling properties are particularly noteworthy due to their extensive surface area in contact with the surrounding environment and the large quantity of adsorbed water in the form of a single monolayer of water molecules. For illustrative purposes, the quantity of water associated with the hydration of swelling clays in the upper 2 kilometers of the Earth's crust is estimated to be approximately ten times that of all the lakes on the Earth's surface or twice the total quantity of drinking water.

The structural and dynamical properties of adsorbed water at the surface of clay minerals, situated halfway between those of liquid water and ice-like water, represent a particularly challenging area of research. These characteristics have attracted significant attention since the pioneering studies of the swelling clays conducted in the 1930s and has largely beneficiated from the development of numerical simulations and their coupling with experiments. In addition, the question of the upscaling of water properties (molecular to decimeter) in the mechanistic description of the parameters controlling macroscopic diffusion processes is particularly important. The preferential orientation of lamellar clay particles indeed leads to wide variability in the geometry and connectivity of the pore network. At these scales, recent progress has been made in calculating transfer properties from 2D/3D models of virtual clay porous media or from imaging techniques.

This presentation will focus on the progress made in understanding the structural and dynamic properties of adsorbed water, and how these properties can be incorporated in the prediction of macroscopic water transfer.

BACK TO PROGRAM

LAYER-STACKING VARIETY IN KAOLIN GROUP MINERALS OF SEVERAL ORIGINS

Kogure, Toshihiro

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Kaolin group minerals, represented by kaolinite, are typical clay minerals along with illite and smectite, and important mineral resources formed under various geological conditions around the Earth's surface. Their structure is well known as a dioctahedral 2:1 type phyllosilicate, and unlike mica or smectite, they exhibit very limited compositional variety. However, their powder X-ray diffraction (PXRD) patterns display various aspects, reflecting the complex layer-stacking structure or stacking disorder. Unlike the stacking variety of micas, which occurs only through mutual layer rotation of $n60°$ ($n = 0$ to 5), the layer-stacking of kaolinite is mainly faulted by changes in the vacant-site positions within the octahedral layer, which can be approximated as layer rotation, and the selection of three directions of interlayer displacement, making its analysis even more complex. Conventional analysis using PXRD has focused on explaining the profile of so-called 01,11 bands to identify the defect structure types and their frequencies. For example, in a given kaolinite sample, models with stacking disorder generated mainly by the two kinds of interlayer displacements ($\boldsymbol{t}_1$ and $\boldsymbol{t}_2$), and the coexistence of two kinds of particles with few defects and with many defects have been suggested to explain the band profiles.

In contrast, the author has conducted research on the layer-stacking structures of kaolin group minerals primarily through direct observation of atomic arrangements using HRTEM (high-resolution transmission electron microscopy). Generally, due to intense electron damage compared to micas, it was considered difficult to record high-quality HRTEM images that would reveal the true nature of stacking disorder. However, we have revealed for the first time in 2005, from HRTEM images of kaolinite/dickite of diagenetic origin, that no stacking disorder was observed in the coexisting dickite, while stacking disorder in kaolinite occurred due to two types of interlayer displacements ($\boldsymbol{t}_1$ and $\boldsymbol{t}_2$). Subsequently, we used HRTEM to investigate the defect structures of kaolin group minerals of different origins. However, due to severe electron damage, image recordings for sufficient number of particles were not achieved, and the analysis of kaolinite stacking structures by HRTEM was only glimpsed in part. However, recent improvements in the performance of imaging cameras for HRTEM are gradually overcoming this challenging situation.

In this presentation, I would like to review our previous analyses of layer-stacking structures in kaolin group minerals, centered around HRTEM, and report my recent findings. In particular, I would like to introduce what has been revealed through high-resolution observations of highly-crystalline samples (Keokuku and diagenetic origin), samples of hydrothermal origin, CMS source samples (KGa-1b, KGa-2), etc.

BACK TO PROGRAM

STANDARDIZATION OF CLAY NANOPLATE MATERIALS FOR QUALITY ASSESSMENT AND CERTIFICATION

Ono, Akira *[1], Ebina, Takeo [2], Yoshida, Hajime [1] and Itoh, Tetsuji [2]

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Clay nanoplate material, distinguished by their unique shape and properties, is an advanced nanomaterial with extensive potential applications across various industries. Ensuring the successful market acceptance of these materials requires a reliable assessment of their overall quality, with testing standards playing a pivotal role. Considering the promising application of these materials in gas barrier technology, a dedicated standard, ISO 21346-2:2021, specifies the characteristics to be measured and measurement methods to be adopted for comprehensively assessing the quality of clay nanoplate materials. This presentation provides an update on the standardization of clay nanoplate materials for quality evaluation and assurance, addressing testing laboratory designation for reliable measurement data and material certification for ensuring the quality.

In accordance with testing standards, manufacturers of clay nanoplate materials report their characteristic values to users. Throughout the processes, testing laboratories play a crucial role in determining reliable characteristic values for the materials, necessitating sufficient capability in relevant techniques. This led to the establishment of a testing laboratory designation system, enabling material manufacturers to identify proficient testing laboratories. The Nanomaterial Standardization and Certification Committee (hereafter referred to as the Committee), one of the AIST Consortia, has played the role of a designating body and provided guidelines for the designation. In the designation processes, the measurement capability declared by testing laboratories is examined by the Committee. The capability is reviewed from a technical viewpoint of the uncertainties in measurement results of characteristics. The Committee initiated the designation process in 2023, designating two testing laboratories as of 2024.

The Committee is currently developing a certification system for clay nanoplate materials. According to the system, material manufacturers will declare the quality of their commercial models of clay nanoplate materials, specifically showing the characteristic values with their tolerance in conformity with the ISO testing standards. The certification system requires that the characteristic values are measured by the designated testing laboratories. The Committee examines the declaration from technical viewpoints of the testing standards and the designation of testing laboratories, as well as an administrative point of the quality management system. The confidence of clay nanoplate materials in the market transactions is enhanced step-by-step through the stages of establishing testing standards, designating testing laboratories, and certifying commercial material models.

BACK TO PROGRAM

ROLE OF ILLITE IN THE GLOBAL CYCLING OF ELEMENTS

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Illite was discovered in 1937, simultaneously in the US and in Hungary (under the name sarospatakite). It is the second (after quartz) most abundant mineral of sedimentary rocks and the most abundant mineral of mudstones. This abundance is related to its relative stability during weathering and at elevated temperatures: during diagenesis other dioctahedral clays turn into illite, while unweathered part of detrital illite becomes recycled. Above 300-350^{o}C (epizone) illite recrystallizes into mica (phengite). Due to its abundance and structure characteristics, illite is a major player in the global cycling of water, potassium, nitrogen, boron, rubidium and cesium.

In subduction zones, illite carries into the mantle 50% more water than chlorite, which is the second most important carrier. In sedimentary rocks, the illite reservoir of potassium is over four times bigger than the potassium feldspar reservoir, supplying potassium in soils developed on such rocks.

During diagenesis, the crystallizing illite fixes nitrogen released from organics as NH_4 substituting for K. NH_4/K ratio of pore water controls the level of NH_4 substitution in illite, which in bentonites may reach 50%, recording migration of hydrocarbons in sedimentary basins. Mudstones are often net importers of nitrogen, as illite capacity to fix it is higher than its local production from the organic matter. The transport of nitrogen fixed in illite in the subduction zones is responsible for the replenishing crust and mantle in nitrogen, to the level comparable with the atmospheric nitrogen pool. In soils, illite acts as the nitrogen supplier.

In similar manner, illite crystallizing during diagenesis fixes boron released from organics, by the substitution of silicon in the tetrahedral sheet. The concentrations up to 1000 ppm B were recorded in illites. Boron in illite is responsible for the good correlation, utilized by the borehole geophysics, between the neutron absorption cross section Sa and CEC of the rock. Oxidized sediments are exceptional, containing two other important carriers of boron: kaolinite and hematite. Thus the concentration of boron in mudstones or in illite is not a proper indicator of the salinity of sedimentary basin, but it may reflect the hydrocarbon generation.

In normal mudstones, three minerals are major carriers of cesium and rubidium: K-feldspar, detrital mica, and illite. Most of Cs and Rb is fixed, substituting for K. Detrital mica is the major source of Cs for diagenetic illite, which concentrates Cs and Rb, compared to the Upper Continental Crust (UCC) values, on average two times and by 60%, respectively. In abnormal mudstones, affected by the hydrothermal fluids, the average Cs and Rb values are 18 and 2.4 times higher than the UCC values, respectively, and illite is their major carrier. The Cs/K and Rb/K ratios in illite-smectite are controlled by the chemistry of fluids, which promote crystallization of illite during burial.

BACK TO PROGRAM

Session 1

Role of Clays in Contaminant Fate and Transport

Conveners: Marcus Flury (Washington State University, USA) and Jianying Shang (China Agricultural University, China), Maximilien Mathian (University of New Caledonia, New Caledonia), and Yingxue Yu (The Connecticut Agricultural Experimental Station, USA)

FATE AND TRANSPORT OF VIRAL PATHOGENS THROUGH CLAYS

Himanshu Yadav[1], Deepa Mehta[2], Tadikonda Venkata Bharat[3], and Sachin Kumar[4]

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Lack of guidelines on safe disposal of pathogenic waste during the recent Covid-19 pandemic forced the policy makers to recommend disposal of pandemic waste to the municipal solid waste landfills. However, the knowledge of transport parameters in clay liners under various conditions is scarce. It is evident that the geosynthetic clay liners present in the landfills fail to seal the macro-voids to arrest the pathogens' movement in the presence of high ionic strength salts, which might lead to contamination of the environment. The knowledge of fate and transport of viruses is thus important under various field conditions for the safe disposal practice. In the present study, the Newcastle disease virus (NDV) and Japanese encephalitis virus (JEV) were used to study their diffusion characteristics in clays in the laboratory through-diffusion set-up. The NDV is an infectious and contagious viral pathogen and it affected more than 250 avian species in the past. Moreover, the JEV causes Japanese encephalitis and leads permanent neurological damage to the survivors. The study utilized two different clays bentonite and kaolin for evaluation of its fate and transport parameters. The interactions of these pathogens with both the clays were studied using batch sorption tests. The influence of clay dose, interaction time, clay type, and virus type will be presented. The studied clays showed an excellent sorption ability for both the viruses. Further, the design parameters i.e., diffusion coefficient and retardation factor of these viral pathogens through the bentonite and kaolin clays will also be presented for design of exclusive biomedical waste disposal facility. The NDV is used as surrogate to the coronavirus in recent studies by the authors due to its structural similarities. Thus the results from the present study are useful for designing a facility for the safe disposal of coronavirus pandemic waste.

Keywords: *clay-virus interaction; Newcastle disease virus; Japanese encephalitis virus; virus sorption; virus diffusion; Biomedical waste disposal facility.*

A MODEL TO PREDICT THE INFLUENCE OF PHYSICOCHEMICAL CONDITIONS ON COLLOID TRANSPORT AND RETENTION IN POROUS MEDIA

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Knowledge of the transport of colloids (including clays, dissolved organic matter, microorganisms, and nanoparticles) and colloid-associated contaminants in porous media is needed for many industrial and environmental applications. However, mathematical models of colloid transport are limited by difficulty in predicting the sensitivity of parameters to a wide range of physicochemical conditions. This paper presents an approach to predict the influence of physicochemical conditions on colloid transport, retention, detachment, and blocking. Collector surfaces can have selected amounts, sizes, and/or distributions of nanoscale charge heterogeneity (CH), nanoscale roughness (NR), and microscopic roughness (MR). The model employs filtration theory to predict colloid mass transfer to and from the collector surface. Upscaled values of attachment and detachment efficiencies, the maximum retention capacity, and the probability for colloids to enter from the primary minimum from the secondary minimum are determined by conducting torque and energy balance calculations over the heterogeneous surface of the porous media. This analysis considered distributions of applied hydrodynamic torques, interaction energy profiles, resisting adhesive torques, and a Maxwellian kinetic energy distribution for diffusing colloids. Simulated breakthrough curves, low concentration tailing, and blocking behavior show expected trends with CH, NR, MR, zeta potential, solution ionic strength, collector size, and Darcy velocity. New insights are gained about the important role of hydrodynamics on colloid retention and release. Parameters also show that colloids in a secondary minimum may rapidly transition to a primary minimum. This has important implications for one-site and two-site kinetic models of colloid retention and release.

REMOVAL OF EMERGING METALS USING CLAY/IRON-BIOCHAR COMPOSITES

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The development of high-tech emerging industries such as semiconductors and optoelectronics has led to the use of gallium (Ga) and indium (In) in related processes, gradually raising concerns among scientists about associated pollution issues. The environmental fate and risks of two emerging metals remain unclear. Biochar produced from agricultural waste exhibits greater carbon sequestration and possesses a porous microstructure with a high surface area, making it a potential adsorbent for soil/water emerging pollutants. However, biochar prepared solely by pyrolysis could lack both abundant pore structures and functional groups. This study aims to determine the structural stability and characteristics of biochar modified with bentonite and iron salts and its removal efficiency for adsorbing emerging metals, such as Ga and In. Both rice husk (RH) and wood sawdust (WS) were modified with various proportions of bentonite (Bt) and/or iron salts (Fe). The samples were categorized into three groups: (1) pristine biochar (RHBC/WSBC), (2) Bt-modified biochar, and (3) Bt/Fe-modified biochar. After carbonization at 600°C in a nitrogen environment, the samples undergo characteristic analyses. The results indicated that clay modification significantly enhances yield and elemental analysis (EA) showed that, after high-temperature pyrolysis, the H/C and O/C decreased, suggesting a transformation of C from aliphatic C to aromatic C. The BET results indicated that, compared to biomass, the surface area of the pristine biochar increases after high-temperature pyrolysis. However, Bt/Fe-modified biochar showed no significant differences, suggesting that Fe may contribute to the formation of crystals during pyrolysis, reducing the surface area. The FTIR spectra of Bt-modified biochar and Bt/Fe-modified biochar samples. showed the presence of aromatic C=C and absorption bands representing C=O bonds in hydrogen-bonded ketones and quinones, suggesting enhancing the carbon stability in biochar modified samples. In addition, the adsorption experiments involving the pH effects on Ga and In showed that both RHBC and WSBC were modified with Bt and Fe exhibited enhanced removal efficiency for Ga. However, similar trends were examined for In only at pH 2.0, while at pH 4.0, the smaller molecules in biochar may form dissolved complexes with In, inhibiting the formation of $In(OH)_3$.

THE ROLE OF THE AIR-WATER INTERFACE ON COLLOID TRANSPORT IN THE VADOSE ZONE

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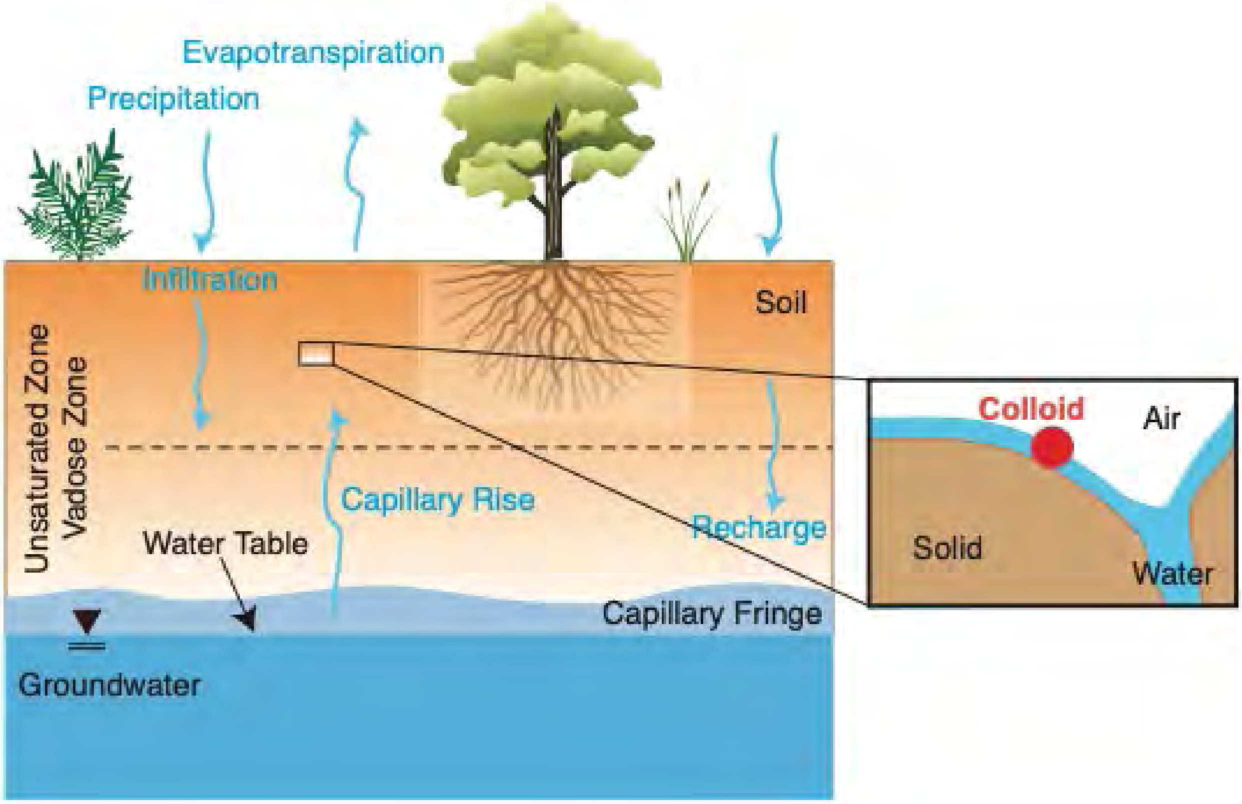
Air-water interfaces play an important role in unsaturated porous media. Phenomena like capillarity or evaporation are controlled by the configuration of air-water interfaces. Less recognized and understood are interactions of colloids with the air-water interface in porous media. Here we discuss experimental and theoretical methods to characterize and quantify interactions between air-water interfaces and colloids and nanoparticles in porous media. We show that these interactions depend on the size of the particles, i.e., particles in the micrometer size range will behave differently than particles in the nanometer size range. We also discuss how interaction with the air-water interface will affect transport of colloids and nanoparticles in soils and sediment.



CHROMIUM OXIDATION ON FERRIHYDRITE UNDER ATMOSPHERIC CONDITIONS WITH UV IRRADIATION: TRENDS AND MECHANISMS

Lin, Li-Pang[1], Kung, Yu-Yu[1], Liu, Yu-Ting[1], and Hsu, Liang-Ching*[1]

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Atmospheric particulate matter (PM) is a major source of air pollution, with heavy metals in PM posing significant health risks due to their potential to increase PM toxicity. Chromium (Cr), commonly found in PM, exists mainly as Cr(III) and the highly toxic Cr(VI), the latter being a known human carcinogen. This study uses an oxidation flow reactor (OFR) to simulate the formation of hydroxyl radicals (HO·) in the atmosphere, exploring how these radicals might promote the conversion of Cr(III) to Cr(VI) through reactions with iron oxides, a typical inorganic component of PM. It also investigates how humidity affects HO· generation and Cr oxidation. This research enhances our understanding of atmospheric chemistry's role in heavy metal transformation and aids in developing methods to reduce PM-associated health risks.

This study investigated chromium species transformation using ferrihydrite to adsorb trivalent chromium (Cr-FH) and an oxidation flow reactor (OFR) for photoreaction studies under varying humidity levels (RH20%, RH40%, RH55%, RH70%). Findings revealed that increasing humidity decreased Cr(VI) production in Cr-FH, while pure trivalent chromium (Cr w/o FH) showed increased Cr(VI) levels with higher humidity. This suggests iron's presence in Cr-FH affects chromium's oxidative reaction, especially at RH20% where oxidation is most pronounced. UV light absorption by water vapor reduces light intensity and enhances Fe(III) to Fe(II) photoreduction, making chromium on ferrihydrite more reactive with Fe(II) and HO·. The accumulation of Fe(II) promotes Cr(VI) reduction. These results demonstrate that atmospheric hydroxyl radicals can oxidize Cr(III) to Cr(VI), with iron significantly influencing chromium's redox reactions under light irradiation.

LATERITIC ENVIRONMENTAL DUSTS CHARACTERIZATION AND QUANTIFICATION: IS MINING EXPLOITATION PROMOTING TRACE METAL-RICH DUST DISPERSION IN THE ENVIRONMENT? A CASE STUDY FROM EASTERN NEW CALEDONIA

France Pattier[1], Maximilien Mathian[1*], Peggy Gunkel-Grillon[1], Sylvie Russet[1], Kapeliele Gutut-auava[1], Mark Patrick Taylor[2], and Estelle Roth[3]

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The geology of New Caledonia (Southern Pacific) is dominated by ultrabasic rocks that have been weathered during the last 34 Ma, allowing the development of metal-rich lateritic regoliths. These regoliths are enriched in Fe but also in various poorly mobiles trace metal elements (Ni, Cr, Co, Mn,...). Due to their high content of trace metals, particularly in Ni, mining is one of the main economic sectors from the archipelago. However, such activities have led to environmental degradation and to the creation of stripped lateritic surfaces, with no vegetation. Excavation, ore transportation and processing as well as stripped surfaces are potential sources for the emission of metal-enriched dust into the environment. Given the potential toxicity of the metals in dust these can pose a long-term threat to the local population.

To quantity such sanitary risks, we explore mineralogical and geochemical characteristics of dust deposits sampled over a year around the Thio Ni-mine in New Caledonia. Eighteen Owen gauges have been placed in the mine and its surrounding, including a local village to sample the dust deposits. The evolution of the dust content (e.g. their weight) and their geochemical composition, using a portable x-ray fluorescence spectrometer, in parallel to climatic events is studied. The dusts mineral composition, and particularly the nature of their metal bearing minerals is also explored, through the crossing X-Rays Diffraction analyses and mineral semi-quantification as well as SEM analyses. This study data identifies that cyclonic weather periods, characterized by strong precipitation and wind, create the optimal conditions for mobilization of mine-contaminated dust. By contrast, dry weather periods promote the remobilization of phyllosilicate-rich dust, which is relatively poor in trace metal-bearing minerals.

THE ROLES OF •OH AND MINERAL FE(IV) FOR PHENOL DEGRADATION DURING FE(II)-BEARING CLAY MINERAL OXYGENATION

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Fe-bearing clay minerals are ubiquitous in soils, sediments, and rocks, representing an important Fe pool in Earth's crust. Electron transfer (ET) from/to structural Fe in clay minerals is an important electron and energy flux in natural environment, which drives numerous biogeochemical processes and contaminant transformation. However, the nature of generated oxidants from Fe(II)-bearing clay mineral oxygenation for contamination degradation remains unclear. In this study, we investigated the production of oxidants from oxygenation of reduced Fe-rich nontronite NAu-2 and Fe-poor montmorillonite SWy-3. We identified the generated •OH and mineral Fe(IV) as the dominant oxidants for phenol degradation. A kinetic model was developed to well reproduce the variation of phenol concentration during oxygenation of rNAu-2 and rSWy-3. The modeling results reveal that the contributions of •OH and mineral Fe(IV) to phenol degradation are 81.2% vs. 14.6% for rNAu-2 and 88.9% vs. 11.1% for rSWy-3, respectively. It is noteworthy that the role of Fe(IV) in phenol degradation mainly occurs within 30 min, aligning with the rapid formation of $\mathrm{Fe(IV)_{edge}}$. Subsequently, with the depletion of $\mathrm{Fe(II)_{edge}}$, the generated Fe(IV) is dominated by $\mathrm{Fe(IV)_{int}}$, which may not react with phenol due to mass transfer resistance. Therefore, the generation of mineral Fe(IV) and •OH should be taken into consideration carefully when assessing the natural attenuation of contaminants in redox-fluctuating environments.

IMPACT OF COUPLED PHYSICAL AND CHEMICAL HETEROGENEITY ON COLLOIDAL TRANSPORT IN UNSATURATED POROUS MEDIA

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Colloids are present in the environment, experiencing processes of environmental aging. Subsurface environments are typically heterogeneous in unsaturated conditions, which may affect the transport of colloids. This study focused on the transport of colloids in physically (clean coarse and fine sand) and physicochemically (iron oxides-coated coarse and clean fine sand) heterogeneous porous media at three different water saturations (100%, 70%, and 40%). In physically heterogeneous porous media, the decrease in water saturation from 100% to 40% led to a shift in the main water flow from the clean coarse sand to the clean fine sand domain, resulting in a continuous decrease in the transport of colloids. In physicochemically heterogeneous porous media, the primary water flow shifted from the iron oxides-coated coarse sand to the clean fine sand domain, resulting in an initial increase and subsquent decrease in colloidal transport. Retention profiles revealed substantial colloidal retention at the interface between coarse and fine sand domains. The release of retained colloids exhibited two peaks at 100% and 70% water saturations, along with a single peak at 40% water saturation. Additionally, the increased irreversible retention was observed at lower water saturation. This study underscores the significance of water content and heterogeneity in colloidal transport. It provides essential insights into the environmental fate of colloids in natural field conditions.

AGGREGATION KINETICS AND STABILITY OF BIODEGRADABLE NANOPLASTICS: EFFECTS OF WEATHERING AND PROTEINS

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Plastic pollution caused by conventional plastics has promoted the development and application of biodegradable plastics. However, biodegradable plastics do not degrade readily in water, instead, they can generate countless micro- and nanoplastics. Compared to microplastics, nanoplastics are more likely to cause negative impacts to the aquatic environment due to their smaller size. The impacts of biodegradable nanoplastics highly depend on their aggregation behavior and colloidal stability, which still remain unknown. Here, we studied the aggregation kinetics of polybutylene adipate co-terephthalate (PBAT) nanoplastics in both NaCl and $CaCl_2$ solutions before and after artificial weathering. We further studied the effect of proteins on aggregation kinetics with both negatively charged bovine serum albumin (BSA) and positively charged lysozyme (LSZ). We found that divalent cations (Ca^{2+}) destabilized PBAT nanoplastics more aggressively than monovalent cations (Na^+); weathering stabilized PBAT nanoplastics profoundly, with no aggregation observed in NaCl nor in $CaCl_2$; both BSA and LSZ promoted the aggregation of pristine PBAT nanoplastics, with LSZ showing more pronounced effect. These results suggest that biodegradable nanoplastics, especially weathered biodegradable nanoplastics, are highly stable in the aquatic environment.

Session 2

Sediment transport mechanics, morphologic expressions, depositional patterns, and climate impacts of clay-rich dispersal systems

Conveners: Judy Yang (University of Minnesota, USA), Hongbo Ma (Tsinghua University, China), and Ian Bourg (Princeton University, USA)

CAN STRONTIUM AND NEODYMIUM ISOTOPES OF THE CLAY MINERAL-RICH COLD-SEEP CARBONATES BE A TRACE TO RECORD THE SOURCE OF THE COLD-SEEP FLUIDS?

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The radioactive strontium (Sr) and neodymium (Nd) are powerful tools to reveal the source of the cold-seep fluids, which are widely used in studies on cold-seep carbonates. However, it remains a disputable question whether it is appropriate to use this technique in the cold-seep carbonated studies. To discuss this problem, we carried out a series of X-ray powder diffraction (XRD) and Sr-Nd isotope studies on the cold-seep carbonates from the Haima cold seep, northern Southern China Sea. The results show that cold-seep carbonates of the two sites both contain high portions of clay minerals, which are mainly illite (31-44%) and chlorite (6-15%). The $^{87}Sr/^{86}Sr$ isotopes of these cold-seep carbonates range from 0.709178 to 0.709278 with calculated $^{87}\delta$ values of 0.01-0.15, which are similar to the $^{87}Sr/^{86}Sr$ isotopes of the modern seawater. The Nd isotopes show that these cold-seep carbonates have constant $^{143}Nd/^{144}Nd$ ratios of 0.512059-0.512092 with calculated εNd values of -11.2 to -10.6 which are much lower than the Nd isotopes of modern seawater and similar to the sediments of the northern South China Sea.

It is indicated that the Nd isotopes of the cold-seep carbonates are mainly inherited from the clay minerals in the carbonates because the clay minerals were mainly sourced from the weathering product of ancient rocks from the nearby continent which will have highly Nd isotopes. However, the Sr isotopes of the cold-seep carbonates are inherited from the authigenic carbonate minerals and record the Sr isotopes of the cold-seep fluids during the deposition of these authigenic carbonate minerals. Therefore, it is concluded that Sr and Nd isotopes have different functions and it needs to be careful when using the Nd isotopes to study the clay mineral-rich cold-seep carbonates.

QUANTITATIVE X-RAY DIFFRACTION ANALYSIS OF CLAY MINERALS IN MINING APPLICATIONS

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Although clay minerals are critical to a number of geological and industrial processes, their quantitative analysis has remained challenging owing to poorly crystalline and fine-grained nature in complex mineral assemblages. Accurate quantitative phase analysis of clay-bearing ores is of considerable interest to facilitate better understanding of their behaviour in industrial applications.

This research incorporates multiple approaches to sample preparation of clay-bearing ores in a variety of geological settings, encompassing classical clay separation, magnetic separations, and chemical treatments. These methods collectively contribute to the targeted purification of specific clay minerals in complex mineral assemblages.

The resulting clay samples serve as a reference for Rietveld-PONKCS (Partial Or No Known Crystal Structure) method with refinements of anisotropic models including peak asymmetry and broadening. Case studies presented herein include geosynthetic bentonite liners, clay-bearing iron ores, clay-hosted rare earth ores, and lithium-bearing hectorite ores. The integrated approach provides a practical and robust foundation for quantitative clay mineralogy, thereby influencing mineral resource characterisation, ore processing efficiency, and decision-making processes within the mining industry.

EXAMINING THE IMPACT OF CLAY AND AQUEOUS PROPERTIES ON THE ERODIBILITY OF SMECTITE USING A COMPUTATIONAL FLUID DYNAMICS FRAMEWORK

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The erodibility of cohesive fine-grained sediment – i.e. clay, has important implications for fluvial geomorphology, pollutant transport, and geochemical cycling. Although known for its importance, the ability to predict erosion thresholds and rates has been difficult due to complex hydrological-mechanical-chemical couplings that exist within clayey media. This model intends to incorporate known physical and chemical properties of clay in a mechanistic manner to predict erosion thresholds, types, and rates.

This model was created using the recently developed Darcy-Brinkman-Biot framework. This framework is Eularian-Eularian in nature and operates within OpenFOAM to discretize equations for its continuum mechanics. The modeled dimensions and operations are based on flume experiments performed by the Yang Group at the University of Minnesota. Clay content and salinity levels were chosen to represent conditions found in rivers and estuaries: regions known for their significance in clay transport. The model currently predicts erosion threshold and rates for smectite clay and allows for changing of parameters including clay content percentage, flow rate, salinity, and yield stress.

In conclusion, this mechanistic model helps resolve the complicated nature of clay erosion through utilizing well-established chemical and physical properties of clay. The ability to easily alter one condition and examine its impact on erosion demonstrates the benefit of this model and proves promising to assist in improving the understanding of fine-grained sediment erosion.

Figure 1. Example of modeled erosion event

DO MICROBES SHAPE LANDSCAPES? BIOPOLYMERS, CLAYS, AND CRUSTS IN MARS ANALOG ENVIRONMENTS

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Clay minerals are considered some of the most powerful cohesive materials in terrestrial sediments. Some field studies have shown a numerical relationship between concentrations of clay minerals in sediments and concentration of extracellular polymeric substances (EPS)—sticky biopolymers excreted by common microbes. EPS are found in low concentrations in soils (<1.5 wt%). But with a cohesive strength an order of magnitude greater than kaolin clay, small quantities of EPS may have a significant impact on sediment strength. Which begs the question: how much of the cohesion from the presence of clay minerals in Earth sediments is due to cohesion from EPS? And could EPS influence the geomorphology of common landforms such as aeolian dunes or meandering rivers on Earth and possibly Mars? Here we investigate the abundance and distribution of EPS from sediment samples collected over a wide range of Mars analog environments spanning from arid basins of the southwestern United States to proglacial plains of southern Iceland. We compared these measurements to results from laboratory experiments in the literature and found that 97% of the 306 field samples contained EPS concentrations above the 0.016 wt% sediment transport reduction threshold value. We also find that EPS concentration correlates positively with clays and iron oxides, which has exciting implications for the search for life on Mars; if microbes were present on ancient Mars, high concentrations of EPS may have impacted ancient geomorphic processes that could be expressed in landscape-scale topography on Mars today.

DIFFERENCES IN TRANSPORT REGIMES BETWEEN SILT-RICH BEDDED AND SAND-BEDDED RIVER SYSTEMS

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The channel bed of world's lowland rivers consists of sand and silt sediment. Two primary types can be identified: (1) sand-bedded rivers who have their beds primarily sand and are thus sand-dominated or (2) silt-sand or silt-rich bedded rivers whose bed is rich in silt. In this presentation, we show that the sediment transport features in these two types of rivers are drastically different. Under the same hydrodynamics forcing, the sediment load can have an abrupt change by one to two orders of magnitude, due to slight change in bed grains size around 125 microns, the border between fine and very fine sand. Our analyses show that the impacts of bedform geometry may be the primary but the only reason for the abruptly change in the sediment load. The underlying reason may be related to the transport modes of the sediment i.e. mixed transport of bedload and suspended load versus the suspended-dominated transport. In the end, we discuss the potential impact of this difference in sediment load on the river and delta morphology.

MICROPLASTIC PARTICLES IN CLAY-SAND SEDIMENT MIXTURES: UNVEILING THEIR CONTRIBUTION TO EROSION

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Due to the wide range of parameters affecting the erosion behavior of clay-sand sediment mixtures, knowledge on governing processes and their complex interactions is still very limited. Plastic in natural sediment mixtures changes the structure of the sediment matrix and, subsequently, the erosion behavior. Even small low-density Microplastic particles (MPs) were found to increase fine sediment resuspension. Zhang et al. (2020) (1) observed this trend in 9 lakes and raised environmental concerns due to the potential high resuspension, which can lead to eutrophication in shallow-water lakes. However, more studies are needed to understand this complex behavior.

In the present study, the influence of MPs on the erosion behavior of artificially produced clay-sand sediment mixtures is investigated by using data from erosion tests. The physical properties of MPs, like the polymer type, shape, and the number of particles, varied during the tests to indicate the dependency of erosion on these factors. The erosion tests were performed in an erosion flume, where the erosion evolution was recorded with high spatial and temporal resolution measurements using the pixel-based topographic change detection method (PHOTOSED, (2)). Erosion rates and critical shear stresses were investigated for increasing MPs (500 and 3,000 particles/kg sediment). Sediment mixtures with 15% kaolinite and 85% fine sand were artificially prepared and spiked with MPs. The polymers used are polystyrene (PS, d50 = 0.023 and 1.5 mm, ρ = 0.96 g cm-3), polyamide (PA, d50 = 0.2 and 2.5 mm, ρ = 1.01g cm-3), and polylactide (PLA, d50 = 3 mm, ρ = 1.38 g cm-3). The tested shapes of the particles were pellets and monofilaments. To estimate the critical shear stress of the mixture with MPS, we proposed a method based on the stochastic erosion model by Winterwerp et al. (2010) (3), which allows for the determination of the predominant physical parameters of MPs and their influence on sediment stability by using probability density functions (PDFs).

The measurements with high spatial resolution (~0.10 mm2) confirmed that the highest erosion rate occurs mainly around the MPs, making the influence of MP on the sediment matrix evident. Experimental erosion tests demonstrated that even a small percentage, such as 1% in weight, of lowdensity MPs (< 1.05 g cm-3) provoked a non-uniformity of the critical shear stress on the sediment mixture, which a PDF could capture. Overall, the results indicated that the presence of MPs decreased the critical shear stress of the sediment mixture, and some affecting factors were the density and surface area of the particle. Also, a predominant stochastic erosion behavior, especially for floc erosion, is visible. The resulting PDFs of sediment mixtures with MPs enable us to understand and predict the potential risk of uncontrolled erosion more realistically. Additionally, this knowledge will enhance our understanding of the complex erosion processes of cohesive sediment mixtures.

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RELATIONSHIP BETWEEN PARTICLE SIZE AND CHARACTERISTICS IN THE SEDIMENT COLLECTED FROM LAKE OKUTAMA, JAPAN

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After the Fukushima Daiichi Nuclear Power Plant accident in 2011, ^{137}Cs tends to accumulate in Lake Okutama sediments within Tama River watershed, Japan[1]. ^{137}Cs mainly adsorbs to clay minerals. Inose *et al.*[2] showed a correlation between sediment particle size and ^{137}Cs concentration in the mainstream of Tama River. In this study, sediment was collected from Lake Okutama and sieved into four categories (less than 75 µm, 75-250 µm, 250-850 µm, 850-2000 µm) according to JIS A 1204[3]. We investigated the relationship between particle size and characteristics in Lake Okutama sediment by analyzing classified samples.

The sediment sample collected at Tozura Pontoon Bridge in Lake Okutama was dried at 105°C for over 24 hours. This was then classified using a horizontal gyratory sieve (ASONE, SKH-01). The crystalline phases in the classified samples were analyzed using an X-ray diffractometer (Rigaku, MiniFlex600).

Clay minerals such as kaolinite, and rock-forming minerals such as quartz were identified. **Figure 1** shows the crystalline phase composition by particle size in the sediment sample. Concentration of quartz decreased with smaller particle size. This result is presumed by quartz having strong resistance to weathering[4]. Other minerals didn't show any relationship with particle size.

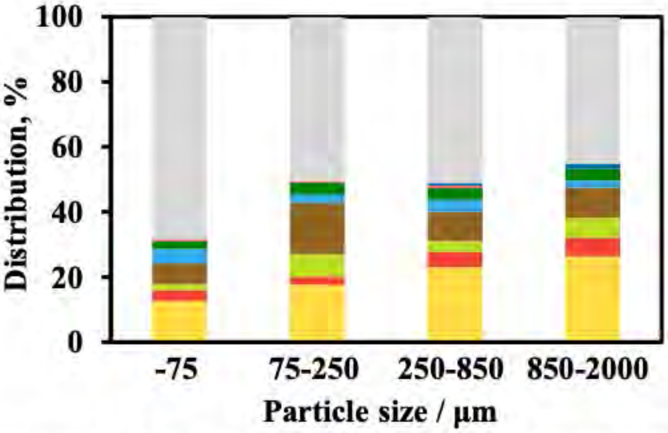

Figure 1 Concentrations of crystalline phases by particle size distribution of sediment collected from Tozura Pontoon Bridge on June 6, 2023.
🟨: Quartz, 🟥: Kaolinite, 🟩: Vermiculite, 🟫: Albite, 🟦: Mica, 🟩: Halloysite, 🟥:Fe_3O_4, 🟦:Siderite, ⬜: Unknown.

We also performed an ignition loss test to simply determine the amount of organic matter in the sediment sample. Future research surveys ^{137}Cs concentration in Lake Okutama sediments and investigates the relationship between ^{137}Cs migration and sediment characteristics.

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IMPACT OF SALINITY ON THE EROSION THRESHOLD, YIELD STRESS, AND GELATINOUS STATE OF A COHESIVE CLAY

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Clay is the main component that contributes to sediment cohesiveness. Salinity impacts its transport, which controls the electrochemical force among the sediment grains. Here, we quantify the impacts of salinity on the erosion threshold, yield stress, and the microstructures of a fluorescently labeled smectite clay, laponite, combining flume experiments, rheometer measurements, and macro- and microscopic imaging. We show that the critical shear stress for clay erosion, increases by one order of magnitude with increasing salinity when salinity <1.5 ppt and slightly decreases when salinity >1.5 ppt showing a weaker dependency upon salinity We further show that the yield stress, of the clay remains roughly a constant at salinity less than 1.5 ppt and decreases by over one order of magnitude at salinity larger than 1.5 ppt. This change in the dependency of and yield stress on salinity corresponds to a change in the gelatinous state of clay, from gel-like structures to phase-separated structures as salinity increases. Our results provide a quantitative characterization of the dependency of clay erosion threshold and yield stress on salinity and highlight the importance of clay gelatinous state in controlling clay transport.

PEDOGENIC-WEATHERING EVOLUTION AND SOIL DISCRIMINATION BY SENSOR FUSION COMBINED WITH MACHINE-LEARNING-BASED SPECTRAL MODELING

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Loess deposits are important records of the evolution of the soil environment and pedogenic weathering. Changes in pedogenic weathering conditions through space and time are important scientific issues in the soil (paleosol) community. Here, 502 soil samples from different climatic zones of China were investigated using portable X-ray fluorescence (PXRF) and visible to near-infrared reflectance (VNIR) in combination with previously published mineralogic and magnetic datasets. A spectral modeling approach was employed to discriminate loess-derived soils from different regions of China. We developed a three-dimensional model to fingerprint loess-derived soils using principal component analysis (PCA), showing that soils accumulating under varying climatic conditions were effectively discriminated with sensor fusion data. Six key soil mineralogic and magnetic attributes serving as pedogenic-weathering proxies were analyzed and predicted with conventional methods and chemometric models. Predictive models were constructed with machine learning methods, including partial least squares regression (PLSR), random forest (RF), and Cubist algorithms. The results indicate that the Cubist algorithm works better than PLSR and RF in predicting pedogenic-weathering proxies. The cross-validation results indicate that, although models derived from single sensors (i.e., PXRF or VNIR) work well in predicting pedogenicweathering proxies, the sensor fusion approach is superior with regard to accuracy and robustness of results in most cases. The sensor fusion models reveal that pedogenic processes in the loess chronosequences are diversified both spatially and temporally in different climate zones of China. Our results suggest that spectral modeling can be an alternative to geochemical, mineralogic and magnetic pedogenic-weathering proxies, and that it has great potential for investigating soilforming conditions and pedogenic-weathering evolution, especially when large-area and/or high-resolution analysis is required.

Session 3

Natural Hazards and Clays: How determining/understanding their physicochemical properties can aid in modeling and mitigation efforts

Conveners: Hiroshi Sakuma (National Institute of Material Sciences, NIMS) and Diane Moore (U.S. Geological Survey, USA)

NATURAL AND EXPERIMENTAL SEISMIC SLIP ON CLAY GOUGE: IN THE CASE OF THE TAIWAN CHELUNGPU FAULT DRILLING PROJECT

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Catastrophic events such as earthquakes, tsunamis, and landslides are often associated with large coseismic slip localized to relatively thin slip zones. During seismic slip, the accumulated frictional heat tends to drive thermally activated physical and chemical processes within the slip zone. At shallow crustal depths, water-saturated clay-rich gouges are common components of fault slip zones. Therefore, recognition of slip zone within clay-bearing fault zone and understanding its strength and frictional behavior, and the associated triggering mechanisms, are critical to earthquake physics and seismic hazard assessment.

The Chelungpu fault ruptured northward along an ~90 km segment as a result of the 1999 Mw 7.6 Chi-Chi earthquake. Later, the Taiwan Chelungpu fault Drilling Project (TCDP) was initiated and penetrated the active fault zone of the Chelungpu fault. By means of optical, field emission scanning and focused ion beam transmission electron microscopies, we recognized the principal slip zone (PSZ) with the evidence of both thermal pressurization (< 300 ˚C) and frictional melting (up to 1000 ˚C) of clay gouges derived from the 1999 Mw 7.6 Chi-Chi earthquake. To investigate how the different mechanisms were triggered within the slip zone, we conduct rotary shear rock friction experiments on water-saturated TCDP fault gouges at approximately the borehole depth expected for seismic slip, under either fluid-drained or -undrained conditions. The results show typical dynamic weakening behaviour regardless of the ambient conditions but with different peaks and steady-state values of the friction coefficient (the ratio of shear stress/normal stress). After the experimental seismic slip on TCDP gouge, we show that frictional melting of gouges can occur after the cessation of thermal pressurization in drained experiments, similar to the PSZ of TCDP. Since water can absorb frictional heat, this suggests that the deficiency of water in the PSZ due to fluid drainage leads to an increase in temperature, resulting in gouge melting. We conclude that the dynamic weakening of fault gouges during the 1999 Chi-Chi earthquake was due to thermal pressurization. Our finding also suggests that spatial hydraulic heterogeneity along fault zones can lead to variable physical and chemical reactions and the associated coseismic products after a seismic event.

MINERALOGY AND PHYSICAL PROPERTIES OF CORE FROM SERPENTINITE MUD VOLCANOES, NORTHERN MARIANA SUBDUCTION ZONE

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We obtained 12 core samples for physical and chemical characterization from three serpentinite mud volcanoes (Yinazao, Asùt Tesoru, and Fantangisña) located on the forearc of the Mariana subduction system, where the Pacific Plate descends beneath the Philippine Sea Plate. The core was collected during International Ocean Discovery Program Expedition 366 of 2016-2017. The materials comprising the mud volcanoes have risen diapirically along normal fault systems in the forearc that extend down to the subducting slab; thus, examination of the core will provide insights on the properties and behavior of the megathrust region. Ten of the samples are thoroughly serpentinized ultramafic rocks that consist of the low-temperature serpentine varieties lizardite and chrysotile, magnetite and, in most cases, brucite and andradite garnet. The other two come from cored intervals into Fantangisña mud volcano that contain some materials derived from the subducting Pacific Plate, and their whole-rock compositions, obtained by X-ray fluorescence techniques, are consistent with the inclusion of a substantial crustal component mixed with serpentinite. These two core samples are rich in the Mg-smectite clay minerals saponite and corrensite, the products of metasomatic reactions between the crustal and ultramafic rocks, and they also contain trace amounts of crustal minerals such as augite, titanite, ilmenite and apatite. The mineralogy of the core samples, in turn, affects their physical properties. The smectite-clay-rich cores have lower frictional strengths ($\mu < 0.2$) than the serpentinites ($\mu = 0.2$-0.4), and their measured permeabilities at 5 MPa effective pressure are also somewhat lower, at 9.6×10^{-20} and 5.0×10^{-19} m^2, compared to 8.9×10^{-19} to 3.9×10^{-18} m^2 for the serpentinite cores. The physical properties of the clay-bearing Marianas samples are consistent with those found in other faulting environments (e.g., the San Andreas Fault Observatory at Depth) where serpentinites and crustal rocks are juxtaposed.

ROLES OF CLAY MINERALS IN SEISMOGENESIS IN SHALLOW SUBDUCTION ZONES INVESTIGATED BY LABORATORY FRICTION EXPERIMENTS

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Clay minerals such as smectite and illite are main components of seafloor sediment. In subduction zones, seafloor sediments on an incoming plate subduct beneath an upper plate and constitute the plate boundary fault. As clay minerals tend to show low frictional strengths, slip on the clay mineral-rich plate boundary fault is critically important for earthquake processes that have the potentials to cause severe damages on surrounding areas. Toward the understanding of fault slip behavior in subduction zones, I have conducted friction experiments on clay mineral-dominated materials simulating the subducting sediments to determine their frictional properties and the roles of clay minerals in seismogenesis in shallow subduction zones.

Among various clay minerals, smectite is one of the mechanically weakest minerals. Therefore, its impact on fault slip behavior has been widely studied either at low velocity conditions (~1 μm/s) or at high velocity conditions (~1 m/s). However, frictional behavior at intermediate velocity conditions is limited despite it characterizes how slip evolves toward coseismic rupture. Toward a better understanding, I conducted friction experiments on gouge materials of smectite-glass mixtures at velocities of 10 μm/s to 1 m/s under water pressurized conditions. I found an anomalous slip-weakening behavior happening at 1-3 mm/s when small amounts of smectite were contained. Considering instability of fault slip associated with elasticity of host rock, the slip weakening offers a fault to have an unrealistically large dimension to accelerate slip. Therefore, upon earthquake nucleation, clay mineral-mixed fault gouge self-arrests fault slip and potentially ends in slow earthquakes (Okuda, Hirose, & Yamaguchi, 2023, JGR Solid Earth).

Illite is another key clay mineral for seismogenesis in subduction zones because smectite-illite transition has been hypothesized as a major control of the onset of the depth range where sources of megathrust earthquakes are located. However, both smectite and illite tend to slip stably in laboratories, although their frictional properties were not fully understood under hydrothermal conditions. To understand the influence of smectite-illite transition in seismogenesis, I simulated *in-situ* pressure-temperature-mineral conditions along the shallow plate boundary of the Nankai Trough and experimentally explored variations of frictional properties. Smectite-illite transition in the Nankai Trough completes at the depth of 5-6 km below seafloor where temperature reaches 150 °C. Even at this depth, the potential for unstable slip was not observed, which implies that the onset of seismogenesis is not controlled by smectite-illite transition. On the other hand, frictional instability emerged at a deeper depth condition associated high-temperature frictional behavior of illite, which is actually important for nucleating megathrust earthquakes (Okuda, Kitamura, Takahashi, & Yamaguchi, 2023, EPSL).

TEMPERATURE DEPENDENT FRICTIONAL PROPERTIES OF SINGLE-CRYSTAL MUSCOVITE

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Earthquakes often occur due to stress release along weak faults. Characterizing the frictional behavior of minerals in faults is essential to understand the dynamics of fault movement. The rate and state friction law (RSF law) (Dieterich 1979; Ruina 1983) achieved great success in characterizing the friction of simulated faults and gouges as a function of slip velocity and holding time. However, the parameters used in the RSF law are semi-empirical and therefore, it is difficult to apply the law at elevated temperatures and pressures beyond the experimentally tested ranges. To develop a non-empirical RSF law, the physics and chemistry behind the parameters must be revealed.

Natural faults often contain layered-structure clay minerals, which exhibit unique frictional properties compared to common rock-forming minerals such as quartz. Here, we chose single-crystal muscovite as a representative of layered-structure clay minerals and have studied its shear-force response for the change in slip rate (direct effect) as a function of temperature. The direct effect has been interpreted as a thermally activated process at asperity contacts (Stesky 1978; Heslot *et al.*, 1994). This thermally activated process requires that the direct effect parameter "*a*" should increase with increasing temperature. However, our shear tests on single-crystal muscovite have revealed that the "*a*" value clearly decreased as increasing temperature from ~25 to 400°C.

To comprehend the physics of the direct effect, we conducted SEM and TEM observations of the muscovite samples recovered from the shear tests. We found wear particles on the slip surfaces and slickenlines along the direction of movement as commonly observed on natural faults. We also observed linear features oriented perpendicular to the slickenlines that are composed of fractures and dislocations within the muscovite layers.

We also conducted non-equilibrium molecular dynamics simulations of single-crystal muscovite to reveal the behavior of the direct effect. The simulated "*a*" value remains constant regardless of temperature. We cannot fully interpret the negative temperature dependence of the "*a*" parameter for single-crystal muscovite yet, however, it is likely that the physics of layered minerals cannot be explained by the thermal activation theory.

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Session 4

New insights into the mechanisms of microbe-mineral interactions in geological processe

Conveners: Jinwook Kim (Yonsei University, Korea), Eric Roden (University of Wisconsin at Madison, USA) and Juan Liu (Peking University, China), and Tae-hee Koo (Yonsei University, Korea).

MANGANESE NANOCLUSTERS IN ROCK VARNISH ANALOGOUS TO PHOTOSYNTHETIC OXYGEN-EVOLVING COMPLEXES

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The Mn-Ca-cluster in Photosystem II (PSII) plays a crucial role in water oxidation and the production of molecular oxygen in all oxygenic photosynthetic organisms. The discovery of a mineral analog to the biological Mn-Ca-cluster would significantly advance our conceptual understanding of the origin and evolution of oxygenic photosynthesis. To date, however, no such occurrence has been found in nature. Here, we conducted a comprehensive examination of the distribution of Mn-oxides and clay minerals in rock varnishes using collocated nano- and atomic-scale analyses, complemented by synchrotron-based X-ray absorption fine-structure (EXAFS) spectroscopy. Our investigation revealed the presence of nano-sized Mn-Ca-clusters on the sunlit side of rocks, acting as a mineral equivalent and potential precursor to the biological oxygen-evolving complex (OEC). Multiple lines of evidence suggest that clay minerals facilitate Mn oxidation by providing nucleation sites for Mn-oxides. These results indicate an intimate association between the formation of organic matter and the Mn-Ca-clusters. Collectively, these observations support a scenario of CO_2 fixation mediated by Mn-Ca-nanoclusters, with the sunlit side of rocks serving as the source of initial inorganic components for photosynthetic systems.

MICROBIAL FE-REDUCTION IN NONTRONITE AT 4°C: EVIDENCE OF PSYCHROPHILIC REDUCTIVE DISSOLUTION OF FE

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Microbial reduction of nontronite and subsequent geochemical modification of nontronite including formation of high-charge nontronite at 4°C by psychrophilic Shewanella species (*S.frigidimarina* and *S.vesiculosa*) has been confirmed by mineralogical assessments. The extent of Fe(III) reduction reached ~21% within 1 year, contrasting with the negligible Fe(III) reduction in the no-bacteria control. The observed increases in Fe, Al, and Si concentrations in the supernatant, along with the formation of vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), provide evidence for the reductive dissolution of nontronite. Furthermore, K-nontronite, layer-collapsed high-charge nontronite with K-saturation, identified in X-ray diffraction profiles (10°C-shoulder after Li-saturation) and transmission electron microscopic (TEM) analysis (Al/Si=~0.3 with K-saturated) suggests the microbially-induced smectite-to-illite reaction despite the extremely low temperatures. These findings collectively indicate that microbial respiration by psychrophiles at low temperatures could serve as new pathway of supplying the bioavailable Fe in cryosphere through the biogenic mineral diagenesis at low temperature.

INVESTIGATION OF MICROBIALLY MEDIATED TRANSFORMATION OF FE-RICH SMECTITE TO ILLITE

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The *in-situ* interactions between microbial populations and introduced materials in a subsurface system are of interest in nuclear waste disposal research. Bentonite (primarily smectite) can be an ideal buffer material for an engineered barrier system (EBS) of a geologic repository, due to its low permeability, high swelling capability, and high ion exchange capacity (Mills et al, 2023, Chem. Geol., 615, 121214). The microbially-assisted transformation of smectite into illite could have implications to the long-term performance of the EBS. The ideal conditions for illitization are elevated temperatures and pressures and the presence of a potassium source. Studies show that iron-reducing microorganisms can catalyze the illitization reaction without the need for high pressures and temperatures. The ability of *Shewanella oneidensis*, a facultative bacterium, to reduce ferric iron into ferrous iron may initiate the illitization of nontronite (Fe-rich smectite) accompanied by silica release in a geologic environment (Koo et al., 2017, Clays Clay Miner. 65, 410).

Previous work has shown the relationship between reduction of the clay ferric iron component and signs of illitization. This experiment aims to further drive the illitization reaction by adding excess potassium in the reacting aqueous solution (0.25M) and/or by using K^+-exchanged nontronite. We will present our findings from a six-month study on the possible illitization in the interaction between nontronite and *S. oneidensis*. Batch reactors containing nontronite, *S. oneidensis*, and potassium modified M1 media were kept in anaerobic conditions at 30°C, with minimal light exposure. The analytical approaches to identifying possible illite transformation include: solution chemistry quantified by optical emission spectrometry (ICP-OES), iron assay spectrophotometry, crystalline structure of the clay assessed via x-ray diffraction (XRD), microbial populations characterized by genome sequencing, and microbial viability observed through plating. Our results show signs of clay alteration, as there is a visible color change and high dissolved Fe. However, XRD does not provide unequivocal evidence of illitization, as the altered clay seems to become less crystalline (amorphous). SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525- SAND2024-02367A.

SYNERGY OF SEMICONDUCTING MINERALS AND ELECTROACTIVE BACTERIA IN ELEMENT CYCLING AND ENERGY CONVERSION

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Semiconducting minerals are widespread on Earth's surface and have the ability to efficiently convert light to electrons through photocatalysis. The influence of photogenerated charge carriers from these minerals on microbial metabolism and related biogeochemical processes energy conversion remains a subject of debate. In this study, we present two recent investigations indicating their significant impacts on microbial metabolism, energy production and biogeochemical nutrient cycling. In one case, sunlight enhances lactate metabolism in the electrogenic microbe Shewanella oneidensis MR-1 when exposed to the semiconducting mineral hematite (α-Fe_2O_3) under anaerobic conditions. This process accelerates the reduction of Cr(VI) or nitrate. In the other example, the sulfate-reducing microorganism Desulfovibrio desulfuricans G20 utilizes photogenerated electrons from extracellular sphalerite (ZnS) to survive under substrate-limited or depleted conditions. These findings suggest that the light-induced synergy between semiconducting minerals and microorganisms for photo-to-electron conversions and elemental cycling could be a key factor in shaping microbial communities and surface environments on Earth.

MICROBIAL COMMUNITY STRUCTURE AND FUNCTIONAL POTENTIALS IN THE QUATERNARY AS-BEARING CLAY LAYERS AT JIANGHAN PLAIN, CHINA

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Arsenic (As) level in the groundwater of Jianghan plain (JHP), China often exceeds the concentration safe for drinking. To evaluate microbial roles in the As enrichment in the groundwater of JHP, the bacterial and archaeal community structure, abundance and functional potentials as well as geochemical properties of six clay layers of different depths (i.e., A1-A6 from top to bottom) in a borehole (112°34’0”E, 30°36’21”N) were comparatively analyzed. Layers A1 and A2 were oxic and rich in NO_3^- and SO_4^{2-}. The remaining layers were anoxic, of which A3 was rich in Fe, Mn and As, while A5 and A6 were rich in the total organic carbon (TOC). Correspondingly, distinctly vertical stratification of microbial communities in these clay layers was evident, which was significantly impacted by the concentrations of SO_4^{2-}, HCl-extractable Fe(II) and TOC in the clay sediments. Alpha diversity of microbial community decreased significantly as the depth increased. The abundance of total 16S rRNA genes in the clay sediments ranged from 9.26×10^5 to 5.96×10^7 copies/g sediment and decreased substantially with the increased depth. The archaeal abundance was approximately 35.5% in all samples, and was mainly found in A5 and A6 (~ 60%) of which the relative abundance of Bathyarchaeia was ~25%.

Functional analyses revealed that A1 and A2 were dominated by ammonia-oxidizing archaea. The facultative or obligate anaerobic microorganisms capable of dissimilatory reduction of NO_3^-, Fe(III) or SO_4^{2-} were found mainly in A3 and A4, while A5 and A6 were characterized by fermentative bacteria and archaea. The TOC and a variety of small molecule organic acids produced by microbial fermentation in the clay sediments could promote the reductive dissolution of As-rich Fe(III) (hydroxyl)oxides by Fe(III)-reducing microorganisms and reduction of As(V) to As(III) by As(V)-reducing microorganisms. SO_4^{2-}-reducing microorganisms might also mediate reductive dissolution of As-rich Fe(III) (hydroxyl) oxides. Most importantly, heterologous expression of identified *arsC* and *arsM* genes showed for the first time that the Bathyarchaeia could directly reduce As(V) and methylate As(III). Thus, the microorganisms in the clay sediments of JHP play important roles in controlling As transport and transformation in the sediments, which could contribute the As enrichment in the groundwater of JHP.

BIOTITE MICRO-STRUCTURE: RECORDER OF REGIONALLY GEOLOGICAL EVOLUTION

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Our recent work show that the micro-structure of biotite is an excellent indicator for reflecting regional magmatic activities, sedimentary environment, and volcanic system evolution.

Studied biotite from rhyolite were investigated via multiple microanalysis techniques including micro-XRD, electron probe microanalyzer (EPMA), micro Raman spectra, laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS), transmission electron microscope (TEM) and related energy dispersive X-Ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS).

Observation revealed a wide existence of multiple ordered structures (i.e., various polytypes of biotite) and disordered structures. Especially, those biotite particles with chemical zoning always have ordered cores and less ordered rims. It was also observed that the alteration at nanoscale led to a phyllosilicate transformation (from biotite to berthierine) during late sedimentation under reducing conditions. Evidence demonstrates that the coexistence of various short- and long- period polytypes in biotite samples indicates a non-equilibrium crystallization during the oscillation of regionally physical-chemical conditions. The regularly core-rim zoning of biotite are formed in two stages, i.e., stable crystallization of cores as deep phenocrysts and the the epitaxial growth around deep phenocrysts during magma mixing and eruption. This process suggested by biotite structural zone provides evidence for the existence of deep magma chamber and shallow crystal storage (crystal mush) in Long Valley volcanic system. Finally, a weak altered structure at the edge of biotite was observed, which is the first report about the formation of nanoscale interstratified twinning berthierine layers in biotite and sheds light on the transformation mechanism from 2:1 phyllosilicate to 1:1 ones.

In conclusion, the observations and analyses support the typomorphic significance of biotite in recording environmental conditions. We also provide a practice of applying biotite micro-structures to delineate corresponding crystallizing and preserving conditions, and to further model the magmatic system as well as describe regionally geological evolution.

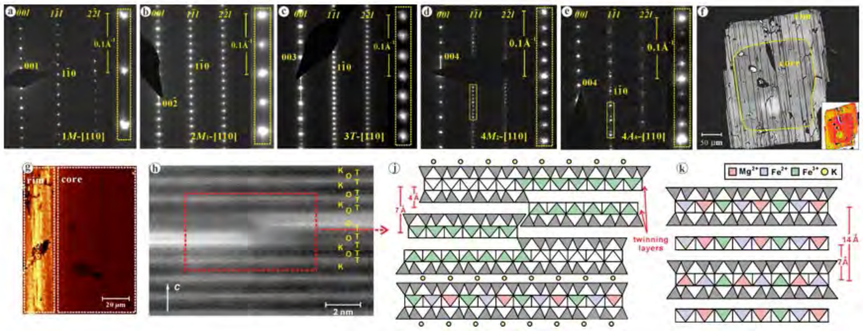

Figure 1. Some micro-structure features observed in biotite samples. (a-c) Basic polytypes of sample biotite, coexisting with **(d-e)** 4M_2 and 4A_8 rare polytypes. **(f)** Chemical zoning of biotite and **(g)** corresponding structure zone represented by Raman map. **(h)** Micro-alteration structure at the edge of biotite and **(g-k)** diagrams of the twinning berthierine structures in (f).

EFFECT OF FE(III)-CONTAINING CLAY MINERALS ON THE METABOLIC ACTIVITY OF METHANOGENS

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Methanogens and Fe(III)-containing clay minerals can co-exist across various environmental settings. Despite numerous studies demonstrating the Fe(III)-reducing capacity of methanogens, our understanding of how microbial iron reduction impacts the metabolic activity of methanogens remains incomplete. To better address this issue, we conducted a series of bench-scale experiments employing iron-containing smectite (montmorillonite or nontronite) as the electron acceptor and methanol as the sole electron donor, with a typical methanogen (*Methanosarcina mazei*) as the reaction mediator. Our findings indicated distinct methane production patterns compared to the biotic controls lacking smectites. In general, montmorillonite with a lower degree of iron reduction promoted methanogenesis by *M. mazei*, while nontronite with a higher degree of iron reduction significantly inhibited it. Proteomic data revealed that the addition of montmorillonite stimulated the methanogenic metabolic pathway, whereas the presence of nontronite up-regulated functional proteins involved in the Fe respiration and down-regulated those linked to methanogenesis. Furthermore, the inhibitory effect of nontronite was attributed to the stress induced by soluble Al produced during bioreductive solubilization. Interestingly, the addition of a low concentration of Fe^{2+} enhanced methanogenesis by *M. mazei*, which is consistent with our findings that montmorillonite increased methane production. Our study sheds light on the metabolic activity of methanogen in the presence of clay minerals, offering significant insights into their interaction dynamics.

Session 5

Mineral-organic matter interactions and their regulation of organic carbon stabilization in terrestrial and aquatic environments

Conveners: Mengqiang Zhu (University of Maryland College Park, USA), Chunmei Chen (Tianjin University, China), Hailiang Dong (China University of Geosciences, Beijing, China), Yuanzhi Tang (Georgia Institute of Technology, USA), and Balwant Singh (University of Sydney, Australia)

THE ROLE OF EXTRACTABLE MINERALS ON MINERAL ASSOCIATED SOIL ORGANIC CARBON

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Minerals (Fe and Al oxides, hydroxides, oxyhydroxides) via mineral surfaces forms an association with soil organic carbon (SOC) termed mineral-organic associations (MOAs) through various interactions is a key to long-term large retention and storage of carbon in the soil.

To measure the relative distribution of SOC associated with pedogenic Fe and Al minerals, soil samples (0 – 20 cm and 20 – 40 cm) were collected from cropped and uncropped soil across New South Wales, Australia and were subjected to separate extraction: dithionite citrate bicarbonate (DCB) (extracts crystalline pedogenic Fe phase), ammonium oxalate (AO) and citrate ascorbate (CA) (extracts short range order (SRO) minerals or organo-metal complexes) and sodium pyrophosphate (NaP) (extracts organically complexed metals or and colloidal or dispersible Fe). The supernatants were analyzed for iron (Fe), aluminum (Al), manganese (Mn) and silicon (Si) using inductively coupled plasma mass spectrometry (ICP-MS). Total carbon (TC) of the soils before extraction and the soil residues after extraction were also analyzed were analyzed using CHN analyzer vario MACO cube Elementar.

Results indicated that the mineralogy of the soils were majorly predominated by kaolinite with high SiO_2 values determined by power X-ray diffractometry (XRD). The predominant extractable minerals for surface and subsurface soil depth where crystalline pedogenic Fe phase SRO Fe phase. Total iron (Fet) was highest followed by the amount of various extractable chemical Fe. The sequence is as follows: $Fe_t > Fe_{dcb} > Fe_{ca} > Fe_{ox} > Fe_{nap}$ while the sequence of Al occurrence is presented as; $Al_{dcb} > Al_{ca} > Al_{ox} > Al_{nap}$. The variables in the principal component analysis explained 83.7% of the total variance. PC1 and PC2 explained 46.4% and 37.4% of the total variance respectively. The major significant factors in PC1 are DCB extractable carbon, while PC2 are Fe_{dcb}, and clay. Pyrophosphate Fe had a significant and positively relationship with total carbon (r = 0.62**, p<0.01), AO extractable carbon (r = 0.34**, p<0.01), DCB extractable carbon (r = 0.38**, p<0.01), NaP extractable carbon (r = 0.47**, p<0.01) and CA extractable carbon (r = 0.31**, p<0.01). Ammonium oxalate Fe and citrate ascorbate Fe had a positive significant relationship with clay (r = 0.41** and 0.52**, p<0.01), TC (r = 0.45** and 0.22**, p<0.01), NaP extractable carbon (r = 0.42** and 0.23**, p<0.01) and CA extractable carbon (r = 0.18**, p<0.05) respectively.

In conclusion, our findings suggest that crystalline pedogenic phase (DCB extractable carbon) accounts for substantial amount of stabilized C retention pool when compared to SRO phases (AO and CA extractable carbon) and organically complexed metals phase (NaP extractable carbon).

PHOTOCHEMICAL ALTERATIONS OF FE-ORGANIC MATTER COPRECIPITATES PROMOTED THE ORGANIC MATTER PRESERVATION OR DEGRADATION: ROLE OF ORGANIC MATTER FUNCTIONAL GROUPS

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To be presented by Yandi Hu if Dawei Cai's visa doesn't come through on time

Soil organic carbon (SOC) plays an important role in the Earth's carbon cycle, and reactive Fe minerals are significant determinants of carbon accumulation. Fe-organic matter (OM) coprecipitates transformation in deep soil under anoxic conditions has been intensively studied, while such mechanisms are insufficient to be applied in surface soil under oxic and sunlight conditions. Here, various characterization techniques were combined to explore the stabilization mechanisms and extended pathways of sunlight-driven Fe-OM coprecipitates transformation. In addition, to investigate the effect of different OM functional groups, sodium alginate (SA), bovine serum albumin (BSA), fulvic acid (FA), and dextran (DET) were selected as model OM compounds containing carboxyl, amine, aromatic, and hydroxyl functional groups which can complex with Fe ions and Fe hydroxide particles. Our results showed that each Fe-OM was not completely dissolved and released in sunlight condition, but reached stabilization after a certain degree of reaction. All Fe-OM coprecipitates released Fe mostly in the colloidal state (>100 kDa, <0.45 m) and OM in the dissolved state (<100 kDa). Interestingly, total organic carbon and ICP-OES analyses showed two trends in the stability of Fe-OM coprecipitates with different functional groups, (1) both Fe and OM were released in Fe-SA, Fe-DET, and Fe-FA systems, and (2) Fe-BSA was very stable under light conditions, with no release of either Fe or OM. Solid-phase XPS and liquid-phase FT-ICR-MS analyses showed that these two trends were due to different photochemical alterations of Fe-OMs coprecipitates. The reactive functional groups (C–O–C/–COOH) of Fe-SA, Fe-DET, and Fe-FA solid phases were degraded, and these OMs with reactive functional groups were released into solution; on the contrary, the reactive functional groups of Fe-BSA solid phases were increased, which led to a tighter Fe-OM complexation and promoted the preservation of OMs. In summary, the properties of organic matter (e.g., functional groups) largely determine the stability of iron minerals to SOC. This study advanced the fundamental understanding of Fe-OM systems, which was essential to predict the fate and transport of OM in the environment.

SUBSTANTIAL AMOUNTS OF REACTIVE FE AND FE-ASSOCIATED ORGANIC CARBON IN COASTAL WETLAND SOILS AT GLOBAL SCALES

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Coastal mangrove and salt-marshes—also termed blue-carbon ecosystems—play an important role in the global carbon cycle. Association of organic carbon (OC) with Fe (oxyhydr)oxides is vital for the persistence of soil organic carbon (SOC). However, the ambulance and speciation of Fe (oxyhydr)oxides as well as their relative importance for OC storage in coastal wetland soils remains unclear. Here, employing both global-scale comparisons across major terrestrial ecosystems and national soil survey of coastal wetlands in China, we show that coastal wetland soils contain greater amounts of poorly-crystalline Fe minerals than upland soils such as forest and grassland soils. Mössbuaer spectroscopy further supports that Fe (oxyhydr)oxides in coastal wetland soils consist mainly of short-range ordered minerals (e.g., nano-geothite) with small amounts of magnetite. Importantly, we find that Fe-bound OC constitutes an equally important proportion of SOC in coastal wetlands as in uplands. The proportion of Fe-bound OC to SOC was positively correlated with poorly-crystalline (oxyhydr)oxides but displayed a negative relationship with exchangeable Ca and Mg, implying a competing role of divalent cations and reactive Fe in controlling SOC accumulation in coastal wetland soils. These findings collectively highlight the important effect of reactive Fe on the preservation of SOC in coastal wetlands at global scales.

IMPORTANCE OF INNER-SPHERE P-O-FE BONDS IN MINERAL-ORGANIC ASSOCIATIONS OF A CREEK SEDIMENT

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Preservation of organic matter and cycling of nutrients is strongly influenced by adsorption to mineral surfaces. The number of bonds and binding mechanisms control desorption, exchange, and probably also microbial degradation of the adsorbates. Strong inner-sphere bonds are known to form between singly coordinated hydroxyl groups of Fe oxides or aluminol-groups of clay mineral edges and carboxyl-, phenol-, and phosphate groups of organic molecules. Here, we investigated the importance of inner-sphere P-O-Fe bonds of mineral organic associations in the sediment of a small, Fe-rich creek by XRF and NEXAFS, using a STXM at the P and C K-absorption edges.

XRF element maps with a spatial resolution of 50 nm showed that Fe was co-located with C, whereas Al was not. We therefore assume that most Fe oxides (ferrihydrites) are completely covered by organic matter, while individual clay minerals are either free of organic matter or covered by less organic matter than the Fe oxides. Relatively high C-signals were found on a clay mineral aggregate. NEXAFS at the C K-edge with a STXM was used to characterize the composition of organic matter on Fe-oxides found in close proximity to bacterial cells. Here, spectra are not similar to spectra of bacterial cells or extracellular polymeric substances, but show considerably more alkyl C and/or aromatic C. Either the fresh bacterial exudates do not have a high affinity to Fe-oxides or there is a strong chemical fractionation during sorption.

Phosphorus was only observed by XRF on ~1/3 of the Fe oxide surfaces by XRF. Corresponding P K-edge NEXAFS spectra usually showed a small pre-edge peak at ~2150 eV, which can be taken as evidence for inner-sphere Fe-O-P bonds. The position of the absorption edge was in most cases in accordance with Fe-complexed organic P compounds. Inner-sphere adsorption of orthophosphates or the presence of phosphate minerals was not detected.

Overall, we found an unexpectedly heterogeneous composition of the mineral surfaces. The binding of organic matter to Fe oxides via the phosphate group obviously plays a role in our sediments, but most of the organic material must be adsorbed by other mechanisms.

MINERAL-ORGANIC ASSOCIATIONS INFLUENCE THE CAPACITY AND VULNERABILITY OF SOIL CARBON STORAGE

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Chemical and physical associations of carbon with minerals play a critical role in soil carbon storage and persistence. At the global-scale, mineral-associated carbon constitutes the largest component of soil organic carbon in non-permafrost mineral soils. However, the capacity and vulnerability of mineral-associated carbon remains uncertain. Leveraging measurements of soil carbon fractions from > 1,100 globally-distributed soil profiles, we present the first spatially-resolved global estimates of mineral-associated carbon stocks and carbon-storage capacity. Critically, we find that the proportion of carbon stabilized through associations with soil minerals can play a dominant role on the emergent climatological temperature sensitivity of bulk soil carbon stocks. Indeed, we find that the temperature sensitivity of particulate carbon can be nearly 30% higher than that of mineral-associated carbon, and up to 55% higher in cooler climates. To improve projections of carbon cycle-climate feedbacks and inform soil management, it is imperative to assess underlying soil carbon fractions to accurately predict the distribution and vulnerability of soil carbon.

INTERACTION BETWEEN PHENOLIC CONTAMINANTS AND DISSOLVED ORGANIC MATTER DURING OXIDATION BY MANGANESE OXIDES

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Manganese oxides are naturally occurring, redox active minerals that can oxidize phenolic contaminants in natural waters and water treatment processes. In environmentally relevant matrices, the oxidation rate of these compounds can be increased or decreased due to the presence of dissolved organic matter (DOM)compared to laboratory studies using buffered, ultrapure water. The mechanisms by which DOM alters the oxidation rate of phenolic contaminants are not well understood. We address this knowledge gap by analyzing the changes to oxidation rate constants by acid birnessite of two brominated phenolic contaminants (i.e., tetrabromobisphenol A and 4-bromophenol) in lake and wastewater effluent samples. Using DOM bulk characteristics (e.g., fluorescence index and electron-donating capacity), we show changes to rate constants are related to DOM composition. Furthermore, we evaluate the role of radical-mediated mechanisms on phenol rate enhancement by examining the incorporation of the brominated contaminants into organic matter using Fourier transform-ion cyclotron resonance mass spectrometry. Our mechanistic investigation provides important insight into the fate and transformation of contaminants in environmentally relevant systems.

ASSESSING THE EFFECT OF MINERALS ON THE OXIDATION OF ORGANIC MATTER BY FENTON CHEMISTRY

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Terrestrial organic matter (TOM) annually contributes 0.7 petagrams (Pg) of carbon to the oceans. Fresh TOM dominated by the remains of C_3 plants has a different chemical and stable carbon isotopic ratio ($\delta^{13}C$) that traditionally has been exploited to distinguish it from oceanic organic matter (OOM). Thus, researchers use two-endmember mixing models to conclude that very little TOM enters the oceans beyond near-shore continental margins and deltaic settings. The fundamental assumption underlying such mixing models is that the $\delta^{13}C$ values of TOM and OOM are minimally altered by degradative processes such as oxidation. In this presentation we will present experiments in which TOM from seven soils was chemically and isotopically transformed by Fenton oxidation. In this process hydroxyl radicals are generated by reacting inherently present metals (e.g., Fe) with hydrogen peroxide. The resulting oxidation of TOM by these radicals can remove functional moieties typical of terrestrial material and lead to a large enrichment in ^{13}C, e.g., oxidize an aromatic-rich peat with $\boldsymbol{\delta}^{13}C$ = -28 ‰ to a marine-like aliphatic-rich residue with $\boldsymbol{\delta}^{13}C$ = -22 ‰. We will then relate the observed carbon losses and $\boldsymbol{\delta}^{13}C$ fractionation kinetics (modeled as Rayleigh distillations) to inherent soil characteristics, such as organic matter (solid-state NMR) composition and mineral composition revealed by X-ray diffraction and ICP-MS analyses after selective dissolutions with pyrophosphate, hydroxylamine, dithionite, and oxalate. The results from this research provide insight to how minerals impact the oxidation of TOM and its conversion to pseudo-OOM with the perspective of developing a new global model for terrestrial-to-marine transfer of organic matter.

CONTROLS OF MINERAL SOLUBILITY ON ADSORPTION-INDUCED MOLECULAR FRACTIONATION OF DISSOLVED ORGANIC MATTER

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The adsorption of minerals induces molecular fractionation of dissolved organic matter (DOM), influencing both the composition of DOM and the organic matter (OM) adsorbed and stabilized by minerals. However, the specific mineral properties governing the extent of DOM fractionation remain unclear. Employing a comprehensive approach that integrates ultrahigh resolution 21 T Fourier transform ion cyclotron resonance mass spectrometry and adsorption isotherms, we delineate the molecular compositional variances underlying fractionation resulting from the adsorption of Suwannee River fulvic acid onto aluminum (Al) and iron (Fe) oxides, as well as a phyllosilicate (allophane) species with divergent properties.

Minerals characterized by high solubility, such as amorphous Al oxide, boehmite, and allophane, demonstrate notably robust DOM fractionation capabilities compared to those with low solubility, such as gibbsite and Fe oxides. Specifically, the former release Al^{3+} ions into solution (0.05-0.35 mM), forming complexes with OM that likely diminish the surface hydrophobicity of the mineral-OM assemblage. This phenomenon enhances the affinity for adsorbing polar DOM molecules. Moreover, interactions with DOM intensify metal release from minerals, exacerbating the effects of mineral solubility.

In the case of sparsely soluble minerals, mineral surface hydrophobicity emerges as the primary determinant of DOM fractionation power, surpassing the influence of solubility. Other chemical properties appear to have comparatively less direct relevance, with surface hydrophobicity and solubility playing pivotal roles in DOM fractionation.

THE ORIENTATION OF GLYCEROL INTERCALATED IN SMECTITE AS A FUNCTION OF HUMIDITY

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Intercalation of organic compounds is an important environmental reaction for preservation or degradation of organic matter but also a strategy for developing hybrid nanocomposites based on clay minerals. The interaction between water molecules, cations and organic compounds in the interlayer control the stability of the intercalated complex. The intercalation capacity is a function of layer charge and the orientation of the intercalated compound with respect to basal planes of smectite. The orientation of intercalated compounds, however, is difficult to measure directly and is thus a source of uncertainty for understanding the properties and stability of intercalated complexes.

To elucidate the influence of cations, layer charge and water content on the orientation of an organic compound in the interlayer, we used glycerol (propane-1,2,3-triol) and a range synthetic saponites with layer charges from 0.8 – 1.4 per formula unit (pfu). Saponite suspensions containing 30% of glycerol were prepared in 1 mM solutions of either CaCl2 or SrCl2 and shaken for 24 h at 90 °C to increase the rate of otherwise sluggish intercalation kinetics. We prepared the oriented slides by filtering method and analysed them in a humidity controlled chamber starting at 90% relative humidity (RH) in steps of 10% until the final rh of 10%, and then back to 90% rh to assess the reversibility of reaction. The whole analysis cycle took approximately 48 h.

We observed that the orientation of glycerol in Ca- and Sr-saturated smectites varies as a function of RH. At high RH, glycerol is oriented parallel to the basal plane (layer-to-layer distance ~16.3 °C) whereas at low RH the glycerol orients vertically with respect to the basal plane (~18.3 °C). There is gradual change in layer-to-layer distance going from high to low RH implying that either interlayer concentration of glycerol increases, or the angle between basal plane and glycerol molecule gradually changes as a function of RH. The lower the layer charge of smectite, the lower the difference between layer-to-layer distance at high and low RH, stressing the interplay between charge density and water content on the orientation of interlayer compounds. The likely process for the variation of glycerol orientation within the interlayer is a simultaneous coordination of secondary hydroxyl group of glycerol to cations and the formation of a hydrogen bond between the primary hydroxyl of glycerol and the hydroxyl groups on the surface of the octahedral sheet at low water activity, and diminished at high. We corroborated this interpretation by observing that the change in molecule orientation occurs also for propane-1,2-diol (high RH ~15.8 °C vs. low RH ~18.0 °C) but not for propane-1,3-diol, which forms a monolayer parallel to the basal plane regardless of RH (high RH ~14.8 °C vs. low RH ~14.4 °C).

Our results suggest that humidity affects the orientation of organic compounds in the smectite interlayer. This finding is important for elucidating the effects of environmental conditions on the stability of intercalated organic compounds and open new avenues for tailoring the properties of hybrid organic-inorganic nanocomposites based on clay minerals.

MINERAL-OM INTERACTIONS AT THE MOLECULAR LEVEL

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Many of us share the understanding that organic matter inputs to soils drive weathering reactions of the mineral matrix and hence create reactive mineral surfaces ready to receive organic adsorbates until an equilibrium stage is reached that is defined by the interplay of the five classic pedogenetic drivers: climate, organisms, relief, parent material, and time.

But there are a few riddles here and holes in our knowledge. For instance, why are mineral surfaces in soil never continuously coated with adsorbates? Why do we often see organics “stack up” on mineral surfaces?

Another, rather fundamental issue is the question: why would a substrate in close contact with a mineral surface be protected against enzymatic or microbial decomposition? We eat our food from plates (= surfaces) – why cant the microbiota do the same, or can they? And if they can, what mechanism would then explain the occasionally reported turnover times for soil organic matter of centuries or even millennia?

A particularly interesting little problem is the matter of the involvement of chemically “labile” organic compounds in the long term cycling of organic matter. Organic compounds present in mineral fractions with particularly slow turnover are frequently of microbial origin, i.e. largely composed of compounds that have traditionally been considered as being chemically labile. The picture that emerges here is that microbial products (also called extracellular polymeric substances, EPS) such as proteins and polysaccharides apparently contribute to the formation of protective microaggregates by “glueing” primary mineral particles and platelets together. The fact that the supposedly “primary” particles in the clay size fraction often tend to be micron-sized aggregates supports a protective mechanism that combines the adhesive (aka “bonding”) effect of extracellular polymeric substances with the physical protection afforded by shielding clay platelets to generate mineral–organic mini-shelters around individual bacteria and bacterial microcolonies.

These and other unresolved issues will be briefly presented and strategies towards their elucidation will be proposed.

APPARENT SATURATION OF SOIL MINERAL-ASSOCIATED ORGANIC CARBON IN THE UNITED STATES

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Soil carbon sequestration is a promising and practical strategy addressing global climate change. It is preferrable to store carbon in the form of mineral-associated organic carbon (MAOC) because of its relatively long turnover time. However, it remains unresolved whether there is a saturation limit for soil MAOC. Using a new dataset from the United States (n > 1,300), we sought to determine whether there is an upper limit of MAOC content. Our data revealed an apparent upper limit of MAOC content at 50 g C kg^{-1} soil when soil organic carbon ranges between 3.2 and 99 g C kg^{-1} soil. In contrast, no upper limit was detected in the content of particulate organic carbon (POM). Using boundary line analysis with the 95th quantile, we also estimated a maximum MAOC loading as a function of clay and silt content at 54 g C kg^{-1} mineral, which aligns with the apparent saturation limit of MAOC content. We will discuss the implications of our findings for soil carbon and soil health management.

MINERALOGICAL CONTROLS ON CLIMATE AND OXYGENATION

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The preservation of organic carbon in marine sediments is fundamentally important for Earth's carbon and oxygen cycles, but the controls on carbon preservation remain unclear. Preservation can be enhanced by limiting exposure of carbon to oxygen, but on continental margins, where the majority of carbon preservation occurs, the relationship between oxygen exposure and burial efficiency is weak. In these environments in particular, additional preservation mechanisms are proposed, including the protection and preservation of carbon with sediment minerals.

We show that the sorption of carboxyl-rich carbon [1] and its chemical transformation [2] with reactive forms of iron and manganese provides a hitherto unrecognised mechanism for the stabilisation and preservation of carbon in sediments, such that the flux of iron and manganese into the oceans may provide a new control on planetary climate and oxygenation [2,3].

References: [1] Curti L., Moore O.W., Babakhani P., Xiao K-Q., Woulds C., Bray A.W., Fisher B.J., Kazemian M., Kaulich B., Peacock C.L. (2021) Carboxyl-richness controls organic carbon preservation during coprecipitation with iron (oxyhydr)oxides in the natural environment. *Communications Earth & Environment* 2:299. [2] Moore O.W., Curti L., Woulds C., Bradley J.A., Babakhani P., Mills B.J.W., Homoky W.B., Xiao K-Q., Bray A.W., Fisher B.J., Kazemian M., Kaulich B., Dale A.W., Peacock C.L. (2023) Long term organic carbon preservation enhanced by iron and manganese. *Nature* 621, 312-317. [3] Zhao M., Mills B.J.W., Homoky W.B., Peacock C.L. (2023) Oxygenation of the Earth aided by mineral-organic carbon preservation. *Nature Geoscience* 16, 262-267.

NANO- AND SUB-NANO SCALE INVESTIGATION ON ORGANIC CARBON DISTRIBUTION IN SOIL MINERALS

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Soil minerals play a critical role in regulating the fate of organic carbon (OC) in the environment through adsorption, precipitation, and sequestration processes. Therefore, a thorough understanding of the preservation mechanisms of OC by minerals is of vital importance in predicting the environmental behavior of OC and the global OC turnover. Overall, the mineral compositions, morphology, structure as well as dynamic environmental conditions are the key factors accounting for the OC stability in soil environment. However, due to the complexity of soil organic matter and dynamic properties of reactive minerals, determining the dynamic interactions between OC and minerals remains challenging.

In this talk, we will introduce our recent efforts in imaging the OC distribution on typical soil minerals (e.g., Fe and Mn oxides) at nano- and even sub-nano scales by employing the spherical aberration corrected scanning transmission electron microscopy (Cs-STEM) coupled with electron energy loss spectroscopy (EELS). Our Cs-STEM results provided direct evidence of the stabilization mechanisms of OC and its species on minerals, and showed how chemical reactivity and physical structure of minerals affected OC interactions with minerals. Our study has also provided insight into the stabilization mechanisms of OC during the Fe oxide transformation processes and OC distribution on Mn oxides during the coupled reactions of adsorption and oxidation. The results would further shed insights into the nanoscale sequestration mechanisms of OC by various soil minerals.

MOLECULAR COMPOSITION OF OGRANIC MATTER IN AN OXISOL DOES ALTER WITH LAND USE CHANGE

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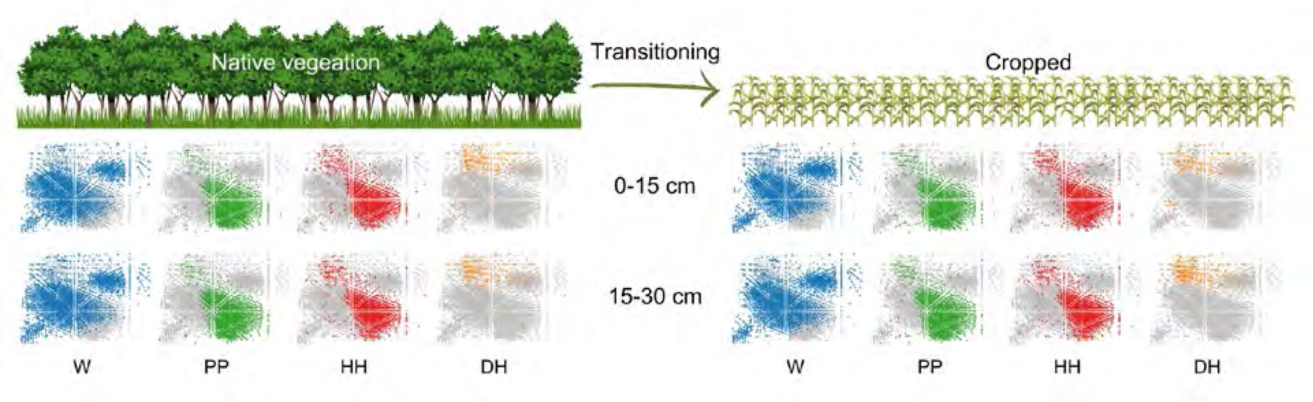
Land use change from native vegetation to cropping can significantly affect the quantity and quality of soil organic matter (SOM). However, it remains unclear how the chemical composition of SOM is affected by the land use change. We employed a sequential chemical extraction procedure to extract four distinct Fe (and Al)-C associations – water-soluble fraction (W), sodium pyrophosphate (PP) to extract organo-metal complexes, hydroxylamine hydrochloride (HH) to extract C associated with short-range ordered (SRO) oxides, and dithionite (DH) to extract C associated with well-crystalline oxides. Soil carbon content was measured after each extraction and extracted SOM was characterized by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). Greater amounts of OM were observed in the PP and HH fractions compared to other fractions, highlighting the importance of organo-metal complexes and SRO in SOM stabilisation. The composition of OM varied in different extracts, with oxy-aromatic compounds being prevalent in the PP and HH fractions, while lipids-like compounds dominated in the DH fraction. Despite a significant decrease in the concentration of soil organic carbon from native vegetation to cropping land use change, there was a little or no influence on the molecular composition of SOM associated with different mineral phases. The results suggest there was no selective loss or preservation of organic carbon compounds in the Fe and Al oxides dominated Oxisol.



STABILIZATION OF ORGANIC CARBON IN TOP- AND SUBSOIL BY BIOCHAR APPLICATION INTO CALCAREOUS FARMLAND

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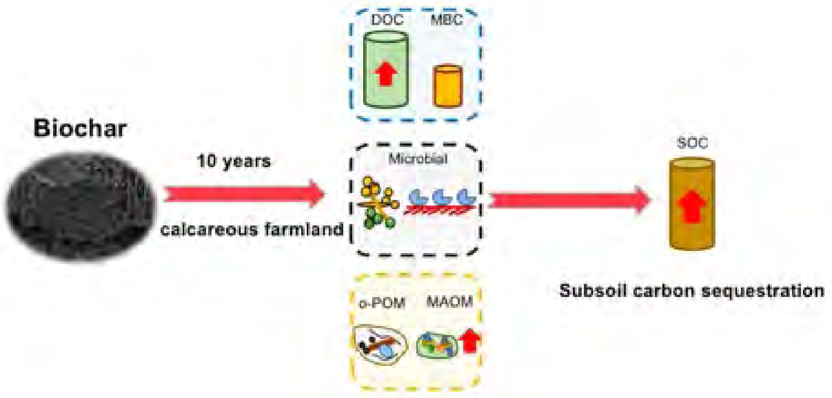
Biochar is recognized for its role in carbon sequestration and emission mitigation in farmland topsoil. However, the mechanisms by which biochar affects soil organic carbon (SOC), its composition, and stability, in the topsoil (0–20 cm) and subsoil (140–160 cm) remain unclear. Applying biochar to the calcareous farmland topsoil significantly increased the topsoil SOC contents by 33 % after a decade, with a 5 % increase in dissolved organic carbon (DOC) contents (topsoil) and a substantial increase of 162 % in subsoil DOC contents. Additionally, humic substances showed an increase of 24 % (topsoil), while low-molecular-weight water-extracted DOC exhibited a remarkable increase of 142 % in the subsoil. The application of biochar significantly increases the contents of SOC, DOC, and microbial biomass carbon (MBC) in the topsoil, as well as SOC and DOC contents in the subsoil. However, a slight decrease is observed for MBC content in the subsoil. Biochar-amended soil significantly suppressed enzyme activity in the topsoil and decreased α diversity in topsoil and subsoil while increasing the content of mineral-associated soil organic matter (MAOM). These observed changes are conducive to stabilizing SOC, emphasizing MAOM formation as a primary mechanism for carbon sequestration in both topsoil and subsoils. This study provides evidence that biochar contributes to the long-term organic carbon sequestration in calcareous farmland, highlighting the importance of considering both topsoil and subsoil when evaluating the dynamic impacts of biochar on SOC.



MINERAL CATIONS MEDIATE FOREST SOC STORAGE IN RESPONSE TO N ADDITION THROUGH PLANT-ORGANO-MINERAL INTERACTIONS

Xia Xu, Chonghua Xu

Zhejiang A and F University

The role of soil organic carbon (SOC) as a regulator of climate has been well recognized, whose gains or losses under nitrogen (N) deposition are still of considerable uncertainty. It is well known that cation availability in soils, as a result of buffering N addition induced soil acidification, mediates SOC storage by influencing plant productivity and SOC stabilization. However, it remains unclear under what conditions plant-mineral and organo-mineral interactions enhance or weaken forest SOC storage. Combing a field experiment and a global meta-analysis, we show that N addition in general stimulated forest SOC storage with increases observed in the low (pH < 4.5) and high (pH > 7.5) soil pH ranges but non-significant changes were found in the intermediate range (4.5 < pH < 7.5). This variation in SOC-N addition feedback could largely attribute to different responses of plant-derived particulate OC (POC) and mineral-associated OC (MAOC) to N addition. POC shifted from neutral at the low to positive at the high soil pH ranges and simultaneously, MAOC increased at the low and high ranges. This switch in SOC-N addition feedback among different soil pH ranges arose dually from plant-mineral interaction indirectly associated with POC as well as organo-mineral interaction directly associated with MAOC. The plant-organo-mineral interactions offer generalizable mechanisms not only to help explain SOC-N addition feedback but also to improve predictions of forest soil C dynamics in response to N deposition.

Keywords: *soil organic carbon; organic carbon components; mineral cations; soil pH; forests; nitrogen addition*

ADSORPTION-DESORPTION OF DISSOLVED ORGANIC MATTER FROM DIFFERENT PLANT RESIDUES WITH DIFFERENT CLAY MINERALS

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Associations of soil organic matter (SOM) with clay minerals have been recognized as a significant process for carbon preservation in soils. However, the nature of association of SOM with different clay minerals is still not well understood. We extracted water-soluble dissolved organic matter (DOM) from decomposed plant residues of four common land use systems in Australia, ie., pine (*Pinus radiata*), Eucalyptus (*Eucalyptus tereticornis*), native pasture, and wheat. DOM composition was characterized using FT-ICR-MS, coupled with soft X-ray spectroscopy. Adsorption and desorption experiments of DOM on six clay minerals were conducted under pH 4.0 and 10 mM NaCl as background solution. The clay minerals included poorly crystalline minerals (ferrihydrite and allophane), metal oxides (goethite and birnessite), and phyllosilicates (montmorillonite and kaolinite). The adsorption and desorption data were fitted to Langmuir and Freundlich equations. Soft X-ray spectroscopy was employed to assess C functional groups involved in adsorption reactions with minerals.

Highly unsaturated aromatic compound group was most prominent in all DOM. Some variations in the abundance of aromatic functional groups (i.e., aromatic and double-bonded C, and aromatic C with side chains) was observed, with DOM from wheat showing the highest and pine the lowest. The poorly crystalline minerals showed the highest adsorption of DOM, followed by metal oxides and least by phyllosilicates. The adsorption of DOM appeared related to mineral properties, such as specific surface area and surface charge, rather than the composition of DOM. The amount of remaining DOM onto minerals after desorption varied among different minerals, however, there was no selectivity in the desorbed DOM with similar abundance of organic functional groups for adsorption and desorption. This study highlights the importance of minerals in SOM stabilization. Despite variations in DOM composition, the affinities of different organic compounds onto minerals are more related to the mineral properties. The desorption strength of the adsorbed organic compounds appears to be similar, and they may not exhibit selectivity for desorption. The consequences of sorption of different DOM to different minerals for stabilization against microbial mineralization needs to be determined.

INCREASE OF HUMIC ACID BIOAVAILABILITY BY HYDROXYL RADICALS PRODUCED UPON OXYGENATION OF FE(II) IN REDUCED NONTRONITE

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Reactive oxygen species, such as hydroxyl radicals (•OH), produced from minerals are considered to accelerate the mineralization and turnover rate of organic matter (OM) in redox-fluctuating environments, but the underlying mechanisms remain elusive. In this study, we investigate the bioavailability of humic acid (HA), a stable OM component, to anerobic microbial communities after HA transformation by •OH produced upon oxygenation of reduced nontronite. Incubation experiments were set up with transformed HA as the sole carbon source and electron donor and nontronite as electron acceptor to anerobic microbial communities.

Results show that transformation of HA by •OH significantly promotes humic acid bioavailability. Specifically, during the initial stage of incubation (0-15d), microbial Fe(III) reduction was coupled with oxidation of transformed HA. However, such redox coupled process was not observed with original HA as substrate. Moreover, acetic acid was also produced during this stage, suggesting that fermentative bacteria could also utilize transformed HA to produce low molecular weight organic acids. These results suggest that HA transformation by •OH increased the bioavailability of HA to both Fe reducing and fermentative bacteria. When Fe(III) reduction process ceased, methanogenesis followed in the experimental groups with transformed HA as substrate (15-30d). Again, no CH4 production was observed in the groups with original HA. The enhanced CH4 production can be attributed to both the production of acetic acid and transformed HA as premium substrates to methanogen. Collectively, these results demonstrate increased bioavailability of humic acid to anerobic microbial communities after its transformation by •OH, which explains the fast turnover rate of OM in redox-dynamic environments.

Session 6

Biogeochemical evolution of Fe and Mn (oxyhydr) oxide and their environmental impacts

Conveners: Tongxu Liu (Institute of Eco-environmental and Soil Sciences, Guangdong Academy of Sciences), Xionghan Feng (Huazhong Agricultural University), Zimeng Wang (Fudan University), and Wei Li (Nanjing University)

INVESTIGATING NATURAL MINERAL TRANSFORMATION PROCESS USING ELECTROCHEMICAL METHODS AND IN SITU CHARACTERIZATIONS

Jung, Haesung[1], Taillefert Martial[1], Yang, Lufeng[2], Chen, Hailong[2]*, and Yuanzhi Tang[1]

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In the study of mineral formation and transformation, it is challenging to replicate the natraul mineralization process in the lab. For example, processes involving ultrahigh temperature and pressure are difficult to achieve in the lab, and some natural processes can spread over long geological time scale, which is impossible to exactly replicate in the lab. However, it is possible to design appropriate lab synthesis procedures to mimic these extremely time-consuming mineralization processes. Particularly, for those that involve redox reactions, electrochemical method can be utilized to greatly expedite the reaction process.

Mn(III,IV) (oxyhydr)oxides (hereafter Mn oxides) are a group of minerals that exist ubiquitously in terrestrial and aquatic environments. Among a variety of polymorphic phases of Mn oxides, tunnel structured todorokite (3 × 3 tunnel size) is one of the most commonly observed phases in natural systems. Yet, laboratory efforts attempting to produce todorokite under low-temperature circumneutral environmental conditions have been surprisingly difficult. Recently, with using a novel cyclic electrochemical method, we successfully achieved the synthesis of todorokite in the lab under ambient temperature and pressure. Ex situ and in situ XRD and EXAFS analysis and electron microscopy results together supported our new hypothesis that todorokite can be formed in natural ambient environments with cyclic redox reactions, which can be driven by the natural cycles such as tidal, daily and seasonal cycles and mimicked by electrochemical redox cycles in the lab[1].

1 Jung, H., et al., *Redox Cycling Driven Transformation of Layered Manganese Oxides to Tunnel Structures.* J Am Chem Soc, 2020. **142**(5): p. 2506-2513.

A NOVEL USE OF ZINC ISOTOPE AS AN ATOMIC TRACER TO REVEAL MOLECULAR-LEVEL INSIGHT INTO ZINC SORPTION MECHANISM ON CALCITE

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Zinc (Zn) is a bioessential trace metal and plays an imperative role in various biological processes, while elevated Zn concentrations may exert toxic effects on lives. Calcite is a widespread mineral on earth, the interaction between Zn and calcite surface critically controls Zn fate in the natural environment.

In this research, batch sorption experiments were conducted under different reaction times, pH values and initial Zn concentrations ($[Zn]_i$), the underlying sorption mechanisms were investigated using a combination of X-ray absorption fine structure (XAFS) spectroscopy, Zn isotope measurement and density functional theory (DFT) calculations. The results demonstrate a continuous conversion from inner-sphere tetrahedral surface complexes (IS Zn_{tet}) to hydrozincite surface precipitate as pH and $[Zn]_i$ increases. A link between Zn isotope fractionation and Zn sorption mechanism was established. At $[Zn]_i$ = 5 μM and pH = 6.5, the $\Delta^{66}Zn_{sorbed-aqueous}$ of +0.40‰ corresponds to IS Zn_{tet} sorption mechanism, at $[Zn]_i$ = 100 μM and pH ≥ 7.5, the $\Delta^{66}Zn_{sorbed-aqueous}$ of +0.20‰ corresponds to hydrozincite precipitation mechanism. The $\Delta^{66}Zn_{sorbed-aqueous}$ of +0.23‰ to +0.37‰ is consistent with the mixture of IS Zn_{tet} and hydrozincite under intermediate conditions, the $\Delta^{66}Zn_{sorbed-aqueous}$ value decreases gradually as the proportion of IS Zn_{tet} decreases and hydrozincite increases.

These results indicate the potential of metal stable isotope as an atomic tracer to probe interfacial sorption processes and provide deep insights into the Zn sorption mechanisms on calcite.

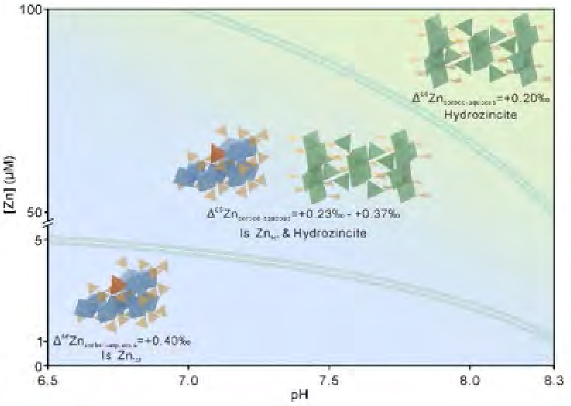

Fig. 1 Schematic diagram of Zn sorption mechanism on calcite in relation to pH and initial Zn concentration ([Zn]i). "IS Zn_{tet}" represents inner-sphere Zn tetrahedra.

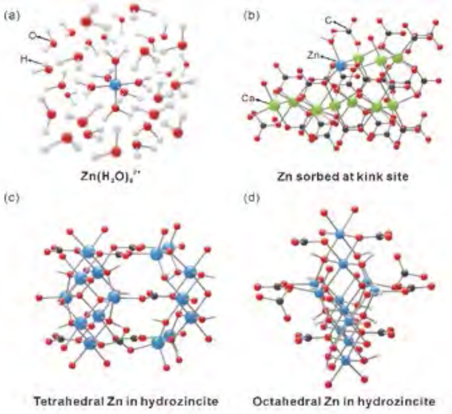

Fig. 2 DFT optimized structural models of $Zn(H_2O)_6^{2+}$ (a), tetrahedral Zn sorbed at kink site (b), tetrahedral Zn in hydrozincite (c) and octahedral Zn in hydrozincite (d).

THE EFFECT OF CRITIC ACID ON THE CATALYTIC OXIDATION OF MN(II) ON FERRIHYDRITE

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Surface-catalyzed Mn(II) oxidation is an important process for abiotic formation of various Mn (oxyhydr) oxides in nature. Previous research has shown that some complex-forming ligands (e.g., citric acid, desferrioxamine B, and tartrate) can significantly bind with Mn(II) to promote its homogeneous oxidation by dissolved O_2. However, there is little to no understanding of the role played by complex-forming ligands in abiotic interfacial oxidation of Mn(II). In this study, the adsorption and oxidation of Mn(II) on ferrihydrite (Fh) surface at a range of citric acid (CIT) concentrations was investigated using batch kinetic studies combined with X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, and wet chemistry analyses. The presence of CIT substantially inhibited the adsorption and oxidation of Mn(II) on Fh, whereas oxidized Mn generated certainly enhanced the degradation of CIT. However, at a high concentration of CIT, the oxidation kinetic of Mn(II) was slightly increased due to ligand-promoted homogeneous oxidation. Moreover, the presence of CIT remarkably altered the distribution and composition of Mn(II) oxidation products by inhibiting the formation of hausmannite on Fh surface and the following auto-catalytic oxidation. At low CIT concentration, the oxidation products were mostly coated on Fh surface with weaker crystallinity and higher Mn AOS, resulting in stronger reactivity. When CIT is greater than 1 mM, Mn(II) oxidation products were mainly distributed in the bulk solution in the form of soluble Mn(III)-CIT/ox complexes, thereby enhancing the mobility of redox active Mn. These results suggested that CIT improved the redox activity of oxidation products and migration of active Mn in the environment although it inhibited Mn(II) oxidation on mineral surface.

HEMATITE-MEDIATED MN(II) ABIOTIC OXIDATION UNDER OXIC CONDITIONS: EFFECTS OF PH AND MODEL QUINONE COMPOUND

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Interactions between manganese (Mn) and iron (Fe) are widespread processes in soils and sediments, however, the abiotic transformation mechanisms and the impact of model quinone compound (anthraquinone-2, 6-disulfonate, AQDS) are not fully understood. Herein, Mn(II) oxidation on hematite were investigated in the absence and presence of AQDS under oxic condition. In the hematite-Mn(II) treatments, Mn(II) oxidation rates increased from 3×10^{-4} to 8×10^{-2} h^{-1} as pH increased from 7.0 to 9.0, whereas hematite enhanced Mn(II) oxidation rates to 1 h^{-1}. In the hematite-Mn(II)-AQDS treatments, Mn(II) was rapidly oxidized, and oxidation rates increased from 4.2×10^{-2} to 8.8×10^{-2} h^{-1} with increasing AQDS concentration from 0 to 1 mM. Interestingly, a co-shell structured nanowire composed of manganite and feitknechtite was observed in the hematite-Mn(II) treatments owing to autocatalytic reactions. Abiotic oxidation of Mn(II) produced granular-like Mn_3O_4, fibrous-like β-MnOOH, and rod-like γ-MnOOH in the hematite-Mn(II)-AQDS treatments. Specifically, in the hematite-Mn(II) treatments, electron transfers between Mn(II) and O_2 occurred on the surface or through bulk phase of hematite, and direct electron transfers in the O_2-Mn(II) complex and indirect electron transfers in the O_2-Fe(II/III)-Mn(II) complex may both have contribution to the overall reactions. For hematite-Mn(II)-AQDS treatments, the proposed mechanism of AQDS-mediated Mn(II)oxidation on a hematite surface is AQDS serving as an electronic medium with semiconductor hematite as a foreign substrate, promoting electron transfer between O_2 and Mn(II) on its surface. The findings provide a comprehensive interpretation of Fe-Mn interaction and the geochemical functions of electron shuttles on the dynamics of redox-sensitive elements, which have implications for the formation of soil Fe-Mn oxyhydroxides with unique properties in controlling element cycling.

COPRECIPITATION OF CR(III)/FE(III) HYDROXIDE IN SOLUTION AND ON MINERAL/ORGANIC SURFACES

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Iron hydroxides are important scavengers for chromium (Cr) via coprecipitation and adsorption processes. These processes can be significantly influenced by the presence of organic matter (OM) and minerals in soils. Here, we studied Fe(III)–Cr(III)-OM coprecipitation under environmentally relevant conditions in solution and on different mineral/organic surfaces. Acetate acid (HAc), bovine serum albumin (BSA), and Suwannee River natural organic matter (SRNOM), were selected as model OM compounds containing –COOH/NH_2 functional group which can complex with Fe/Cr ions and Fe/Cr hydroxide particles. SiO_2 and Al_2O_3 were selected as model soil surfaces with Si-O and Al-O bonds. Our results showed that OM and mineral surfaces significantly affected Fe/Cr hydroxide coprecipitation. More precipitates formed on Al_2O_3 than on SiO_2, due to electrostatic forces between Fe hydroxide polymers and substrates. With Cr adsorption onto SiO_2 surfaces which altered the surface charge of SiO_2, heterogeneous precipitation of Fe/Cr hydroxide particles on SiO_2 was greatly inhibited; while SRNOM adsorption onto Al_2O_3 also altered its surface charge, and promoted heterogeneous precipitation of Fe/Cr hydroxide particles on Al_2O_3. Total organic carbon analysis showed that more than 80% of SRNOM can coprecipitate with iron hydroxide, while no detectable organic carbon within iron hydroxide was observed in the presence of HAc, which implied that the strong complexation between SRNOM with Fe led to its coprecipitation with iron hydroxide. The incorporation of Cr in the lattice and at the surface of the Fe hydroxide precipitates were also greatly controlled by the complexation capability of organics and mineral surfaces with Fe/Cr ions and hydroxide particles. Furthermore, the (de)protonation of minerals and organic coatings on minerals could alter local solution pH, controlling Cr/Fe ratios of the coprecipitates. BSA and SRNOM were also found to affect the crystallinity and stability of the newly formed Fe(III)–Cr(III)-OM complex. This study advanced the fundamental understanding of Fe(III)-Cr(III)-OM/mineral systems, which was essential to predict the fate and transport of Cr in the environment.

CARBONATE-ENHANCED TRANSFORMATION OF FERRIHYDRITE TO HEMATITE IN ALKALINE MEDIA

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Alkaline media widely exist in natural and engineered systems such as semiarid/arid areas and radioactive waste sites. Due to the substantial increased atmospheric CO_2 concentration, carbonate stands to increase in these media. However, how increasing carbonate affects the transformation of poorly crystalline iron (oxyhydr)oxides (e.g., two-line ferrihydrite) under alkaline condition still remains unclear. Here, kinetics of ferrihydrite transformation were evaluated at pH ~10 as a function of [carbonate] = 0-286 mM using synchrotron-based X-ray and vibrational spectroscopic techniques. Results showed that carbonate slowed down the ferrihydrite transformation slightly and suppressed the goethite formation, but promoted the hematite formation regardless of its concentration. At low carbonate addition (11.42 mM), the effect of carbonate on the product formation was obvious due to the weak inner-sphere complex, however, at high carbonate concentration (80-286 mM), the effect was retarded because of the adsorption equilibrium of carbonate as well as the initial carbonate adsorption followed by desorption. Moreover, carbonate modified the morphology of hematite from rhombic to honeycomb and goethite from rod-like to rugby-like due to the inner-sphere adsorption-desorption of carbonate and adsorption of hydroxyl ions on reactive sites of iron (oxyhydr)oxides. Results suggest carbonate can control the transformation/occurrence of iron minerals and have important implications for the biogeochemical cycles of iron and carbon.

AUTHIGENIC TITANIA ALTERED FROM VOLCANIC GLASSES IN MODERN DEEP OCEAN: IMPLICATION FOR TI MIGRATION DURING DIAGENETIC PROCESSES

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Titanium (Ti), a typical rock-forming element, is traditionally considered to be lithophile, incompatible, and fluid-immobile. This study aimed to get comprehensive understanding of the mobility of Ti in volcanic sediments. The element composition and structural characteristics of the volcanic sediment specimens from the Mariana Basin and Marshall Archipelago were systematically examined using multiple micro-analytical methods. Both the specimens consist primarily of mixed-layer illite/smectite, phillipsite, and carbonate-bearing fluorapatite. These composition characteristics are indicative of volcanic glasses that have undergone palagonization processes. Scanning electron microscopy images of the cross section and powdered samples revealed the presence of numerous spherical smectite aggregates enveloped by thick coatings of Ti-rich shells, measuring approximately 450-1000 nm in thickness. Further analysis using transmission electron microscopy confirmed the presence of authigenic titania particles within these Ti-rich shells. Additionally, numerous titania nanoparticles were observed within the pore spaces of the smectite aggregates. The concentration of Ti, as well as the quantity of titania particles exhibited a negative correlation with the degree of volcanic glass alteration, which indicate a potential migration of Ti associated with the aging of smectite and subsequent release into the porewater. Brookite was identified as the predominant titania phase in both the titania shells and the smectite pores, with rutile and anatase occasionally present in the titania shells. This observation suggests that mineral phase evolution occurs continuously during the growth of titania particles, possibly influenced by the heterogeneity of Ti concentration and size-dependent thermodynamic stability of titania. The growth of the titania particles could be largely attributed to crystallization through particle attachment, as supported by the abundant alignment of titania particles in both the titania shell and the pores of the smectite aggregates. For the first time, this work provides solid evidence for the mobilization of Ti and formation of authigenic titania along with the alteration of volcanic glasses in basic and oxygen-rich environments in the modern marine system.

MOBILITY OF METALS IN TYPICAL ROCKS FROM ULTRAMAFIC SUBSTRATES IN NEW CALEDONIA

Dubernet, Chloé[1], Barats, Aurélie[1], Renac, Christophe[1], Gunkel-Grillon, Peggy[2], Mathian, Maximilien*[2], Pattier, France[2] and Gututauava, Kapeliele[2].

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Presented by M. Mathian on behalf of C. Dubernet

The aim of this study is to evaluate the mobility of potentially toxic elements (PTE: Cr, Fe, Ni, Mn, Co, and As) from typical rocks of New Caledonia, i.e. PTE transfers from solids to freshwaters due to water-mineral interactions. Different lithotypes with dominant magmatic, hydrothermal or weathering minerals were sampled in the southern ultramafic massif of New Caledonia. To determine the total metal content of each sampled lithotypes, sample mineralizations were conducted using acids assisted by microwaves. Sequential extractions were also performed to assess the retention of metals into lithotypes during changes of physicochemical conditions (T, pH, Eh). Acid digested samples and extracts were analyzed by ICP-AES (Cr, Fe) and ICP-MS (Ni, Mn, Co, As). Mineralogical characterization of these lithotypes by X-Rays Diffraction (XRD) reveal the occurrence of phyllosilicates and Mn- and Fe- oxides.

PTE concentrations were the lowest in lithotypes covered by pink laterite or hosting black and white serpentinite (21 $g.kg^{-1}$ for Fe, 1,7 $g.kg^{-1}$ for Ni, 0,56 $g.kg^{-1}$ for Mn, less than 0,20 $g.kg^{-1}$ for Cr and 0,05 $g.kg^{-1}$ for Co on average). Comparatively, the PTE concentrations were the highest in the lithotypes covered by iron duricrust, Mn-oxides rich laterite and unconsolidated laterite (in the order of hundreds of $g.kg^{-1}$ for Fe, tens of $g.kg^{-1}$ for Cr and Ni, less than tens of $g.kg^{-1}$ for Mn and less than 2.0 $g.kg^{-1}$ for Co). The results of sequential extractions highlight the strong retention of Fe, Ni, Cr and As in solids, whereas Mn and Co are the most mobile elements, especially under reducing and acidic conditions. In the first three steps of sequential extractions, they can be significantly transferred: 45% of the total Mn and 37% of the total Co. This study indicates that the strong mobility of Mn and Co may stem from specific phyllosilicates (black serpentinite and pink laterite) as well as from Fe and Mn oxides (goethite and birnessite) containing important concentrations of Mn and Co. Attention must also be paid to Fe, Ni and Cr in lithotypes due to their high content. Although, they are demonstrated strongly retained by minerals, their transferable concentrations can still be significant, and thus transfer processes must be taken into account.

POST-OBDUCTION HISTORY OF NEW CALEDONIA: NEW TEMPORAL CONSTRAINTS FROM GOETHITE (U-TH)/HE DATING OF DURICRUSTS IN REWORKED LATERITES.

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New-Caledonia is an archipelago from Southern Pacific where a third of the whole surface is covered by ultramafic rocks due to obduction at *ca* 34 Ma. In contrast with the pre-Oligocene geological history, the post-obduction evolution is not time-constrained. Accordingly, the Neogene and Quaternary paleoenvironmental and paleoclimatic evolution of this diversity hotspot is still poorly known.

The Fluvio-lacustrine Formation of southern New-Caledonia is an intra-montain sedimentary system, the overall sedimentological features point to a fluvial depositional environment with dominant floodplain and subordinate channel sequences. It consists of a basal conglomerate containing peridotite and iron crust boulders (≤1m) a few m thick, and an overlying fining upward (sand to clay size) sequence of reworked iron-rich lateritic material, 50 to 80m thick at most. Occasional light-colored clay levels (kaolinite and nontronite) are also observed. The whole sequence displays evidence for intra-formational iron mobility (pseudo-layering) and locally contains dense horizons of fossil roots or stumps and fossil leaves. The top of the sequence consists of an iron crust, a few dm or m thick, providing evidence for post-depositional weathering. Such features could potentially enlighten the paleo-environmental conditions that prevailed in southern New-Caledonia after the obduction; however, this was still impossible due to the lack of geochronological constraints.

In this contribution, we shall present a new goethite (U-Th)/He geochronological dataset obtained on iron duricrust pebbles from the base of the sequence and samples from its overlying duricrusts, all from outcrops of the Fluvio-lacustrine System. The obtained ages will then be discussed in term of paleoenvironmental and climatic conditions by considering the sedimentary organization and structure as well as the regional geomorphology.

ADSORPTION MECHANISMS OF GLYPHOSATE ON FERRIHYDRITE: EFFECTS OF AL SUBSTITUTION AND AGGREGATION STATE

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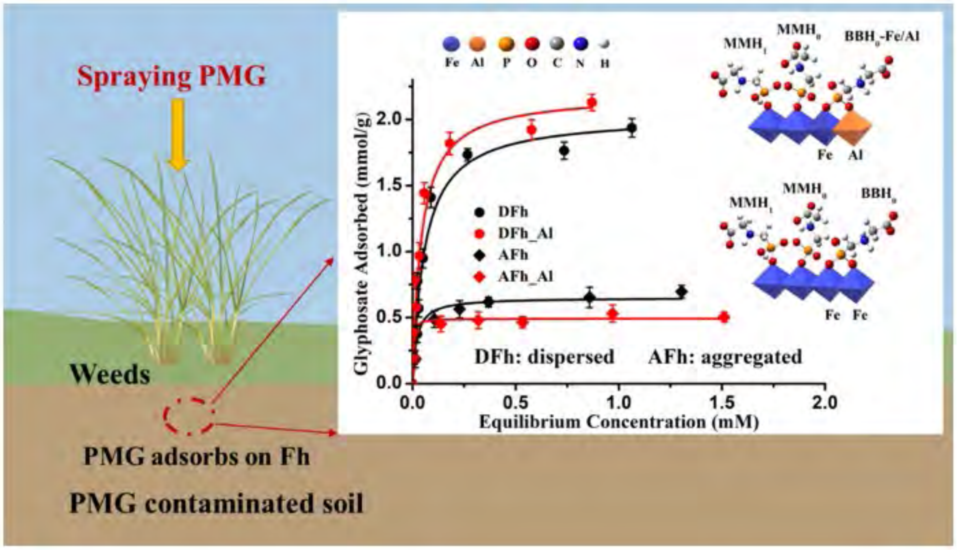
Ferrihydrite is one of the most reactive iron (Fe) (oxyhydr)oxides in soils, but the adsorption mechanisms of glyphosate, a most widely used herbicide, on ferrihydrite remain unknown. Here, we determined the adsorption mechanisms of glyphosate on pristine and Al-substituted ferrihydrites with aggregated and dispersed states using macroscopic adsorption experiments, Zeta potential, P K-edge XANES spectroscopy, in-situ ATR-FTIR with two-dimensional correlation spectroscopy, and multivariate curve resolution analyses. Aggregation of ferrihydrite decreases the glyphosate adsorption capacity. The partial substitution of Al in ferrihydrite inhibits glyphosate adsorption on aggregated ferrihydrite due to the decrease of external SSA, while it promotes glyphosate adsorption on dispersed ferrihydrite ascribed to the increase of surface positive charge. Glyphosate predominately forms protonated and deprotonated, depending on the sorption pH, monodentate-mononuclear complexes (MMH1/MMH0, 77% - 90%) on ferrihydrites, besides minor deprotonated bidentate-binuclear complex (BBH0, 23% - 10%). The Al incorporation and a lower pH both favor the formation of BB complex. Adsorbed glyphosate preferentially forms MM complex on ferrihydrite and preferentially bonds with Al-OH sites on Al-substituted ferrihydrite. These new insights are expected to be useful in predicting the environmental fate of glyphosate in ferrihydrite-rich environments.



MINERAL SURFACE-CATALYZED FORMATION OF MN OXIDES ON MARS

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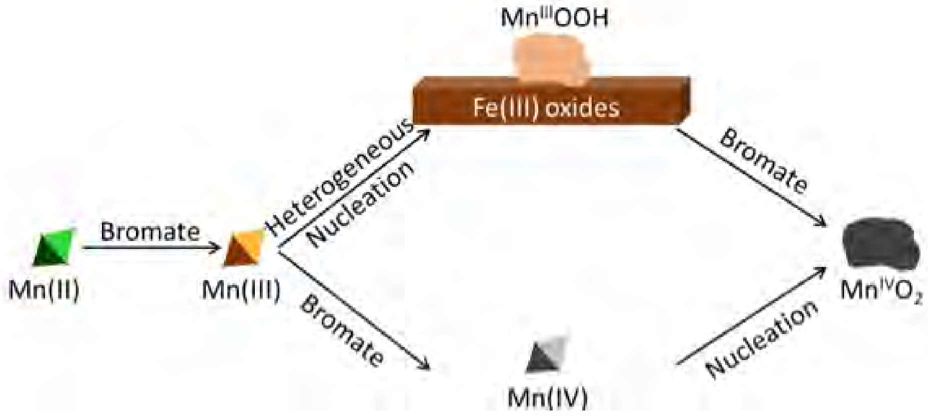
Concentrated manganese (Mn) oxides have been detected on Mars and may indicate an O_2-rich paleoenvironment on Mars because Mn oxides often form through the oxidation of Mn(II) by O_2 on the surface of Earth. Recently, an alternative formation pathway involving bromate (BrO_3^-, a common oxidant in Martian regolith) was proposed, but its kinetics at Mars-like conditions are questionable. In our laboratory simulations, iron (Fe) oxides (hematite and goethite) but not montmorillonite, common minerals on Mars, were found to catalyze Mn(II) oxidation by bromate at low concentrations (1 mM). This reaction is initiated by Fe oxides at the early stage, and subsequently autocatalyzed by Mn oxide products, leading to a mixture of Mn(III)OOH and Mn(IV)O_2 phases. As an intermediate product, Mn(III) OOH rapidly forms because of the surface-enhanced nucleation and growth on Fe oxide surfaces and its higher resistance to oxidation by bromate than Mn(III) ions or clusters, but it can be further oxidized to Mn(IV)O_2 phases. The mineral-surface catalyzed oxidation, favoring both thermodynamics and kinetics, could be a major pathway for Mn oxide occurrence on Mars in the absence of microbial catalysis. Our study also enhances the understanding of thermodynamic and kinetic controls on Mn(II) oxidation.



Schematic for the homogeneous and heterogeneous formation of Mn oxides on Mars

EVALUATION THE REMOVAL OF GLYPHOSATE BY TWO DIFFERENT COLLOIDAL MNO2

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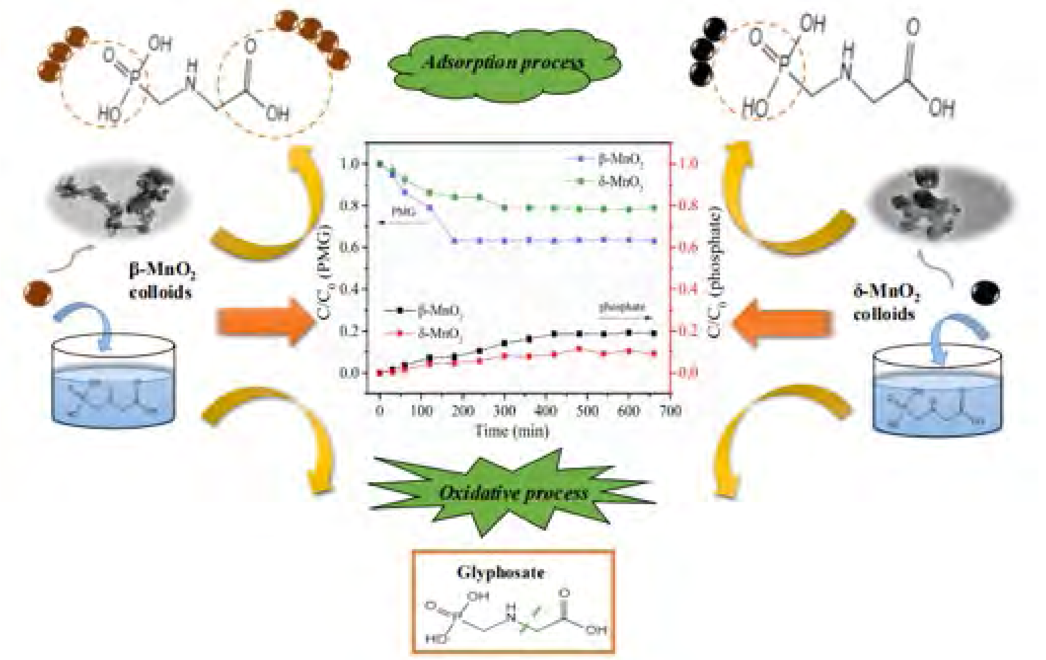
Mn(oxyhydr)oxide, as one of essential clay minerals, has been played significant roles on the transport and fate of contaminants in subsurface environment. However, the differences between nanosized or nanostructured MnO_2 will present different performances. This study investigates the comparative removal of PMG on colloidal β-MnO_2 and δ-MnO_2, the effect of reaction parameters including solution pH, water matrix constituents was evaluated. PMG removal by colloidal β-MnO_2 was higher than that of δ-MnO_2 at pH 4.0. The removal effect of PMG by two colloidal MnO2 within 300min significantly influenced by solution pH. The coexisting metal ion Ca2+ significantly increased PMG removal by colloidal MnO_2, especially colloidal δ-MnO_2. The presence of SO_4^{2-} and NO_3^- had little influence on the PMG removal, whereas phosphate had an obvious inhibitory effect. Humic acid (HA) also inhibited the PMG removal, the removal of PMG by δ-MnO_2 colloids was less affected at low concentration of HA (1mmol). Transformation intermediates were identified to show that PMG degradation involved C−N bond cleavage. δ-MnO_2 colloids showed dramatically slower solid settlementand and better PMG removal efficiencies than that of β-MnO_2 colloids after being placed for hours. Moreover, the TOC evolution displayed a volcano-profile. Therefore, this study provides meaningful information on the functionalization and application of different nanostructured MnO_2.



MOLECULAR COMPOSITION OF OGRANIC MATTER IN AN OXISOL DOES ALTER WITH LAND USE CHANGE

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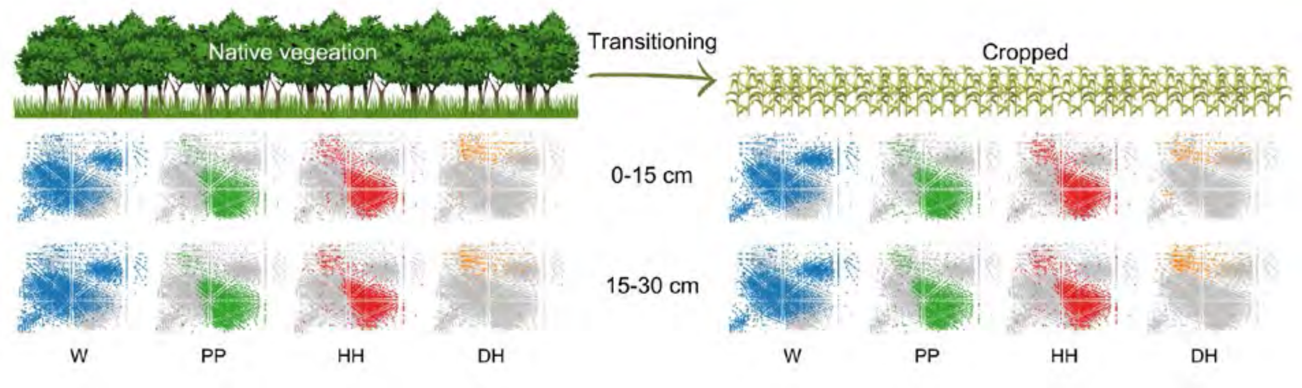
Land use change from native vegetation to cropping can significantly affect the quantity and quality of soil organic matter (SOM). However, it remains unclear how the chemical composition of SOM is affected by the land use change. We employed a sequential chemical extraction procedure to extract four distinct Fe (and Al)-C associations – water-soluble fraction (W), sodium pyrophosphate (PP) to extract organo-metal complexes, hydroxylamine hydrochloride (HH) to extract C associated with short-range ordered (SRO) oxides, and dithionite (DH) to extract C associated with well-crystalline oxides. Soil carbon content was measured after each extraction and extracted SOM was characterized by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). Greater amounts of OM were observed in the PP and HH fractions compared to other fractions, highlighting the importance of organo-metal complexes and SRO in SOM stabilisation. The composition of OM varied in different extracts, with oxy-aromatic compounds being prevalent in the PP and HH fractions, while lipids-like compounds dominated in the DH fraction. Despite a significant decrease in the concentration of soil organic carbon from native vegetation to cropping land use change, there was a little or no influence on the molecular composition of SOM associated with different mineral phases. The results suggest there was no selective loss or preservation of organic carbon compounds in the Fe and Al oxides dominated Oxisol.



Session 7

Geochemical behaviors and mineralization of rare earth elements in near surface settings

Conveners: Hongping He (Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China), W. Crawford Elliott (Georgia State University, USA), Yoshio Takahashi (University of Tokyo, Japan), Yuanzhi Tang (Georgia Institute of Technology, USA), and Xiaoliang Liang (Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China).

CRITICAL MINERALS IN COLD-CLIMATE CLAYS: REGOLITH-HOSTED RARE EARTH ELEMENTS IN POLAR DESERT BASINS (DRY VALLEYS, ANTARCTICA)

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Rare earth elements (REEs) are critical materials for high-tech applications, including low-carbon energy technologies. Regolith-hosted ion-adsorption deposits (IADs) supply most heavy REEs exploited globally (e.g., South China IADs supply ~80% of all HREEs). IADs mostly form via (sub)tropical weathering of igneous bedrock that produces lateritic clay minerals (e.g., kaolinite, halloysite) onto which REEs are weakly adsorbed. Despite the "criticality" of REEs, gaps remain in understanding formation of regolith-hosted REEs, including questions ranging from adsorption mechanisms at atomic scales to clay mineral development and elemental concentration in m-scale to km-scale weathering systems.

Here, we focus specifically on polar-region weathering profiles and REE behavior. We share results of mineralogical and geochemical characterization of supra-permafrost regolith from both intermittent and perennial brine ponds (VXE-6 Pond and Don Juan Pond, respectively) occurring in xeric, endorheic basins of the McMurdo Dry Valleys, Antarctica.

At the site of the shallow, transient VXE-6 brine pond, we document cm-scale mineralogical and chemical changes in the upper 24 cm of sediment, including distinct variations in REEs. At 4–7 cm depth, we document a finer-grained horizon comprised of poorly crystalline aluminosilicates (similar to Al-rich phlogopite or mica) as well as ferric oxides/hydroxides, indicative of chemical weathering and leaching. This horizon is characterized by REE abundances roughly equal to those of the average upper continental crust (AUCC), but notably elevated (15–48%) above REEs at any other depth in the 24-cm-thick regolith profile.

At the shallow but perennial Don Juan Pond (Earth's most saline lake), we document 100-m-scale mineralogical and chemical changes from the center to 300 m SW of the lake. Sediment major and trace element variations indicate a transition from dominantly chemical alteration processes at the center of DJP to physical alteration processes away from the lake. REE concentrations show a trend of increasing abundances with increasing distance from DJP: the 10-cm regolith profile at the center of DJP has the lowest REE abundances (depleted relative to AUCC) and the profile furthest from DJP has

the highest REEs (abundances ~equal or slightly depleted relative to AUCC; slightly lower than those at VXE-6’s 4–7 cm horizon).

Our documentation of REE leaching and concentration in endorheic basins of Antarctica’s Wright Valley carries implications for aqueous alteration and chemical cycling in cold, water-limited settings on Earth, and in planetary analog environments such as on Mars. Understanding REE behavior is important to critical resources on Earth, and also to planetary exploration and the potential for in-situ resource utilization on the Moon, Mars, and beyond.

RARE EARTH ELEMENTS IN THE GEORGIA KAOLIN DEPOSITS.

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Kaolin ore deposits are found in the late Cretaceous and in the early Tertiary sedimentary rocks in the upper Coastal Plain in Georgia. These kaolins comprise the leading domestic source of kaolins. They were formed by the combined effects of sedimentological processes followed by in-situ chemical weathering. The mined kaolins are found as lens within sand rich sediments of the Oconee Group. These kaolin lenses are found and mined from the Cretaceous Gaillard Formation (Buffalo Creek Member) and Eocene Huber Formation (Jeffersonville Member). Rare earth elements (Sc, Y, and La-Lu) are found in both the fine clay fraction as well as in the coarse fractions informally called “grit” of the Buffalo Creek Member. They are also found more abundantly in the Buffalo Creek Member. The fine fraction (< 45 μm) of the Cretaceous Buffalo Creek Member kaolins contain both primary and secondary light (La, Ce, Nd) REE phosphate minerals (Cheshire et al., 2018). The coarser grit fraction is enriched by 50 to 150 times in the heavy (Y, Dy-Lu) REE relative to their concentrations in Upper Continental Crust (UCC, Elliott et al., 2018). These HREE are found primarily in xenotime (YPO_4) and xenotime overgrowths on zircon (Boxleiter and Elliott, 2023). The redistribution of the REE into secondary REE phosphates and xenotime overgrowths demonstrated the mobilization of the REE from their original mineral hosts. The REE are “critical” metals as they are vital constituents for many technologies. The mined kaolins and the bauxites interbedded within these kaolins represent novel domestic REE resources.

Cheshire et al., ACS Earth and Space Chemistry, ***2***, 506-520.

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Boxleiter and Elliott, Clays Clay Miner, ***71***, 274-308.

ENRICHMENT AND FRACTIONATION OF RARE EARTH ELEMENTS (REES) IN ION-ADSORPTION-TYPE REE DEPOSITS: CONSTRAINTS OF AN IRON (HYDR)OXIDE–CLAY MINERAL COMPOSITE

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Ion-adsorption-type rare earth element (REE) deposits are the source of more than 90% of global heavy REEs (HREEs). Thus, understanding the ore genesis of REEs, particularly the distribution characteristics and enrichment mechanisms of HREEs, is vital for efficient exploration and mining of ion-adsorption-type REE deposits worldwide. The characteristics and petrogenesis of bedrock, and the aqueous mobility of REEs, are known to be important factors controlling REE accumulation and fractionation in the weathering crust of REE deposits. However, the effect of REE adsorption on secondary minerals, which is a crucial step in deposit formation, remains poorly understood.

This problem was addressed by the study described herein, which involved a systematic analysis of the complete weathering profile (78 m) of the Renju ion-adsorption-type REE deposit in South China and a simulated adsorption experiment. X-ray diffraction, Mossbauer spectrometry and transmission electron microscopy analyses were conducted to identify the mineralogical phase composition and microscopic morphology of the fine-grain component. Analysis revealed that clay minerals and iron oxides usually form composites, which restrict the enrichment and fractionation of REEs. The clay minerals in the composite are primarily illite, kaolinite and halloysite, while the iron oxides are primarily ferrihydrite, goethite and hematite. Mineralogical phase of the composite changes from feldspar/illite-ferrihydrite/goethite to kaolinite/halloysite-goethite/hematite and finally to kaolinite-hematite.

In the fine-grain component of the humic and completely weathering layers, REEs of ion exchangeable fraction account for approximately 25% and 80%, respectively, and that of Fe-oxyhydroxides combined fraction account for approximately 75% and 20%. In the humic layer, the enrichment of Ce results in a high light-rare-earth-element (LREE) content. In the completely weathering layer, the fractionation of ion exchangeable REEs changes from LREE-rich to heavy-rare-earth-element (HREE)-rich with increasing depth, while the Fe-oxyhydroxide combined REEs remain HREE-rich. The enrichment and fractionation of the ion exchangeable REEs are primarily controlled by clay mineral–REE interactions and eluviation-illuviation processes, but those of Fe-oxyhydroxide combined REEs are affected by the phase and crystallinity of iron oxides and the pH of the weathering crust. These results aid in understanding the mechanism of REE enrichment and fractionation by iron oxide-clay mineral composites in ion-adsorption REE deposits.

EVALUATION OF CLAYS AND CLAY-RICH SEDIMENTS IN THE SOUTHEASTERN UNITED STATES AS POTENTIAL RARE EARTH ELEMENT & LITHIUM FEEDSTOCK MATERIALS

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Identifying unconventional domestic sources of rare earth elements (REEs) and lithium is important because of U.S. dependency on importation of these critical minerals. Recent studies have shown that clays and clay-rich sediments (kaolin, ball clay, bentonite, and organic shale) contain significant amounts of REE+Y+Sc (REE+) and Li. This study focuses on the potential for clay resources found in the Southeastern United States to support the domestic critical mineral supply chain.

Samples of kaolin (N = 7), bentonite (N = 2), organic shale (N = 7), and ball clay (N = 8) were collected and analyzed for REE, Y, Sc, and Li concentrations using ICP-MS (EPA 200.8) following complete digestion (ASTM D6357). The REE+ concentrations in kaolin samples ranged from 141.96 – 565.29 ppm, with an average of 317.24 ± 143.01 ppm. Bentonite sample REE+ contents ranged from 196.93-518.6 ppm, with an average of 357.765 ± 227.46 ppm. Organic shale samples ranged from 163.76 – 431.68 ppm REE+, with an average of 291.48 ± 87.8 ppm. Ball clay REE+ contents ranged from 226.42 – 407.01, with an average of 309.30 ± 57.86ppm. Average Li concentrations were highest in ball clay (66.13 ± 34.03ppm) and organic shale samples (56.71 ± 31.28ppm), and lowest in bentonite samples (10.9 ± 7.63 ppm).

Of the feedstock materials analyzed, 10 individual samples and 3 sample types (kaolin, bentonite, and ball clay) had REE+ contents >300 ppm. Organic shale had the lowest average REE+ concentration. Moderate correlations were found between Y and CaO, P_2O_5, and Sr (r = 0.68, 0.67, 0.73, respectively), suggesting phosphate hosts for these elements. A moderate correlation was also found between Al_2O_3 and Ce (r = 0.53), Pr (r = 0.59), and Nd (r = 0.60), indicating clay mineral hosts for these elements through adsorption. Further characterization of the samples will be conducted to better understand the geochemical behavior and extractability of REE and Li from these materials, using XRD to determine major and minor mineral contents and SEM-EDX analysis and micro-XRF mapping to identify trace mineral/REE associations.

REE DISTRIBUTION IN GNEISSIC REGOLITHS OF THE SOUTH CAROLINA PIEDMONT: EVIDENCE FOR CERIUM AND EUROPIUM REDOX MOBILITY IN THE CRITICAL ZONE

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One mechanism contributing to the accumulation of rare earth elements (REE) involves supergene enrichment, wherein primary REE-bearing minerals undergo oxidation and hydrolysis in response to seasonal cycles of wetting, drying, biological respiration, and organic matter production. To gain a deeper understanding of this process, eleven deep weathering profiles (~8 meters) from the Piedmont region of the Southeastern United States were analyzed for mineralogy, chemistry, and textural properties. Chemical alteration indices of the deepest saprolites varied from 95 to 65, with factors such as land plant cover (including cultivated crops, regenerative pine, and deciduous trees), parent rock, hillshed order, and recent anthropogenic erosion considered as potential influences. A general trend of increasing total REE content was observed in the B-horizons, ranging from 30 to 1048 ppm. Ce anomalies (Ce/Ce* = 3Ce/(2La+Nd)) and Eu anomalies (Eu/Eu* = 2Eu/(Sm+Gd)) were assessed at all depths in the profiles. Across all profiles, regardless of absolute REE concentrations, the ratio (Ce/Ce*)/(Eu/Eu*) was found to be lowest in the argillic horizons, with increases occurring in the A-horizons and C-horizons. It is suggested that oxidized Ce^{4+} and Eu^{3+} released from hydrolysis are adsorbed onto Fe (oxyhydr) oxide, kaolinite, and interstratified clay surfaces, which are predominant clay-sized minerals. Microbially mediated low pH and organic-acid-rich conditions in the A-horizon may preferentially reduce, chelate, and mobilize Eu, while also affecting Ce^{3+} to a lesser extent. A broader trend of increasing (Ce/Ce*)/(Eu/Eu*) with higher hillshed order indicates a geomorphic influence on the extent of redox weathering. Long-term monitoring of CO_2 and O_2 concentrations in 5-meter-deep profiles in the same area reveals seasonal winter patterns of dysoxic and CO_2-rich conditions, most pronounced in deciduous plots and progressively less pronounced in pine and cultivated plots. This pattern correlates with rooting densities, which vary with plant cover type (deepest in deciduous and shallowest in cultivated plots). Apart from the mineralogy of the parent material and plant cover, other mechanisms affecting REE concentrations include biological uptake, erosion, hydrolysis reactions with groundwater, chelation, lessivage, adsorption to clay minerals and (oxyhydr)oxides, and precipitation as nanophases.

EFFECTS OF PHOSPHATE ON RARE EARTH ELEMENT (REE) UPTAKE BY KAOLINITE

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Inorganic and organic ligands play critical roles in controlling the mobilization and redistribution of REEs during weathering and development of secondary REE deposits. This study investigates the effects of phosphate on the sorption of REEs on kaolinite surface at near neutral pH conditions.

Co-sorption and sequential sorption experiments on kaolinite were conducted using Y as a representative REE in the presence of phosphate. The evolution of Y and P solution concentration was monitored. The morphology, mineralogy, and local coordination environment of reacted solids were characterized using a range of complementary techniques, such as X-ray diffraction, scanning electron microscopy, high resolution transmission electron microscopy, and solid state nuclear magnetic resonance spectroscopy. The results revealed two types of phosphate species on kaolinite surfaces, inner-sphere surface complex and a ternary surface complex. The interfacial interactions among Y, phosphate, and kaolinite surface suggest the involvement of complex surface sorption, ternary complexation, and surface nucleation/precipitation processes in controlling REE fate and mobility during weathering and redistribution.

ADSORPTION OF RARE EARTH ELEMENTS ON DISTINCT PLANES OF KAOLINITE

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Regolith-hosted rare earth element (REE) deposits are predominant repositories for critical heavy REE (HREE). However, the formation mechanism, particularly the atomic-level adsorbed state of REE on kaolinite (the primary host for REE) in weathering crusts has never been directly observed. Here, we use atomic force microscope (AFM) to study adsorption characteristics and high-resolution AFM (HR-AFM) to visualize the atomic-level adsorption of both light REE (LREE) and HREE on distinct planes (i.e., Si-basal and Al-basal planes) of kaolinite in aqueous solutions. We suggest that REEs are truly adsorbed on Si-basal plane in weathering crusts (pH=4~6.5), in a zigzag arrangement. Furthermore, Si-basal plane exhibits a higher affinity for HREE than LREE, which contributes to REE fractionation. This study, from an atomic view, visualizes the adsorption of REE on different planes of kaolinite, offering a deeper insight into the enrichment and fractionation mechanisms of REE in the mineralization process of regolith-hosted REE deposits.

Session 8

Iron Redox Processes in Clays and Clay Minerals

Conveners: Joseph W. Stucki (University of Illinois at Urbana-Champaign, USA)
and Anke Neumann (Newcastle University, UK; PSI, Switzerland)

MOLECULAR H_2 GENERATION *VIA* OXIDATIVE DEHYDROGENATION IN FE(II)-PHYLLOSILICATES AND THEIR H ISOTOPE SIGNATURE

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Dehydroxylation and dehydrogenation are two competing reactions of Fe(II)-bearing phyllosilicates occurring upon their heating. The former reaction produces one H_2O molecule from two OH groups, leaving one oxygen in the structure. Dehydrogenation employs electron transfer between ^{VI}Fe(II) and hydroxyl H, resulting in the oxidation of octahedral Fe(II) and generation of H radicals, which - under O_2-free ambient conditions – form a H_2 molecule at the crystal surface. With ambient O_2 present, dehydrogenation results in H_2O formed by hydroxyl (mineral) H and ambient oxygen, and thus the excess H_2O in respect to dehydroxylation. Dehydroxylation and dehydrogenation are separate reactions, resulting in different structural alterations, albeit acting simultaneously, which often produces misinterpretations. Those two thermal reactions can be distinguished quantitatively and separated kinetically: with dehydrogenation preferred at slow heating rates and dehydroxylation at fast ones. Also, oxidizing atmosphere enhances dehydrogenation.

Depending on the interlayer environment and width, dehydroxylation of phyllosilicates may or may not result in H isotope fractionation within the residual hydroxyls. Dehydrogenation always results in H isotope fractionation, much stronger than that during dehydroxylation, leading to deuterium enrichment in the structural hydroxyls and thus controlling the evolution of H isotope composition of the released H_2 and/or H_2O. Such a strong fractionation implies a specific model of proton hopping through the structure and long-range electron transfer, throughout the 2:1 layer, not only in the interlayer. The differences and implications between oxidative dehydrogenation in the 2:1 layer and the hydroxyl interlayer sheet (ie. in chlorites) are discussed based on Fe(II)-Fe(III) transition and H isotope fractionation.

MICROBIAL REDUCTION OF FE(III) IN NONTRONITE: ROLE OF BIOCHAR AS A REDOX MEDIATOR

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Biochar naturally occurs in soils and sediments, but its role in Fe redox cycling is poorly known. In this study, bioreduction experiments were conducted with lactate as the electron donor, Fe(III) in nontronite (NAu-2) or ferric citrate as the electron acceptor, and *Shewanella putrefaciens* as the Fe(III)-reducing bacterium in the absence and presence of biochar. High biochar concentrations promoted but low concentrations inhibited Fe(III) bioreduction. When NAu-2 was replaced with ferric citrate, while the rate was enhanced, the extent of bioreduction remained unchanged at low biochar concentration but declined at high biochar concentration. These different redox behaviors can be explained by four factors: (1) the electron shuttling role of biochar; (2) the electron buffering capacity of biochar; (3) the effect of biochar surface on cell distribution; (4) the effect of biochar on cell attachment and growth. Without biochar, the electron transfer pathway is from cells directly to Fe(III) (Pathway 1). However, with biochar, there is a second pathway (Pathway 2), i.e., from attached cells through biochar to Fe(III). At low biochar concentrations, the efficiency of Pathway 1 decreases because some cells are diverted to biochar surface, but this deficiency is not made up by Pathway 2 because of physical separation between biochar and NAu-2. Therefore, when biochar receives electrons from attached cells, it cannot transfer them to NAu- 2, thus retaining a proportion of electrons. Possible cell clumping on biochar surface may decrease effective cell concentration and thus pose additional inhibition. However, in soluble Fe(III)-citrate complex, Pathway 2 is still effective, because there is no physical barrier between biochar and soluble Fe(III). The electron shuttling role of biochar actually increases the rate of Fe(III) bioreduction. As biochar concentration increases, large surface area of biochar spreads out cells and increases the probability of encounter between cells and NAu-2 particles. Thus, both pathways are effective. Increasing biochar concentrations result in fewer electron retention per gram of biochar. Possible cell growth would further enhance Pathway 2. Therefore, the overall result is the enhanced Fe(III) bioreduction. However, for soluble Fe(III)-citrate complex, both pathways may be impaired because of toxicity to cells, which would inhibit Fe(III) bioreduction. As biochar accumulates in soils, the role of biochar is expected to greatly impact Fe redox reactions and other environmental processes.

FORMATION OF FE- AND MG-RICH 1:1 PHYLLOSILICATES: INFLUENCE OF PH

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In the context of nuclear waste geological disposal, the neoformation of phyllosilicates have been observed at the vitrified waste-steel overpack and steel casing-claystone interfaces. The thermodynamic constants of these phases are not well-established due to their limited availability in Nature. Thus, a synthesis in laboratory can be foreseen to obtain samples in a sufficient quantity and with controlled chemical composition. It can then allow to verify geochemical models used to predict the evolution with time of such engineered system. In general, the synthesis conditions of clay minerals (kaolinite, smectites) by hydrothermal method are well established. However, the synthesis conditions of iron-rich 1:1 tri-octahedral phyllosilicate are not well known.

In this study, we investigated the formation of iron and magnesium rich 1:1 type phyllosilicates (M/Si molar ratio of 1.50) in function of pH. The hydrothermal method was used. The treatment was carried out for 2 days at 160 °C. Synthesis products were characterized by powder X-ray diffraction, Mössbauer, Raman and infra-red spectroscopies, transmission and scanning electron microscopies. The formation of precursor was followed during 2 hours by pH and conductimetry measurements.

Results showed that the two systems, $FeO-SiO_2-H_2O$ and $MgO-SiO_2-H_2O$, differed in terms of products obtained with increasing pH. Above pH 11, in $MgO-SiO_2-H_2O$ system, antigorite-like (1:1 phyllosilicate) phase was neoformed whatever the pH. In $FeO-SiO_2-H_2O$ system, serpentine-like phase (1:1 phyllosilicate) was synthesized below pH 11, and both, serpentine and 2:1 type phyllosilicate phase, were obtained above pH 11. The differences in both systems will be discussed in terms of species solubility and speciation in aqueous solutions.

IRON REDOX PROCESSES IN CLAYS AND CLAY MINERALS

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Iron redox processes play a crucial role in the behavior and properties of clays and clay minerals, influencing their environmental, geological, and industrial significance. This paper provides a comprehensive review of the mechanisms, factors, and implications of iron redox reactions within the context of clays and clay minerals. Key aspects covered include the interplay between iron oxidation states (Fe^{2+} and Fe^{3+}), mineralogy, environmental conditions, and microbial activity in controlling redox transformations. The influence of redox processes on the structure, reactivity, and stability of clays and clay minerals is discussed, highlighting their importance in various natural and engineered systems. Moreover, the implications of iron redox dynamics on pollutant fate and transport, nutrient cycling, and soil fertility are examined. Insights from this review contribute to a better understanding of the intricate interplay between iron redox chemistry and clay mineralogy, with implications for diverse fields including environmental science, geology, and materials science.

MICROBE AND MINERAL INTERACTION DURING FREEZE-THAW CYCLES

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Microbial association with Fe-reduction in Fe-bearing minerals significantly improves our understandings of mineral diagenesis, elemental cycling, biomineralization, and deep biosphere. These reactions, however, have never been elucidated at the low to freezing temperature, typical in cryosphere. We present that structural Fe in nontronite (NAu-2) and maghemite (γ-Fe_2O_3) can be reduced by *Shewanella vesiculosa*, isolated from sea ice in Antarctica, in the freezing and thawing process (-10 °C to 15 °C), and soluble form of Fe is released through the reductive dissolution of bioreduced minerals. The activity of biotic Fe-reduction at various temperatures and the consequent mineralogical and geochemical modification of both minerals will be discussed.

FORMATION OF MIXED STRUCTURES OF 2:1 TYPE PHYLLOSILICATES AND LEPIDOCROCITE (Γ-FEOOH) IN PADDY SOIL

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Various iron hydroxides are present in soil. Generally, these iron hydroxides are very fine and amorphous or low crystalline, resulting in a large surface area and high reactivity, deeply involved in the adsorption of trace components and microbial activity. It is believed that in paddy fields, iron hydroxides undergo dissolution and precipitation due to changes in redox potential caused by field water management during rice cultivation. Representative examples of such iron hydroxides include amorphous or near-amorphous ferrihydrite, as well as goethite (α-FeOOH) and lepidocrocite (γ-FeOOH). However, it is difficult to clearly confirm their presence in soils using bulk analysis techniques such as XRD, and their details remain largely unknown. In this study, by observing paddy soil samples mainly using FIB-TEM/STEM, we found that lepidocrocite with a layered structure is formed at a high density inside 2:1 type phyllosilicates such as smectite. Additionally, we found that in the areas around the soil surface where cementation occurred due to the leaching from pure-iron powder dispersed on the soil, a “mixed structure” of smectite and lepidocrocite close to the unit layer level was formed.

The paddy soil samples were obtained from the plow layer of a paddy field (Nagaoka City, Niigata Prefecture, Japan) after draining (December 2020). The Fe content in the dried soil was approximately 5 wt.% and the major clay mineral was iron-containing smectite (beidelite). On the soil core section, stained areas with brownish mottled contrast were observed in the dark green soil, and μ-XRF confirmed the enrichment of iron in the areas. Thin film samples were prepared by FIB, and observations and analyses by TEM/STEM revealed that ferrihydrite, which appeared amorphous and dendritic was observed in the iron-stained areas, and a layered substance considered to be hydroxylated iron, was formed within the microcleavage of the smectite. The iron hydroxide was determined to be lepidocrocite based on the lattice spacing. On the other hand, lepidocrocite was hardly observed within the phyllosilicates in non-iron-stained areas. Therefore, it is suggested that ferrihydrite and lepidocrocite are essential components of the iron stain, and that 2:1 type phyllosilicate minerals in the soil, such as smectite, serve as a substrate for the formation of lepidocrocite.

In another experiment, agricultural-grade iron powder was spread on the surface of moist soil and left at 30 °C for 7 days, with the surface moistened with distilled water to prevent drying during this time. As a result, orange-colored iron hydroxides were formed around the iron powder, determined to be lepidocrocite by μ-XRD and electron diffraction. The soil immediately below the iron powder was also cemented with orange-colored iron hydroxide. It was confirmed by TEM that lepidocrocite intercalated with smectite as well as ferrihydrite was formed in this portion.

REDOX PROCESSES OF CLAY MINERAL-BOUND IRON

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Reactions at and with clay minerals significantly contribute to the biogeochemical cycling and environmental fate of contaminants, elements, and nutrients in soils and sediments and have even been connected to the advent of life on Earth. In addition to sorption/desorption and acid/base catalysis, redox reactions at clay mineral surfaces are key processes. In naturally occurring clay minerals, redox reactions are mainly linked to the presence of the environmentally ubiquitous element iron in clay mineral octahedral and tetrahedral sheets. This talk will summarize own work and that of others to date on electron transfer reactions to and from clay mineral iron and concentrate on the mechanistic understanding of clay mineral iron redox reactions and their quantitative description with the aim to better predict contaminant fate and remediation. An outlook on current and emerging intriguing questions pertaining to clay mineral redox reactions will conclude this keynote presentation.

FE(II)-PILLARED MONTMORILLONITE

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Redox-activated smectites have much potential as agents for scrubbing undesirable pollutants from aqueous solutions. Flow-through reactors are important devices for remediating large volumes of contaminated water, but the utility of redox-activated smectites in such systems is hindered by the very small particle size of the clay, which inevitably requires low permeability filters to contain the smectite, resulting in extremely slow flow rates. One possible way to overcome this problem is to pillar the smectite and thereby increase its particle size while preserving its high surface area, thus enabling the use of higher through-put membranes. The objectives of the present study were (1) to pillar Wyoming montmorillonite (Mnt) with Fe(III) and determine the optimum level of pillaring, (2) to reduce Fe(III) to Fe(II) in both the Mnt structure and in the pillar, and (3) to test the reactivity with a known pollutant in aqueous solution. Fe pillared smectites were prepared, giving pillaring levels of 0, 5, 10, and 15 mmole Fe/g Mnt. Pillaring was confirmed by XRD and XRF, and the Fe(III) state in the pillar was confirmed by Mössbauer spectroscopy. The zeta potential increased with increasing Fe pillar content from -43 to + 17 mV; and, the greater the pillaring extent, the greater the particle size. Samples were reduced with CB-buffered Na-dithionite, and the relative number of Fe(II)-O-Fe(III) entities formed was estimated from the color change. In unpillared Mnt, little or no color change was detected by the eye, which is normal for this low-Fe smectite in which Fe ions are scattered throughout the octahedral sheet with few residing adjacent to one another, thus precluding the color response. In the pillared Mnt, the color changed from yellow-orange in the unreduced samples to blue to light blue in the reduced samples, confirming that Fe(III) in the pillar was reduced to Fe(II) and that the pillar remained intact. The oxidation state and speciation of Fe in the pillars was examined by Mössbauer spectroscopy and confirmed the presence Fe(II) in the pillars. The reactivity of the samples with nitrate (NO_3^-) was measured. The hypothesis was that the increased zeta potential of the more highly pillared sample should attract the nitrate and reduce it, whereas the less positive zeta potential should repel the nitrate. The results allowed testing of the hypothesis.

ADVANCING UNDERSTANDING OF BIOTITE WEATHERING REACTIONS: XAFS AND *AB INITIO* SIMULATION INSIGHTS

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This study investigates the electronic states of iron (Fe) in weathered biotite, a common mica mineral, using X-ray absorption fine structure (XAFS) measurements and *ab initio* molecular calculations. Chemical reactions such as adsorption, precipitation, and redox affect the environmental behavior of elements. Knowledge of the chemical state and local structure of the elements is necessary to understand the causes of changes in their behavior. XAFS, including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), is a valuable tool due to its sensitivity. However, interpreting XANES spectra is challenging mainly due to the resolution limitation. The study employs high-energy resolution fluorescence detection (HERFD)-XANES to detect subtle differences in Fe speciation, overcoming the limitations of conventional XANES. Artificially weathered biotite samples show systematic changes in XANES and HERFD-XANES spectra, indicating the oxidation of Fe(II) to Fe(III) during weathering. The spectra were consistent with XANES spectra simulated by *ab initio*, validating the biotite and weathered biotite models. The detailed microstructures of the cesium-adsorbed weathered biotite were obtained using the models.

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THE CRITICAL ROLE OF MINERAL FE(IV) FORMATION IN LOW HYDROXYL RADICAL YIELDS DURING FE(II)-BEARING CLAY MINERAL OXYGENATION

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In subsurface environments, Fe(II)-bearing clay minerals can serve as crucial electron sources for O_2 activation, leading to the sequential production of $O_2^{\bullet -}$, H_2O_2 and •OH. However, the observed •OH yields are notably low and the underlying mechanism remains unclear. In this study, we investigated the production of oxidants from oxygenation of reduced Fe-rich nontronite NAu-2 and Fe-poor montmorillonite SWy-3. Our results indicated that the •OH yields are dependent on mineral Fe(II) species, with edge surface Fe(II) exhibiting significantly lower •OH yields compared to interior Fe(II). Evidence from *in situ* Raman, Mössbauer spectra, and chemical probe experiments substantiated the formation of structural Fe(IV). Modeling results elucidate that the pathways of Fe(IV) and •OH formation respectively consume 85.9–97.0% and 14.1–3.0% of electrons for H_2O_2 decomposition during oxygenation, with the $Fe(II)_{edge}/Fe(II)_{total}$ ratio varying from 10% to 90%. Consequently, these findings provide novel insights into the low •OH yields of different Fe(II)-bearing clay minerals. Since Fe(IV) can selectively degrade contaminants (e.g., phenol), the generation of mineral Fe(IV) and •OH should be taken into consideration carefully when assessing the natural attenuation of contaminants in redox-fluctuating environments.

MULTI-SCALE ELECTRON TRANSFER PROCESSES ASSOCIATED WITH FE-BEARING CLAY MINERALS

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Fe-bearing clay minerals represent an important electron source or sink for the redox reactions in the subsurface. Electron transfer (ET) processes associated with Fe-bearing clay minerals cover multiple scales: (1) within the mineral particle between interior to edge sites, (2) at the interface between mineral surface and aqueous species as well as between different mineral or solid surface, and (3) across a long distance mediated by a series of minerals and electron shuttles. Previous studies have well documented the ET at the interface between clay mineral surface and aqueous species. Here we present the results from our group about the short-distance ET from reduced interior to oxidized edge within nontronite particles and from reduced nontronite particles to ferrihydrite particles, and about the long-distance ET from reduced to oxidized zones of experimental columns filled with real clayed sediments. Our results implicate that Fe-bearing clay minerals are both “geo-battery”, which can store and release a large number of electrons during redox oscillations, and “shuttles”, which can function as the carriers for electron hopping between different sites with redox potential gradients.

Session 9

Honoring Dr. Goro Uehara and his work in variable charge clay systems in Hawai'i & beyond

Conveners: Jonathan L. Deenik (University of Hawai'i at Mānoa, USA), Susan E. Crow (University of Hawai'i at Mānoa, USA), Tai McClellan Maaz (University of Hawai'i at Mānoa, USA), Luiz F. Pires, (State University of Ponta Grossa, Brazil), and Kristy I. Lam (University of Hawai'i at Mānoa, USA)

FROM VOLCANIC ASH TO ABUNDANT EARTH: UNDERSTANDING ANDISOL ORGANIC MATTER DYNAMICS AND SOIL HEALTH IN TWO MINERALOGICALLY DISTINCT MOISTURE REGIMES ON HAWAI'I ISLAND

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High concentrations of poorly and non-crystalline minerals in Andisols (i.e., volcanic ash-derived soils) favor greater soil organic matter (SOM) accumulation than in phyllosilicate-dominant soils, yet the abundance and distribution of SOM vary greatly across volcanic landscapes. In Hawai'i, steep climatic gradients drive disparities in mineralogy between soil suborders. High leaching intensity in Udands increases metal oxide concentrations while drier conditions in Ustands favor the formation of halloysite, allophane, and imogolite. Differences in mineralogy play a major role in (sub)tropical Andisol organic matter dynamics and soil health that is largely unexplored. In this study, we measured the effects of moisture regime and current land use on SOM physical fractions and soil health in Andisols and identified carbon (C) and nitrogen (N) pools that predict soil health. We collected soil samples from 24 sites across two moisture regimes (Udands and Ustands) and three land use intensities (cropland, pasture, forest) on Hawai'i Island. We quantified the C and N distribution of three SOM size and density fractions, including mineral-associated organic matter (MAOM), heavy particulate organic matter (HPOM), and light particulate organic matter (LPOM). We then measured nine dynamic soil properties and integrated them into a soil health score. We found that Udands contained greater MAOM-C and HPOM-C content (mg C g soil^{-1}) and higher fraction C:N ratios than Ustands. Pastures held greater proportions of C and N in the sand-sized HPOM fraction than croplands and forests, implying the presence of dispersant-resistant soil aggregates in HPOM. These aggregates represent a mineral control on Andisol SOM dynamics that should be considered when parameterizing ecosystem models that leverage soil size and density fractions. Carbon stabilized in MAOM and N held in the POM fractions best predicted the soil health score ($R^2 = 0.82$), showing the importance of the mineral-associated fraction in Andisol soil health.

DR. GORO UEHARA: FROM CLAY MINERALS TO GLOBAL SOLUTIONS

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Dr. Goro Uehara was born in 1928 in North Kohala, Hawai'i Island where he experienced the hardships of life on a sugar plantation and came to appreciate the importance and value of agriculture. After receiving his BS from the University of Hawai'i, he served in the U.S. Army in Korea and returned to Hawai'i to complete a MS degree in soil science. He earned his Ph.D in soil science from Michigan State University and returned to Hawai'i where he served as a globally recognized professor of soil science and agronomy in the Departments of Agronomy and Soil Science and Tropical Plant and Soil Sciences from 1959 to 2011. In his early career he was engaged in pioneering research on the physical and chemical properties of variable charge clays in highly weathered tropical soils and their behavior in relation to soil structure, water retention and transmission, and nutrient retention. This phase of his career culminated in his acclaimed book entitled "The Mineralogy, Chemistry, and Physics of Tropical Soils with Variable Charge Clays" published in 1981. Dr. Uehara devoted his career to what he referred to as the three purposes of research: 1) to understand process in nature; 2) to use this understanding to make predictions; and 3) to enable others to use these predictions to manage the environment in a sustainable and equitable manner. This axiom of research guided his work and accomplishments. While Dr. Uehara's contributions to elucidating the unique properties of variable charge clays were pioneering and critical to improving our understanding the soils of the tropics, his work in international development with a focus on the global south was remarkable and exceptionally impactful. He was the lead scientist on numerous projects supported by the U.S. Agency for International Development including the Benchmark Soils Project (1974-1983), the International Benchmark Sites Network for Agrotechnology Transfer (IBSNAT) Project (1983-1993), the TropSoils Project/Soil Management CRSP (1984-2007), and a technical assistance and capacity building grant in East Timor (2003-2006). He was the beloved advisor for 34 graduate students and served on thesis committees for another 100 graduate students. In the words of his friend and colleague Hal McArthur "Goro was just as much at home digging soil samples in a farmer's field as he was in the office of the Prime Minister of Sri Lanka discussing recovery strategies following the 2004 Tsunami."

DIGGING DEEP: AGGREGATE STABILITY ACROSS SOIL DEPTHS IN A FERRIHYDRITIC ANDISOL

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Minerals play an important role enhancing the persistence of aggregates and their constituent soil organic matter. Understanding the factors that control soil carbon dynamics is critical for predicting and mitigating the impacts of climate change. This study investigates changes in aggregate stability and aggregate size distribution along a depth gradient in a ferrihydritic Andisol. We characterized the physicochemical and biological attributes across an aggregate size gradient at three depths and subjected macroaggregates to sonication and oxidation treatments. This approach allowed for us to compare organic vs. mineral contributions of aggregate stability and identify factors that drive macroaggregate stability. Our results indicate that ferrihydritic Andisols exhibit robust aggregate stability across all soil depths, and suggest a shift in the primary binding agents from organic matter in surface layers to minerals in subsoils. The ability of the deepest soils to resist chemical oxidation suggests that mineral binding agents played a dominant role in stabilizing macroaggregates in deep soils, contrasting with the significant role of organic binding agents in topsoil. We also found that the water stable aggregate size distribution was correlated with pyrophosphate extractable aluminum, fungal richness, and the distribution of carbon and nitrogen.This nuanced understanding contributes to our knowledge of the mechanisms influencing aggregate stability at different depths. Our findings highlight the importance of considering both biological and mineralogical components in the processes behind carbon persistence and turnover, which is essential for developing strategies aimed at conserving soil organic matter as greenhouse gas concentrations increase.

MODELING PEDOGENIC THRESHOLD OCCURRENCE IN HAWAIIAN VOLCANIC SOILS ACROSS A CHRONOSEQUENCE FROM ~5 KY TO ~4 MY OLD

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Pedogenesis, or the process of soil formation, is often described by a system of pedogenic thresholds where soil properties change rapidly and soil process domains where soil properties change very little across an environmental gradient (time, climate, topography, etc.). Pedogenic thresholds are a response to the exhaustion of a buffer system which accentuates a drop in soil pH and is followed by a descent into the next dominant buffer system and soil process domain. From a soil fertility perspective, the most important soil domain is the domain buffered by primary mineral weathering and cation exchange which, along with buffering pH, also supplies nutrients and nutrient retention to the soil. The exhaustion of the primary mineral pool through progressive weathering leads to a clear pedogenic threshold (a "fertility threshold") between this primary mineral buffered domain and subsequent domain buffered by Al-hydrolysis and characterized by low fertility. Hawai'i's wide gradients in climate (both rainfall and temperature) and geologic age, while relatively consistent parent material and biotic component, offer a study system in which the effects of climate and time on pedogenesis can be examined effectively. Here, we use a semi-quantitative statistical approach to identifying pedogenic thresholds across a chronosequence of 8 substrate ages (5, 15, 20, 120, 150, 450, 1400, and 4100 ky). For each substrate, we sampled on intact volcanic shield surfaces and analyzed soils along climosequences from ~-1000 to ~3000 mm/yr of water balance (precipitation minus evapotranspiration). We identified the pedogenic "fertility" threshold for each substrate by analyzing soil properties that indicate mineral weathering, leaching, and soil fertility. We found that this fertility threshold moves to a lower and dryer water balance as the substrate gets older and follows a logarithmic decay pattern. We also suggest that the occurrence of these fertility thresholds can be modeled with an empirical equation, which can then be used to spatially predict the upper boundary of this fertile, primary mineral weathering process domain as a function of water balance and geologic age.

WHAT IS ISOTIC ANYWAY? A SOIL TAXONOMY MINERALOGY CLASS REVISTED

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The concept of isotic soils and it's use in Soil Taxonomy at the family level was first introduced in 1996 to capture soils that did not meet the criteria to classify as having amorphic mineralogy or andic intergrades but exhibited soil properties akin to andic soils. These properties include having a colloidal fraction dominated by short-range-order mineralogy, higher than normal pH-dependent charge, and a greater ability to fix soluble P than other soils. Isotic soils key out at the family level under mineralogy class in sections D and E of Soil Taxonomy. Some have argued that there is an apparent lack of interpretive value of the isotic versus the mixed mineralogy class, and that it is difficult to apply the class based on easily observed landscape/landform characteristics and correlation guides. The purpose of this study is to reassess not just the necessity of the isotic class, but to investigate the setting, context, and proxies for soil-forming factors associated with isotic versus mixed mineralogy taxa. In doing so, we will determine if there is any practical significance to both its use and the properties used to classify the isotic class. The KSSL laboratory data and other landscape data will be extracted, and various statistical analyses performed to compare differences in defining isotic properties, phosphate retention, and selective dissolution data between pedons classified as isotic or mixed mineralogy. Results of our assessment to date will showcase which soil properties—both those that are and are not currently used to classify isotic soils—appropriately capture the purpose of the isotic class and what gaps and questions remain to direct continuing analyses.

MINERALOGICAL AND MANAGEMENT EFFECTS ON SOIL PORE SIZE DISTRIBUTION OF AN ALLOPHANIC ANDISOL AND HALLOYSITIC MOLLISOL

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Soil pores are often used as a proxy to understand soil water retention behavior. The soil water retention behavior and soil porous system vary among different soil types due to their differences in soil texture, clay mineralogy, and organic matter content. Management practices such as tillage can alter the soil porous system. However, certain clay minerals promote aggregate stability due to their chemical and physical characteristics, and make some soils more resistant to alterations in the soil porous system . This study addresses the following questions: (1) does the total porosity and pore contribution (macro-, meso-, micro- and ultramicro-pores) differ between clay mineralogy?; and (2) how does management (cultivation) affect pore size distribution? This research examined the soil porous system changes in two soil types with contrasting clay mineralogy (allophanic, halloysitic) and two management types (cultivated, uncultivated). Results showed that the allophanic soil behaves differently from the halloysitic soil. Main conclusions are 1) the allophanic soil had the largest increase in mesopores under cultivation; 2) the halloysitic soil exhibited the largest increase in the micropore region; and 3) the general behavior (i.e., modality) of the pore size distribution changes are contrasting in the allophanic and the halloysitic soils. The former is likely due to the combined effects of cultivation intensity, soil organic matter loss, and irreversible drying. Overall, the distinct behavior of the allophanic soil suggests that non-crystalline clay mineralogy drives pore size distribution changes and that mesopores contribution could be a potential indicator of soil damage in allophanic Andisols. Understanding the effects of clay mineralogy on soil porous system changes can elucidate soil water retention behavior.

SOIL MINERAL AND CHEMICAL GRADIENTS STRUCTURE MICROBIAL COMMUNITIES IN AN HAWAIIAN VOLCANIC ASH SOIL ACROSS DEPTH AND SPACE

Tai McClellan Maaz, Casey McGrath, Christian Fullmer, Caitlin Pries Hicks, Susan Crow, Nhu Nguyen

Volcanic soils have a very high potential to sequester carbon due to their unique mineralogical and physical properties. Therefore, more attention should be given to microbial dynamics and conditions that promote and protect carbon stabilization in volcanic soils. We examined the prokaryotic (bacteria and archaea) and fungal communities along chemical, biological, and physical gradients in volcanic soil on the island of O'ahu. Both communities of prokaryotes and fungi changed significantly vertically with soil depth. Key soil properties were important drivers of microbial community structure, including soil carbon, nitrogen, non-crystalline minerals, active iron index, and pH. Bacterial and fungal communities exhibited similar ordinations along one axis of resource constraints, with carbon/nitrogen alleviating resource limitations and non-crystalline minerals/higher active iron index imposing greater limitations. A second, weaker axis was also observed in both communities, which was characterized by environmental conditions (pH, temperature). These conditions are connected with soil depth. Microbial networks were also shaped by the active iron index—a key gradient driving compositional changes. Our results support the emerging organo-metallic glue hypothesis that the interactions with microbes along soil environmental gradients provide the conditions needed to alter *and* sequester carbon deep in the volcanic soil.

X-RAY COMPUTED TOMOGRAPHY FOR SOIL PORE CHARACTERIZATION

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X-ray computed tomography (XCT) is a well-established, non-destructive investigation technique that has been in use since the mid-1970s. Although initially developed for medical purposes, it was quickly employed in other fields of knowledge. In particular, CT was first used in the early 1980s for determining soil bulk density and soil water content for soil science studies. Afterward, the CT technique was adapted to develop high spatial resolution scanners exclusively dedicated to material analysis. In recent years, CT scanners have advanced significantly, enabling time-resolved CT scans on nanometer scales. Also, the development of powerful computers and better image analysis programs permitted significant advances in soil science studies related to the architecture of the soil's inner structure. With the introduction of 4D tomography, the technique is also employed nowadays to investigate dynamic processes inside the soil structure. The dynamic of solute transport and water conduction and retention is directly related to soil structure. Many agents are essential in forming the soil structure, with clays playing a central role due to their high capacity to establish bonds between soil particles. Clay particles contribute to form the intra and inter-aggregate soil structure, which encompasses pores in vast classes of sizes. In this way, CT scan has been recognized as a valuable technique to link different physical processes in porous media to soil aggregation characteristics. Distribution of soil pores by size and shape, soil pore connectivity and tortuosity, soil pore morphology, soil pore function, and soil water retention properties are some important soil physical properties that can be measured using the CT technique. The use of CT in soil science has grown exponentially in Brazil and worldwide. In our presentation, we selected some studies we conducted in our study group to address some answers to important questions related to soil pore characterization using the CT technique.

EVALUATING ORIENTATION OF CLAY MINERALS BY POWDER X-RAY DIFFRACTOMETRY

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Clay minerals are analyzed using powder X-ray diffractometry (PXRD) owing to crystalline material. When clay minerals are filled into a sample holder for PXRD with Bragg-Brentano optics as a conventional measurement method, the preferred orientation occurs due to pressure filling. Clay minerals have a layer structure, and the layers are aligned in a particular direction by pressure filling. Thereby, the intensities of specific diffraction peaks are varied[1]. In this study, the variation of diffraction intensity of montmorillonite as clay minerals in sediment sample was investigated. Two samples, the montmorillonite reference sample having a cleavage plane and the layered structure, and fluorite having a cleavage were used for the evaluation.

Fluorite (Flu; natural stone from China) and montmorillonite (Mon; JCSS-3101, reference sample) were refilled several ten times using an aluminum sample holder. Each sample was analyzed using an X-ray diffractometer (Rigaku, MiniFlex600). Sediment sampled at the Tama River watershed in Japan was used as an actual sample.

The intensity distributions of normalized X-ray diffraction intensity ratio for Flu ((111) / (220)) and Mon ((001) / (021)) are shown in Fig. 1. Diffraction intensity ratio of both crystalline phases showed larger values than each normalized relative intensity ratio ((Measured intensity ratio) / (Reference intensity ratio) = 1.0) due to showing preferred orientation. However, the intensity ratio of Mon was more varied than that of Flu. Also, the X-ray diffraction intensity of Mon (001) showed a bimodal distribution in the actual sample. Clay minerals are expected to have different interlayer distances in the structure due to their formation process. Therefore, random interstratification and heterogeneous composition would affect diffraction intensity variations.

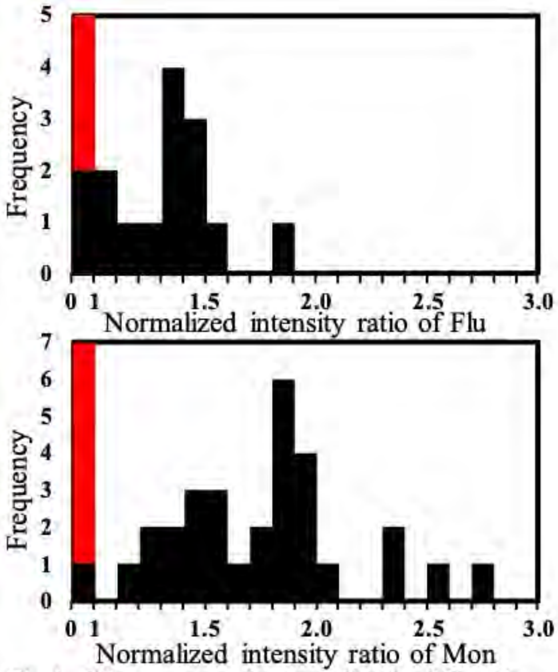

Fig.1 Histogram of normalized diffraction intensity ratio of Flu ((111) / (220)) and Mon ((001) / (021)).

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Session 10

Functional soft materials from clays and related compounds Topics: Colloids, Nanocomposite gels and plastics, Self-assembly, Soft materials

Conveners: Nobuyoshi Miyamoto (Fukuoka Institute of Technology, Japan),
Yasutaka Suzuki (Yamaguchi University, Japan), and Fengxia Geng

PARTICLE SIZE EVALUATION OF CLAY-DYE COLLOID BY MEANS OF TWO-PHOTON FLUORESCENCE CORRELATION SPECTROSCOPY

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Hybridization of organic compounds with exfoliated clay nanosheets improves photofunctionality. However, the hybridization causes the clay nanosheets to become hydrophobic, resulting in aggregates. Two-photon fluorescence correlation spectroscopy (TP-FCS) is a technique to determine the size and number of particles by measuring the speed at which fluorescently labeled particles move. In this study, by applying this technique to hybrid dispersions, direct observation of the aggregation behavior of hybrids was attempted. Synthetic saponite (SSA) was used as the host clay mineral and fluorescent 2,5-dimethoxy-1,4-bis[N-methyl-4-(1,3-butadien-1-yl)pyrinium]benzene iodide as the organic compound. The light source for TP-FCS measurements was an ultrashort pulse fiber laser with a wavelength of 1030 nm, and the fluorescence signal was acquired for 30 s.

Figure 1 shows the autocorrelation curves for hybrids with different dye loadings, which denoted %CEC which is percentage of dye adsorption versus cation exchange capacity of clay, 1 to 10%CEC (top) and 10 to 50%CEC (bottom). Hybrid colloid with 1 to 10% CEC showed almost the same decay of the autocorrelation curves. On the other hand, the decay time became slower with increasing %CEC above 20%CEC. This indicates that the particle size is 90-100 nm and SSA are dispersed for 1-10%CEC, while aggregated particles of 200-500 nm were observed for 20-50 %CEC. Thus, it was found that TP-FCS can be used to evaluate hybrids in colloids.

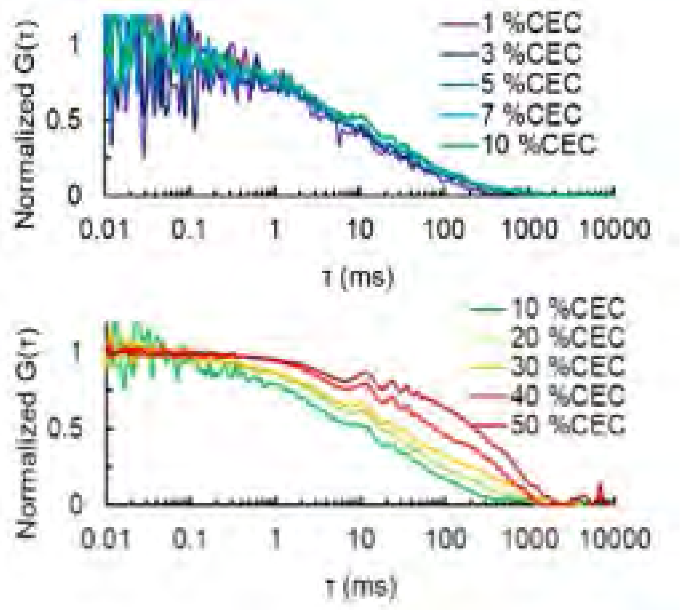

Figure 1. Autocorrelation curves for hybrids with 1 to 10%CEC (top) and 10 to 50%CEC (bottom).

OPTICAL MANIPULATION AND MICROSCOPE OBSERVATION OF DELAMINATED CLAY LAYERS DISPERSED IN WATER

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Optical manipulation using the radiation pressure of a tightly focused laser beam is a popular technique for non-contact and non-invasive trapping of object which is colloidal particles with sub-μm to several tens of μm [1] and thus trapped object can be invasively transported. Spherical colloidal particles such as latex particles, glass beads, metal nanoparticles, semiconductor nanoparticles, liquid crystal droplets, and biomolecules have typically been trapped at a focal point, so far. Optical manipulation of several one-dimensional (1D) rod-like materials have also been demonstrated [2].

We have extended optical manipulation to two-dimensional (2D) materials, nanosheets, including delaminated clay layers [3, 4]. When a linearly polarized laser beam was irradiated to a nanosheet dispersed in water, a nanosheet was trapped at the focal point. The trapped nanosheet was then oriented with its long axes parallel to the propagation direction and the polarization direction of the laser beam. This method was applicable to manipulation of not only a variety of oxide nanosheets, but also clay nanosheets hybridized with organic compounds [5]. Illumination of circular polarized laser beam induced rotation of an exfoliated clay nanosheet [6]. While the rotational motion, the clay nanosheet was optically trapped with maintaining its center of gravity position at the focal point. As the illuminated laser power increased, the rotation speed accelerated. The direction of rotation could be switched by alternating the handedness of polarized light.

In the course of these studies, nanosheets were optically manipulated under optical microscope observation. In-situ microscope observation revealed interesting aspects of clay nanosheets. Several novel findings of colloidal clay nanosheets revealed by the optical microscope observation will be discussed.

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DYNAMIC SELF-ASSEMBLY OF MONODISPERSE NANOSHEETS

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Inorganic nanosheets are usually obtained by exfoliation of layered crystals such as clay minerals and are known to form intriguing colloidal liquid crystals (LC) under a certain condition[1]. They have been applied for fabrication of anisotropic polymer composite materials, structural color materials,[2] etc. However, large polydispersity in lateral size limited more precise design of the self-assembled structures and materials properties.

Here, we demonstrate that very unusual mesophases are reversibly formed by self-assembly of monodisperse titanate nanosheets that were synthesized by the bottom-up method. Small angle X-ray scattering (SAXS) and transmission electron microscopy revealed the formation of one-dimensional long columns of stacked nanosheets. With the increase of nanosheet-nanosheet interaction, the columnar nematic LC phase appeared as confirmed by polarized microscopy and SAXS; this is the very first observation of columnar nematic LC phase in a nanosheet colloid. In some cases, the columns were further assembled into micrometer-scale fibrous bundles with well-defined supercrystalline nano-structures. The formation and dissociation of these structures were reversible and controllable by several factors such as temperature and electric field. The formation of these superstructures is rationalized by weak nanosheet-nanosheet attractions as well as by an entropic excluded volume effect.

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SPECTROSCOPIC BEHAVIOR OF AN ANIONIC PORPHYRIN INFLUENCED BY COLLOIDAL CLAY PARTICLES

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Smectite-type clay minerals form aqueous colloids, where negatively charged clay particles are dispersed in water. The clay colloids have been employed as heterogeneous media for photofunctional organic molecules, where the organic species has been limited to cationic or polar species because of their immobilization mechanism onto the clay particles. However, we have found impacts of aqueous clay colloids on the spectroscopic properties of anionic xanthene dyes [1]. In the present study, we have examined spectroscopic behavior of another organic dye, 5,10,15,20-tetrakis(4-sulfophenyl)porphyrin ($TPPS^{4-}$), in clay colloids in order to establish generality of our finding.

$TPPS^{4-}$ dissolved in aqueous clay colloids (1×10^{-5} and 1×10^{-7} mol L^{-1} dye, 1 to 30 g L^{-1} clay) of synthetic saponite exhibits spectroscopic behavior reflecting the clay particles. Figure 1 shows visible spectra of $TPPS^{4-}$ in the colloids. The spectra clearly indicate the existence of an equilibrium between $TPPS^{4-}$ in aqueous solution (λ_{max} at 413 nm) and that interacting with clay particles (λ_{max} at 423 nm), and most of the dye molecules are interacting with the clay particles at the clay concentration of 30 g L^{-1}. Influence of the clay concentration on the spectra is similar regardless of the difference in dye concentration in two orders of magnitude; hence, the spectroscopic impact of the clay colloids is not ascribed to the adsorption of $TPPS^{4-}$.

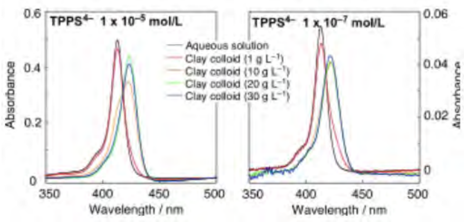

Figure 1. Visible absorption spectra of $TPPS^{4-}$ dissolved in clay colloids. Background due to scattering by the clay particles was subtracted.

[1] T. Nakato, Y. Kawanami, K. Taninaka, E. Mouri, *Bull. Chem. Soc. Jpn.*, **2022**, *22*, 1486.

UV PROTECTIVE CLAY FILM WITH TUNABLE GAS/MOISTURE TRANSPARENCY CONSISTING OF LIGNIN, A PLANT AROMATIC POLYMER

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To realize decarbonized society for sustainable social development, breaking away from petroleum-based material science is essential. Lignocellulosic biomass is the main component of non-edible plant biomass consisting of polysaccharides and lignin. Lignin, an aromatic polymer consisting of phenylpropane units, has potential as a renewable alternative to petroleum-origin aromatic products. In plants, polysaccharides and lignin are linked in a complex manner and are thus difficult to separate efficiently. The ordinary methods for extracting these compounds have required treatment of plants by strong chemicals such as acids, bases, and organic solvents under high temperature. However, the extracted lignin also cause deterioration such as dark coloring that prevent its utilization for functional materials.

In this presentation, we report creation of functional clay materials from lignin via novel sustainable extraction process.

Here, the non-denatured lignin with light brown color, which acts as functional materials such as heatproof filler and ultraviolet absorber, was obtained by simultaneous enzymatic saccharification and comminution (SESC) that realizes lignin extraction only by physical comminution of plants with enzymatic reaction in water1). Furthermore, we prepared nonflammable UV protective films consisting of platelet clay and obtained lignin derivative (SESC lignin). The nonflammable transparent clay films were produced by simple mixing clay with a SESC lignin in water. The preparation procedure did not require hazardous chemicals. The optical properties and gas/moisture permeability of the clay films could be tuned by the components and phase separation structure of the platelet clay and SESC lignin. The present clay film uses mineral and plant components as high-value industrial materials and reduces the environmental load of extracting limited petroleum-based resources.

This work was supported by a grant from JST-Mirai R&D Grant Number JPMJMI19E8 and JSPS KAKENHI Grant Number 21H02007.

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IONIC CONDUCTIVITY OF ION DEFECT INTRODUCED LAYERED DOUBLE HYDROXIDE

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Layered double hydroxide (LDH) is known as a hydroxide ion conductor. In order to realize high ionic conductivity, ionic conductors need to have defects in the crystal that allow ion migration within the crystal. Therefore, it is believed that ion transfer by the so-called vehicle mechanism does not occur in the LDH structure. In the present study, we attempted to improve the conductivity of LDH by introducing hydroxide ion defects into MgAl-based LDH, which exhibits hydroxide ion conductivity, and discussed the conductive mechanism based on these results.

LDH is known as a layered compound with anions inserted between the layers to compensate for the positive charge, and is characterized by the free exchange of anions between the layers. By taking advantage of this structural feature, we introduced defects into LDH. The hydroxide ion defect was introduced by inserting hydrogen carbonate ions into the interlayer of LDH, and some hydroxyl groups were decomposed by acid-base reactions.

We tried to introduce hydroxide ion defects into LDH by heat treatment at 150 to 200°C to desorb protons from LDH after ion exchange to bicarbonate ions. The 003 diffraction peak in the XRD diffraction pattern was shifted to the low-angle side by the heat treatment. This is thought to be due to the introduction of hydroxide ion defects in the host layer. The positive charge in the host layer increased due to the desorption of hydroxide ions, and the interlayer space expanded due to increased repulsion between the host layers. Fig. 1 shows Arrhenius plots of the conductivity of samples containing carbonate ions as interlayer ions in the initial state after heat treatment at 150 and 200˚C. In the system with carbonate ions, the conductivity decreases significantly with heating, and in the sample annealed at 200˚C, the conductivity drops to the detection limit, indicating that the ionic conductivity is almost lost. On the other hand, in the hydrogen carbonate ion system, no significant change in conductivity was observed, only a change in slope. This suggests that in the bicarbonate ion system, a new ionic conductivity mechanism was activated by the introduction of ion deficiencies.

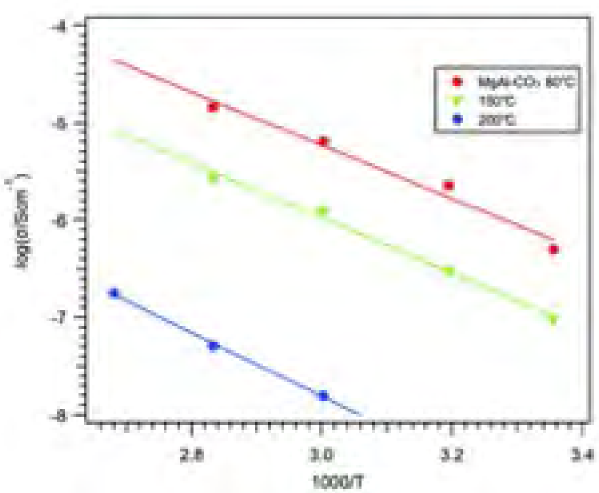

Fig. 1 Ionic conductivity for LDH-CO_3 annealed at 150 and 200˚C.

CONTROL OF ADSORTPION REACTION OF AN ORGANIC COMPOUND TO SMECTITE BY OPTICAL MANIPULARION TECHNIQUE

Suzuki Yasutaka

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Hybridization of clay layer and a cationic organic compound is occurred homogeneously in simple mixing of clay water dispersion and the organic compound solution. Herein, we propose a novel hybridization technique by combining the optical manipulation and slow distribution of relatively hydrophobic organic compounds at water-toluene interface. Typically, colloidal clay nanosheets are tended to be settled down after keeping for a while. After pooling a toluene solution of cationic organic compound onto a clay dispersion, one of the clay nanosheet settled down to the bottom of the sample cell was optically manipulated to near the water-toluene interface. As a result, the manipulated clay nanosheet was hybridized with organic compounds distributed from the toluene phase to the water phase. After hybridization, the nanosheet was optically transported again to the bottom of the sample cell. As a result, hybridized and non-hybridized single clay nanosheets coexist. The technique proposed in this study is a pioneering study of selective adsorption reaction of organic compounds on nanosheets, and thus novel clay-organic hybrid materials.

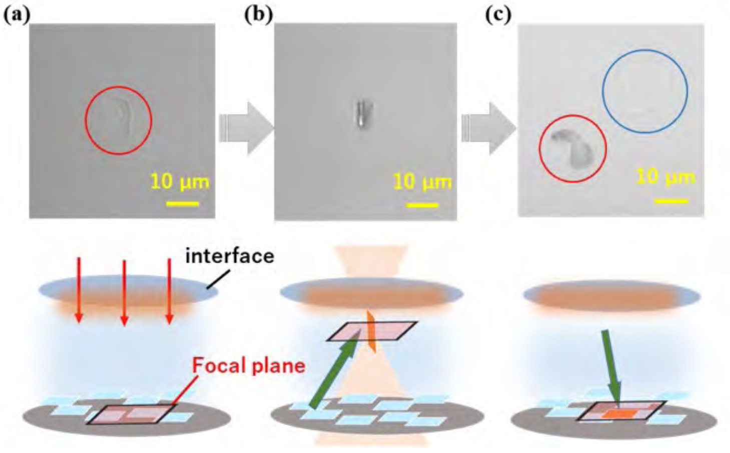

Figure 1. Microscopic images and schematic representation of process of adsorption of organic compound on a specific FHT nanosheet.

Session 11

Clay as nanomaterials: modification, functionalization, and application

Conveners: Chunhui Zhou (Zhejiang University of Technology), Runliang Zhu (Guangzhou Institute of Geochemistry, Chinese Academy of Sciences), Xiaofeng Guo (Washington State University, USA), Yu-Ting Liu (National Chung Hsing University, Taiwan), and He Hongping (Guangzhou Institute of Geochemistry, Chinese Academy of Sciences)

UPTAKE BEHAVIOR OF TWO HEAVY METALS AND AN DIMETHYLATED POLYCYCLIC AROMATIC HYDROCARBON ON RAW AND ALUMINUM PILLARED QUICK CLAYS

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Natural materials such as clays are used to enhance the efficiency of wastewater treatment. Quick clays (QC), a non-expandable clay mainly composed of illite and chlorite, come from glacial erosion of rocks during the last glaciation. No research has yet reported on the capacity of QC to uptake and trap pollutants. In addition, pillaring is a promising technique to enhance the adsorptive capacity of clays. However, pillaring is mainly carried out on swelling clays such as montmorillonite or kaolinite. This study focuses on the development of a new way for pillaring non-expandable QC and the assessment of sorption, desorption and hysteresis processes of two heavy metals (Cu, Cd) and 9,10-dimethylanthracene (DiHAP) on QC. The effects of temperature and salinity on the sorption capacity of clays are also investigated. Sorption models are used to characterize sorption behaviors.

The sorption kinetics show that raw QC rapidly uptake (30 min.) the studied contaminants. Partitioning coefficients show a very high affinity for heavy metals (0.2 - 51.7 $\mathrm{L \cdot g^{-1}}$) and DiHAP (1.9 - 8.0 $\mathrm{L \cdot g^{1}}$). The adsorption capacities of QC for Cu and Cd (kf : 3.41 - 10.7 and 0.60 - 1.07 $\mathrm{mg \cdot g^{1} \cdot (L \cdot mg^{-1})^{1/n}}$ for Cu and Cd, respectively) are 10 and 2.5 times greater than those of montmorillonite (MMT), a clay known for its high adsorption capacity. For the DiHAP, the kf value was similar to the value obtained with the MMT. Moreover, the QC adsorption capacity increases with temperature for all contaminants (38 - 62 %). Our results also suggest that an increase in salinity increases the sorption of Cu, DiHAP and greatly decreases the sorption of Cd. The desorption investigations show a sequestration process with a hysteresis index of 0.4 to 1.9 and 0.22 to 0.43 for Cu and DiHAP, respectively.

Preliminary results show that the pre-treatment of QC with exchangeable cations (Na^+ and Li^+) showed an increase in the basal spacing from 10 to 12 Å. Furthermore, QC expanded in contact with ethylene glycol and their spacing increased to 17 Å. These results suggest promising prospects for the QC pillaring as their d-spacing are like MMT, an easily pillared clay.

EFFECTIVENESS OF NANOMATERIALS AND THEIR COUNTERPARTS IN IMPROVING RICE GROWTH AND YIELD UNDER ARSENIC CONTAMINATION

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Arsenic (As) pollution in rice (*Oryza sativa* L.), a staple food for over 3.5 billion people, is a global problem. Mixed effects of Zn, Cu, and Si amendments on plant growth and yield, including in the presence of As pollution have been reported in previous studies. To better investigate the effectiveness of these amendments on rice growth, yield, and As accumulation, we conducted a rice greenhouse experiment with 11 treatments, including control pots with and without As contamination and pots with amendments of ZnO, CuO, and SiO_2 nanoparticles (ZnO NPs, CuO NPs, and SiO_2 NPs), their ionic counterparts ($ZnSO_4$, $CuSO_4$, and Na_2SiO_3), and bulk particles (ZnO BPs, CuO BPs, and SiO_2 BPs). Compared with the background soil, the treatment of adding As decreased rice plant height, panicle number, and grain yield by 16.5%, 50%, and 85.7%, respectively, but significantly increased the As accumulation in milled rice grains by 3.2 times. Under As contamination, the application of Zn amendments increased rice grain yield by 4.6–7.3 times; among the three Zn amendments, $ZnSO_4$ performed best by fully recovering grain yield to the background level and significantly reducing grain As^{III}/total As ratio by 46.9%. Under As contamination, the application of Cu amendments increased grain yield by 3.8–5.6 times; all three Cu amendments significantly reduced grain As^{III}/total As ratio by 20.2–65.6%. The results reveal that Zn and Cu amendments could promote rice yield and prevent As accumulation in rice grains under As contamination. Surprisingly, NPs do not have advantages over ionic counterparts and bulk particles in promoting rice growth under As contamination. Future field research using a broader range of rice varieties, investigating various As concentrations, and encompassing diverse climate conditions will be necessary to validate our findings in achieving more extensive understanding of effective management of arsenic contaminated rice field.

STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATION OF MONTMORILLONITE MODIFIED WITH POLY(2-N-ALKYL-2-OXAZOLINE)S

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Poly(2-oxazoline)s (POxs) are non-ionic polymers suitable for different bio-applications. Composites of montmorillonite (Mt) and poly(2-methyl-2-oxazoline) (PMeOx), poly(2-ethyl-2-oxazoline) (PEtOx) and poly(2-propyl-2-oxazoline) (PPrOx) were prepared for the first time and the effect of polymer loadings and the side chain length on the adsorption and structural characteristics was examined. The interlayer space of Mt increased with increasing POxs loading from 0.5 to 5.0 $\mathrm{mmol \cdot g^{-1}}$. Gradual transformation of the polymer chain arrangement from monolayer to bilayer up to pseudotrilayer was observed for individual polymers in dependence on the side chain length. The intensities of the bands related to the vibrations of the C=O and CH groups increased with rising amounts of polymers. A slight shift of the bands position reflected the transition from disordered to more ordered polymer arrangement. The thermal stability of PMeOx-Mt at elevated temperatures was determined by thermogravimetric analysis. The first mass loss (~90 °C) is related to desorption of water. Second and third around 370, 450 °C is attributed to the degradation of intercalated PMeOx. The fourth mass loss of the organoclay, at a temperature of around 540 °C, was ascribed to the oxidation of carbon soot, or the in-situ creation of condensed polymeric species by partial thermal decomposition of polyoxazoline. Unexpected and very high adsorption of POx on Mt interlayer and outer surfaces, markedly exceeding the CEC of Na-Mt, was discovered for the first time. Adsorption isotherms of polymers revealed a sharp increase in adsorption at low polymer loadings. When the surface of Mt was saturated with POxs, a plateau not changing with the loading of the polymer appeared. The high adsorption of various polyoxazolines was found for PMeOx (353 $\mathrm{mg \cdot g^{-1}}$) followed by PEtOx (383 $\mathrm{mg \cdot g^{-1}}$), and PPrOx (355 $\mathrm{mg \cdot g^{-1}}$).

The authors acknowledge financial support from the Slovak Research and Development Agency (project No. APVV-19-0487) and Slovak Grant Agency VEGA (No. 2/0166/21).

ESTABLISHMENT OF PEDOTRANSFER FUNCTIONS FOR SOIL ORGANIC CARBON SATURSTION

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Soil organic carbon (SOC) plays a critical role in various agricultural ecosystem services such as nutrient and water retention, aggregate stability, and crop production. SOC has also been considered to an important parameter to contribute to climate change mitigation in recent years. Past studies have indicated that although mineral-associated organic carbon (MAOC) exhibits long-term stability. Therefore, the maximum amount of soil MAOC is considered the soil organic carbon saturation (Csat). The difference between Csat and MAOC represents the soil organic carbon storage potential (Csp), serving as an indicator of the soil's potential for carbon sequestration. However, previous studies have shown varying estimates of MAOC and Csat across different regions. Hence, this study aims to establish region-specific Csat soil transformation equations using the nationwide soil survey database by employing pedotransfer functions (PTFs), and further mapping their spatial distribution through digital soil mapping (DSM). Furthermore, it seeks to estimate the total stocks of surface soil (0-30 cm) Csp at the national scale. This study compiled soil physicochemical analysis data from agricultural experiments conducted between 2008 and 2020. Using the content of fine particles and organic carbon, Csat PTFs were established through boundary line analysis (BL) and quantile regression (QR), and Csp was estimated based on the difference between Csat and existing fine soil organic carbon (Cfine) content. The results indicate that Csat estimated by BL is higher than QR, yet the carbon saturation values estimated by linear and quadratic equations derived from BL and QR show no significant difference. The distribution of soil organic carbon storage potential suggests that most high mountain forest soils are in a carbon-saturated state, with lower carbon storage potential compared to plain and sloped areas. Numerical calculations reveal that the Csp stocks estimated by BL-based PTFs are more than twice those estimated by QR. Furthermore, the results of this study closely resemble those obtained using the Hassink (1997) equation. The soil carbon storage potential maps produced in this study can serve not only as a reference for estimating soil carbon sink targets but also as a basis for planning locations for implementing carbon-negative agriculture.

EFFECT OF PRIMARY ALCOHOLS ON PHOTOCATALYTIC WATER SPLITTING FOR HYDROGEN PRODUCTION OVER CUO/NIFE-LAYERED DOUBLE HYDROXIDE AND CUO/NIO/NIFE$_2$O$_4$ COMPOSITE

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Green hydrogen energy has increased much attention in the two decades. Hydrogen produced by water splitting using renewable resources include sunlight is the most promising energy carrier of the low-carbon economy, where catalysts and sacrificial reagents play a key role in the hydrogen evolution reaction. In this work, the effect of primary alcohols, which typically used as a sacrificial reagent, on the photocatalytic hydrogen evolution over CuO/NiFe-layered double hydroxide and CuO/NiO/NiFe$_2$O$_4$ composite was investigated. CuO/NiFe-layered double hydroxide was hydrothermally synthesized and subsequently calcined at 700 °C for 4 h to form CuO/NiO/NiFe$_2$O$_4$ composite. The composite revealed the higher photocatalytic activity under UV-visible irradiation and the hydrogen evolution increased from 50.3 μmol to 265.3 μmol with changing the sacrificial reagent from methanol to butanol. This result was consistent with the computational calculation, which showed that the adsorption of butanol on a CuO active site was higher than methanol. Moreover, the presence of butanol also affected the charge of adsorbed proton, resulting in the decrease of free energy or higher hydrogen evolution. The amount of hydrogen decreased while using longer chain alcohols, i.e., pentanol and hexanol due to the immiscibility with water.

HYBRID LDHS: ADVANCING FOOD SECURITY AND CLIMATE ACTION THROUGH SLOW-RELEASE FERTILIZATION AND CARBON CAPTURE

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Introduction: This study aimed to create a phosphate slow-release fertilizer using synthesized Layered Double Hydroxides (LDHs) with Chitosan (CTS) and Carboxymethyl Cellulose (CMC), both recyclable agricultural wastes. Synthesizing LDHs is cost-effective and straightforward compared to other carriers. We used synchrotron radiation X-ray spectroscopy to examine how phosphorus species and Fe bonding in LDHs affect release rates and carrier structure. The goal is to develop a biocompatible, eco-friendly fertilizer that enables waste recycling and reduces agricultural pollution, supporting sustainable agriculture.

Methods: Mg-Fe LDH was synthesized using a coprecipitation method, later hybridized with biopolymers CTS and CMC to enhance phosphate sorption and release characteristics, aiming for improved slow-release P fertilizers. The process involved mixing metal nitrate solutions with biopolymer gels, followed by NaOH addition under controlled conditions. Sorption experiments were conducted to evaluate phosphate capture efficiency, while release kinetics studies simulated rhizosphere conditions to assess the controlled release of phosphate.

Results: The phosphate sorption isotherms, fitted by Freundlich models, reveal that hybrid LDHs have higher PO_4 adsorption capacities (57.9 to 71.8 mg/g) than traditional Mg-Fe LDHs[1]. This suggests their potential as efficient P fertilizers. The PO_4 release kinetics from P-loaded LDHs show release rates influenced by polymer content (Fig. 1). Spectroscopic analysis using P K-edge XANES spectra indicates dominant phosphate species in LDHs and how their composition changes over time. Composites with 0.5M LDH showed consistent exchangeable and absorbed P forms during release. Fe-EXAFS results revealed structural differences in hybrid LDHs, influenced by polymer ratios, leading to distinct release mechanisms. Post-phosphate loading, the LDHs transformed into ferrihydrite. This is significant as iron plays a crucial role in soil carbon stabilization[2] absorbing 31.13% to 68.00% of dissolved organic carbon, thus enhancing carbon sequestration.

Conclusion: We developed innovative Mg-Fe LDH materials with biopolymers CTS and CMC, aiming to create effective slow-release P fertilizers. These materials showed promising phosphate sorption and extended-release capabilities, overcoming the limitations of traditional LDHs. The structural transformation during weathering, including the formation of Fe (hydr)oxides, suggests the potential for enhanced soil carbon sequestration. This advancement aligns with Sustainable Development Goals, offering a dual solution for food security and climate change mitigation.

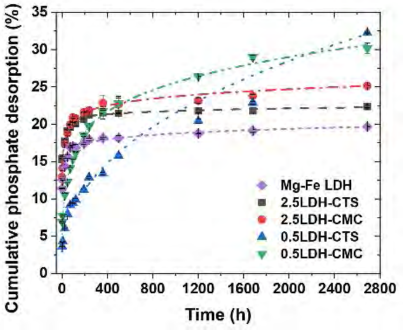

Fig. 1. Release kinetics of PO4 from Mg-Fe LDH and that hybridized with CMC and CTS.

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REVERSE EXCHANGE OF FELDSPATHOIDS FORMED IN CARBONATE-RICH ALKALINE SOLUTION

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Sodalite (SOD) and cancrinite (CAN) are two feldspathoids commonly found under high alkaline conditions such as nuclear waste sites and Bayer process solids, aka bauxite residues, for alumina production. Sodalite and cancrinite have high theoretical cation and anion exchange capacities (CEC) of up to 800 and 200 cmol/kg, respectively, which indicate their potential as nutrient carriers or nutrient-supplying materials. Several studies have reported the cation exchange of hydrosodalite, a sodalite with only water and sodium ions as extraframework species. No cation exchange research has been conducted to date on other feldspathoids with structural anions. The objectives of this study were 1) to characterize the synthesized feldspathoids formed in a carbonate-rich alkaline solution, and 2) to study the forward and reverse exchange with common nutrients, K^+, NH_4^+, Ca^{2+}, and Mg^{2+}, in these feldspathoids, and 3) the corresponding structural adjustments of the minerals during the exchange.

Bayer-SOD and Bayer-CAN were formed by reacting kaolinite with NaOH and Na_2CO_3 at 100 and 230 °C, respectively. Bayer-SOD was identified as an intermediate phase between sodalite and cancrinite, while Bayer-CAN closely resembled pure cancrinite. XRD peak shifts and infrared band changes suggested unit cell expansion after K^+, NH_4^+, and Ca^{2+} exchange. Some Mg-rich particles found under SEM were attributed to the formation of $Mg(OH)_2$, whereas insufficient amounts NH_4^+ to balance the negative charge from the aluminosilicate framework resulted in additional H_3O^+ exchange. Both feldspathoids observed the same exchange preferences with Na: $K^+ > NH_4^+ > Mg^{2+} > Ca^{2+}$ and Bayer-SOD had higher CEC than Bayer-CAN. The incorporated carbonate, hydroxide, and accompanied sodium ions were released partly or completely during cation exchange, reducing the maximum potential exchange capacity. Almost complete Na^+ reverse exchange was achieved on the monovalent cations, K^+ and NH_4^+, but only small fractions of reverse exchange were observed on the divalent cations, Ca^{2+} and Mg^{2+}. No anion exchange was found in our study.

ENHANCING PHOSPHORUS FERTILIZATION EFFICIENCY AND SOIL ORGANIC CARBON SEQUESTRATION WITH MG-FE LAYERED DOUBLE HYDROXIDES

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The urgent need for sustainable agricultural practices is underscored by the dwindling reserves of rock phosphate, increasing pollution of water bodies due to inefficient fertilizer use, and the overarching challenge of global warming. This study introduces a novel approach to address these multifaceted issues through the development of a slow-release phosphate fertilizer synthesized from Mg-Fe layered double hydroxides (LDH) combined with biopolymers such as chitosan (CTS). Building on previous research that demonstrated the potential of LDH for controlled phosphorus release, this project delves deeper into the comparative effects of LDH-based fertilizers and traditional triple super phosphate (TSP) fertilizers on plant growth.

A pivotal aspect of our research is the innovative use of Mg-Fe LDH as both a phosphorus fertilizer and a medium for enhancing soil organic carbon (SOC) sequestration. The dual-function fertilizer ensures the controlled delivery of essential nutrients and produces $Fe(OH)_3$ as a byproduct. This byproduct plays a critical role in SOC stabilization, leveraging its large surface area and complexation capabilities for the adsorption and co-precipitation with SOC (Fig. 1.) Such processes are essential for maintaining and enhancing the SOC stocks in agricultural soils, offering a path toward mitigating global warming through carbon capture.

To evaluate the effectiveness of this novel fertilizer, a comprehensive growth trial was conducted featuring lettuce and bok choy plants grown in pots using sand (washed sea sand) and soil. These plants were subjected to varying phosphorus concentrations (65.0, 130.0, 260.0 mg P kg-1) from LDH and TSP fertilizers. Assessments on Day 28 included plant height, weight, biomass, and elemental contents. Furthermore, the study explored the LDH-PO4 amendment's capacity for carbon stabilization by integrating dissolved organic matter or organic ligands, thereby assessing its environmental benefits beyond nutrient delivery.

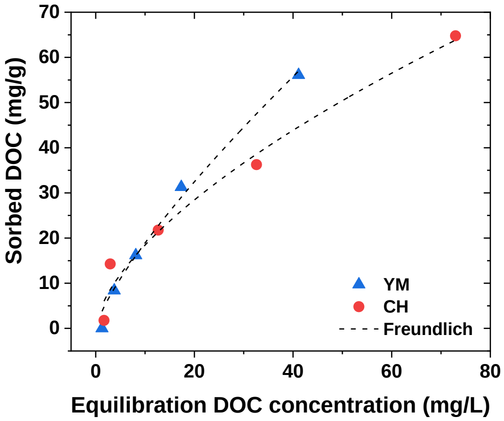

Fig. 1. Sorption isotherms of DOC on Mg-Fe LDH and that hybridized CTS.

The results of this study not only affirm the efficiency of LDH as a phosphate fertilizer in promoting crop growth and enhancing phosphorus bioavailability but also illuminate its significant contribution to sustainable agriculture through SOC sequestration. These findings lay the groundwork for future research into the application of LDH fertilizers across various soil types, application rates, and their long-term environmental impacts, marking a significant step forward in the quest for sustainable agricultural solutions.

EFFECT OF ORGANIC ACID LEACHING ON THE STRUCTURE OF MIXED-DIMENSIONAL ATTAPULGITE CLAY

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Mixed-dimensional attapulgite clay (MDAPT) is mainly composed of one-dimensional attapulgite, and two-dimensional illite, chlorite, kaolinite, illite-smectite mixed-layer clay, etc., which often exhibits brick-red, gray, or earth-yellow colors. Although MDAPT was previously deemed as low-grade ores due to the complex mineral components and darker color, our researches have revealed the industrial application potential by overall structural regulation. Based on organic acid leaching, the coloring Fe^{3+} ions were efficiently removed while preserving the intrinsic properties of one-dimensional/two-dimensional clay minerals. Furthermore, the simple, cost-effective, and efficient solid-state leaching and microwave-assisted leaching methods were developed to transform MDAPT into highly dispersed mixed-dimensional nanostructured minerals. After being applied in polymer composite materials and inorganic functional materials, it demonstrated distinctive synergistic advantages compared with individual minerals as reinforcing and carrier materials. By embracing a novel perspective of "coexistence and harmony, unity in diversity", the unique mineral properties of MDAPT were deeply explored, effectively promoting the efficient and high-value utilization of natural MDAPT.

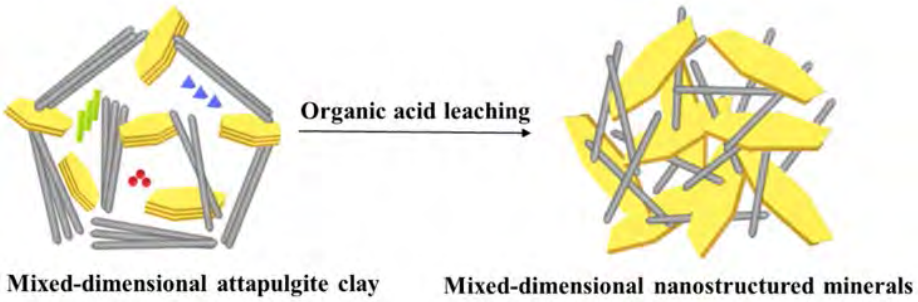

Figure 1. Organic acid leaching induced transformation of MDAPT into mixed-dimensional nanostructured minerals.

HYBRID MATERIALS PREPARED BY INTERCALATION OF ALKYL-AMMONIUM AND -PHOSPHONIUM SURFACTANTS INTO MONTMORILLONITE

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This study describes the potential of infrared (IR) spectroscopy in both middle (MIR) and near (NIR) regions to characterize the samples from two series of structurally analogous alkyl-ammonium- and alkyl-phosphonium montmorillonites. The XRD, TA and IR analysis confirmed the profound effect of the type of the central atom (N *vs* P) of surfactant, overall size of the organic cations and the alkyl chain length on the structural and vibrational features of organo-montmorillonites (O-Mt). The first series was prepared with Me4-N/P, Bu4-N/P and Oc4-N/P cations and the second with Bu3-N/P-C*X* cations with increasing number of carbons in the fourth chain (C*X*= 4, 8, 12, 16). For each corresponding pair, the phosphonium-Mt showed slightly larger d-values and higher initial temperature of decomposition than ammonium-counterparts. The mid-IR spectra of O-Mt show the bands related to the stretching vibrations of the CH_3 and CH_2 groups absorb in the 3000-2800 cm^{-1} region while in the near-IR region the CH overtones and combination modes occur at 6100-5600 cm^{-1} and 4700-4000 cm^{-1}, respectively.

Different charge density of the nitrogen and phosphorus cationic centers affected the positions of the CH bands in both IR regions. The CH_3 and CH_2 bands of phosphonium-Mt were shifted to lower wavenumbers compared to their ammonium counterparts. The effect of the N/P was significant for smaller cations, but gradually decreased with increasing size of the surfactant. For example, difference in the νCH_3 band position between Me4-N-Mt and Me4-P-Mt was 45 cm^{-1} in contrast to Bu4-M/P-Mt showing only 3 cm^{-1} difference. The impact of the central atom of the head-group on the CH vibrations almost completely disappeared for Oc4-N/P cations as confirmed the shape and positions of the CH stretching and overtone bands. Similar trends in the positions of the CH bands were observed also for Bu3-N/P-CX montmorillonites.

Financial support of the Slovak Research and Development Agency (APVV-19-0487) and the Slovak Grant Agency VEGA (2/0166/21) are highly acknowledged.

STABLE DISPERSION METHOD OF K-TYPE MONTMORILLONITE

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Dispersibility of montmorillonite depends on the valence and ionic radius of exchangeable cation. Na-type montmorillonite disperses stably in water by exfoliating layer to layer. On the other hand, Ca-type montmorillonite has only limited swelling in water. K^+ has a lager ionic radius than Na^+, resulting in limited dispersion. However, we found a method to stably disperse K-montmorillonite by using the dehydrated cake obtained in the process of ion exchange operation.

The material used in this study was Na-type montmorillonite (Kunipia-F, Kunimine Industry Co. Lid., Japan). Ion exchange to K-type was performed using potassium chloride solution[1]. After the ion exchange operation, excess chloride ions were washed away using a suction filter. Suction filtration produced a dehydrated cake of K-montmorillonite. The water content of this cake was 79.1%. When this cake was directly put into water and stirred, it was found to be stably dispersed in the water compared to the normal K-type, which is static dried (at less than 100C) and milled from this cake (Fig.1).

Dehydrated cakes were prepared with various ions and XRD measurements were performed (Fig.2). The (001) peak of the K-type cake was broad, indicating less order in the stacking in the cake. The particle size of montmorillonite in the water dispersion was measured by dynamic light scattering method. K-type cake dispersion had a particle size of 838nm, while the normal K-type had that of 1476nm. Kunipia-F was 500 nm, and the dispersion of K-type cake was close to that of Na-type. Drying and crushing are thought to cause the interlayers of K-type to stick together. H-type montmorillonite also shows a similar tendency, and dispersibility increases when spray drying is used instead of static drying[2].

Keyword: K-type montmorillonite, dispersion, ion exchange, dehydrated cake

References: [1] S. Morodome and K. Kawamura, Clays and Clay Minerals. 57, 2, 150-160 (2009) [2] Japan patent JP 5841414 B2

Fig.1: Dispersibility after one week of standing

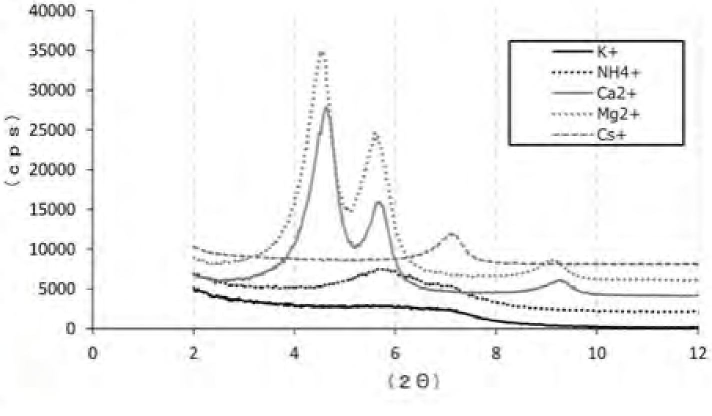

Fig.2: XRD patterns of the dehydrated cake of each ion

INFRARED SPECTROSCOPIC DETECTION OF LUMINOPHORE COMPONENTS IN ORGANOCLAY PIGMENTS

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Hybrid materials comprising organoclays and laser dyes are frequently investigated for their luminescent properties. However, due to the predominance of smectites and organic species, identifying minor luminophore constituents within such systems presents challenges. In this context, infrared spectroscopy emerges as a valuable tool for characterization. This study focuses on the detection of a minor luminophore component, rhodamine 6G (R6G), incorporated into organoclay pigments. The samples were prepared using smectite, tetraoctylammonium, and -phosphonium cations, along with R6G dye. The concentration of organic surfactants varied from 0 to 100% relative to the cation exchange capacity of smectite, while the dye concentration ranged from 0.001 to 0.08 mmol/g. Infrared revealed absorption bands of the C-H vibrations attributed to surfactants. The intensity of these bands increased with higher organic phase content. R6G detection at a concentration of 0.08 mmol/g was feasible in spectra of organoclays, evidenced by bands assigned to C=O and C-H vibrations of aromatic rings or methyl groups at 1717, 1650, 1610, 1533, and 1502 cm^{-1}. The bands remained detectable even in samples with high organic cation loading, despite overlapping with more intensive bands from both organic surfactants. However, dye band visibility decreased significantly at lower dye concentrations (0.005 mmol/g) and was undetectable in samples with the lowest concentration (0.001 mmol/g). Detection in higher wavenumber (> 2700 cm^{-1}) proved challenging, even at higher dye concentrations. An intriguing observation was the appearance of distinct bands at 3440 cm^{-1}, not present in the pure dye spectrum. The intensity of these bands correlated with water content, diminishing with increased organic surfactant loading. This phenomenon suggests interactions between dye cations and water molecules via hydrogen bonding through N-H bonds.

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CHARACTERIZATION OF SMECTITE-CLAY POLYMER HYBRIDS BY DENSITY FUNCTIONAL THEORY METHOD

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The clay-polymer hybrids are perspective materials which can be used in green chemistry, e.g. for wastewater treatment. Clays can enhance the mechanical properties of the polymers together with their thermal stability. In present study, the density functional theory (DFT) method with employed D3 scheme for corrections of dispersion interactions was used to examine the stability of clay-polymer hybrid structures and their mechanical properties. The mechanical properties of the pristine clays from smectites family, dioctahedral (montmorillonite – Mt and beidellite – Bd) and trioctahedral (hectorite – Ht and saponite – Sap) were also examined for a comparison with their clay-polymer hybrids built on the poly(2-methyl-2-oxazoline), polymer – PMeOx. The results revealed a good stability of clay-polymer hybrids and reduction in elastic constants and elastic moduli following the intercalation of smectite clay minerals with the PMeOx polymer. The findings highlight a distinctive ranking of mechanical properties among pristine smectite clay minerals and clay-polymer hybrids, with hectorite and its hybrid (Ht-PMeOx) demonstrating better performance compared to saponite, montmorillonite, and beidellite and their respective hybrids.

Acknowledgements. Financial support by the Scientific Grant Agency VEGA (Grant, 2/0026/23 and 2/0166/21), Slovak Research and Development Agency (APVV-19-0487, APVV-22-0150) and grant Program of Slovak Academy of Sciences (SAS) for PhD students (2022 - APP0426-Doktogrant) is gratefully acknowledged.

INTERACTIONS OF AFLATOXIN B1 WITH BENTONITE – ADSORPTION AND CATALYTIC TRANSFORMATION

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Aflatoxin is a type of mycotoxin, with common variants being B1, B2, G1, and G2. Among these, B1 is classified as a group 1A carcinogen by the World Health Organization (WHO) due to its high content and potent toxicity. Improper storage of human food and animal feed can lead to the growth of various fungi and molds, which produce aflatoxin through metabolism under appropriate temperature and moisture conditions. In this study, Smectite-rich Japanese bentonite (JS) underwent calcination at 200 and 400 °C for 1 hour to produce heat-modified bentonite (JS2-1 and JS4-1) as adsorbents for aflatoxin B1 (AFB1). The heat treatment resulted in a slight increase in the maximum adsorption capacities for AFB1, from 82.7 to 88.50 mg g-1. Besides, the addition of sodium metaphosphate dispersant facilitated a significant elevation in the adsorption capacity of the bentonite to AFB1, particularly for the JS4-1 sample, which saw an increase in maximum adsorption capacity by nearly 60 %. At pH 3, bentonite exhibited the highest efficiency in removing AFB1; however, AFB1 removal was attributed to the transformation of AFB1 to AFB2a rather than adsorption onto bentonite. The optimal adsorption capacity of AFB1 on JS bentonite was observed between pH 5 to 7, with a range of 70-80 mg g-1. If used as a feed additive, bentonite can adsorb AFB1 in the animal esophagus (pH 7), but it may catalyze the conversion of adsorbed AFB1 to AFB2a, which is then released in the stomach (< pH 3) due to the low adsorption capacity of bentonite to AFB2. A wood-biochar bentonite composite could serve as an effective scavenger to remove both AFB1 and AFB2 from the solution.

Keywords: : Aflatoxin; Bentonite; Catalytic transformation; Heat-modification

FUNCTIONAL LAURAMIDOPROPYL BETAIN AND LI CO-MODIFIED MONTMORILLONITE AND ITS COLLOIDAL PROPERTIES IN A MIXTURE OF ETHANOL AND WATER

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Montmorillonite (Mt) is a hydrophilic clay mineral with a generally high cationic exchange capacity and a remarkable swellability in water. Yet the application of Mt, as a functional colloidal component, to cosmetics, paints, polymer nanocomposites, drug delivery systems, tissue engineering, and ethanol/water solvent-based catalytic processes are limited due to it unfavorable swelling and dispersion in a mixture of alcohol and water, which are different from water alone or organic media alone. Improving the swellability and dispersibility of Mt in mixtures of ethanol and water remains challenging. Here, we showed that the swellability and dispersibility of Mt in ethanol/water could be significantly enhanced when lithium-Mt (Li-Mt) was intercalated by a zwitterionic surfactant lauramidopropyl betaine (LPB). The binding of the LPB intercalate to the Li-Mt originated from a combination of van der Waals forces, ion-dipole interaction and electrostatic attraction. Due to the synergistic effect of Li^+ and LPB, the co-modified Mt (LPB-Li-Mt) exhibited tunable swellability, dispersibility and rheological properties, the structure, morphology, zeta potential, dispersibility and gel-forming performance of LPB-Li-Mt can be adjusted by the ethanol concentrations in the ethanol/water mixtures. When the ethanol concentration was 75wt% (ethanol/water), LPB-Li-Mt still showed a good swellability. The results from X-ray diffraction, thermos-gravimetric analysis, Fourier transform infrared spectroscopy, X-ray photoemission spectrometry and small-angle X-ray scattering confirmed remarkable exfoliation of LPB-Li-Mt in the mixture of ethanol/water of 75% v/v. The formation of a stable colloidal LPB-Li-Mt dispersion in a mixture of ethanol/water might be derived from the ion-dipole and hydrophobic interaction of ethanol with LPB and LPB-Li-Mt. The inherent interactions between Li, LPB, Mt nanoparticles, water and ethanol make the system from colloid to gel upon different condition. The findings provide a guide for improving dispersion and swelling of Mt and modified ones in water-miscible organic solvents. Such co-modification of Mt by Li^+ and LPB may extend the application of Mt in a system involving a mixture of ethanol/water, including green-solvent catalysis, biological engineering and environmental-friendly paints, and so forth. [The authors wish to acknowledge the financial support from the National Natural Science Foundation of China (22072136; 41672033)]

NANOSILICON DERIVED FROM CLAY MINERALS AS HIGH PERFORMANCE LITHIUM-ION BATTERY ANODE

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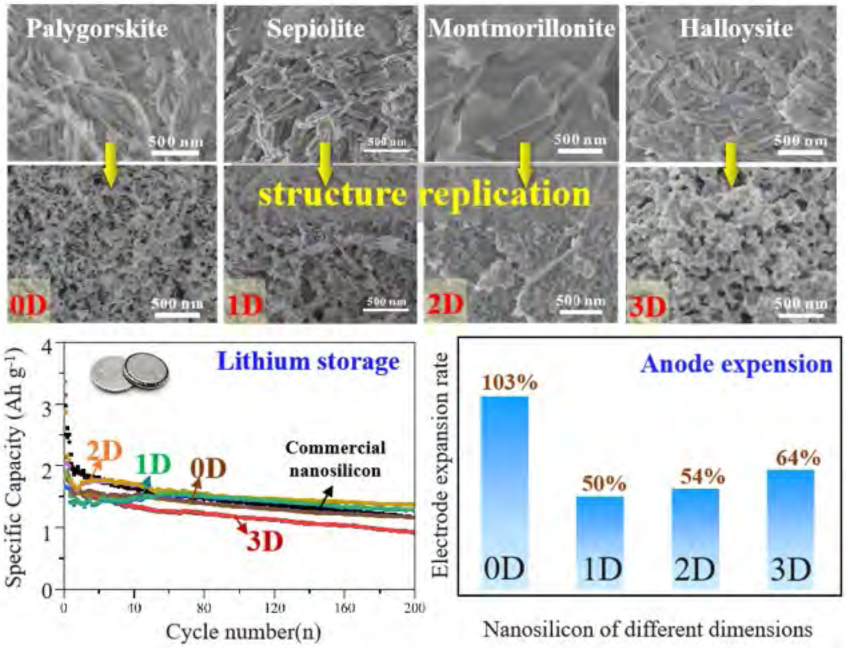
The quick advancement of electric vehicles and portable electronics requires high-performance lithium-ion batteries (LIBs). Silicon (Si) has been recogenized as one of the most appealing anode thanks to its large theoretical specific capacity (3579 mAh g^{-1}). However, Si anodes suffer from severe capacity decay because of the massive volume variation (over 300%) during cycling. Downsizing bulk Si to the nanoscale may be the solution, and a variety of nanosilicon materials have been developed through various strategies. But large-scale synthesizing cost effective nanosilicon materials is still a big challenge.

With high silicon content, uniform nanosized architectures, low price, and abundant reserves, clay minerals have recently been regarded as one of the most attractive precursors for synthesizing nanosilicon materials. Our group have applied various types of clay minerals to synthesize 0D, 1D, 2D, and 3D silicon nanostructures through simple thermal magnesium reduction reaction, and the resulting materials showed impressive performance as anodes in LIBs. The 1D silicon nanorod synthesized from sepiolite and 2D silicon nanosheet from montmorillonite showed particularly good performance due to their smaller expansion rate during cycling (following figure). Besides, we applied modified clay minerals (e.g., organoclays) to synthesize C/Si and SiC/Si nanocomposites, which showed better stability than nanosilicon during the charge-discharge cycling. In all, our studies have demonstrated that clay minerals and their modified products can be ideal precursors for scale up synthesizing nanosilicons for LIB anodes.



ADHESION AND MICROMECHANICAL PROPERTIES OF NANOSTRUCTURAL LAYERED DOUBLE HYDROXIDE COATINGS DEVELOPED ON ZN ALLOY FOR SMART CORROSION PROTECTION

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Zinc is known as an important non-ferrous metal with large application in metallic coatings. It can be used for corrosion protection of steel to extend the service life of steel structures. The galvanized layers improve the corrosion resistance to atmospheric attacks, and fast degradation occurs only in highly polluted air. Zinc is corrosion resistant to fresh water and slightly alkaline solutions; however, weak acidic solutions promote the corrosion rate, so the corrosion resistance property decreases in seawater. The application of polymer-based coatings does not always provide the stable, continuous protection layer of metals against the environment, particularly when aggressive species flow amplifies the damage in place of the imperfection of the coating, intensified by mechanical stress.

Therefore, in this project, we focus on the development of layered double hydroxide (LDH) films directly grown on a metal surface using the substrate alloy as an internal source of Zn metal cations to form naturally adherent, self-healing coatings. In this study, we focus on a correlation between the structural aspects of the formed LDHs coating, the adhesion of the obtained coating to the substrate, and their corrosion performance. A series of ZnAl-NO_3 LDHs coatings were formed in situ on the surface of Zn alloys under the control of pH. The degree of alloy substrate polishing, the time of growth influenced the crystallinity and the thickness of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}]_{x/n}\cdot mH_2O$ LDHs structure coatings formation (where M^{2+} and M^{3+} are respectively two- and three-positive cations) were comparatively investigated towards the formation of adhesive, self-healing protective film. The effects of the preparation methods on the microstructure, composition, mechanical properties, and assessment of corrosion degradation were investigated by means of SEM/BSE/EDS, X-ray diffraction methods, as well as advanced XPS and FTIR spectroscopies. The adhesion and micromechanical properties of the synthesized nanostructural LDH coatings deposited on Zn alloy substrates were evaluated. The hardness and elastic modulus were determined using the nano-indentation technique with the Berkovich indenter. In the first step, scratch tests with the use of a spherical Rockwell diamond indenter were done to assess the coating's adhesion to the substrate. The results of the scratch tests indicated the good adhesion of the coatings to the substrates. The influence of coating structure, its crystallinity, particularly the dimension of the single plate-like particles of LDH, compactness and thickness on the obtained hardness and elastic modulus was examined. The results show that elongation of the exposure time of the Zn alloy to the reaction mixture containing Al ions (from 3h to 20h) increases the thickness of the formed LDH layer from 100nm to 500nm. Meanwhile, the diminution of the roughness of the Zn alloy substrate significantly improved the scratch resistance of the LDH layers tested. The acoustic emission signal measured in the scratch tests indicates the brittle nature of the layer fracture. The cohesive cracks formed are superficial and do not propagate into the substrate.

Session 12

Synthetic and Natural Clays for Nanomedicine and Nanocosmetics

Conveners: Jae-Min Oh (Dongguk University, Korea), Goeun Choi (Dankook University, Korea), Keith Morrison (LLNL, USA), and Youjun Deng (Texas A&M University, USA)

BORON NEUTRON CAPTURE THERAPY ASSISTED BY CLAY-BASED DRUG DELIVERY SYSTEM

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An attempt was made to apply anionic clays, layered double hydroxides (LDHs), 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 μg B/10^6 cells) in U87 glioblastoma cell line was found to be ~ 2000 times larger than the minimum boron requirement (~ 0.02 μg B/10^6 cells) for BNCT, and also orders of magnitude higher than the previous results (0.2 ~ 1.5 μg B/10^6 cells) by those applied with other targeting strategies, and eventually resulted in excellent neutron capture efficiency even under such low dose (30 μg B/mL) and weak irradiation (1×10^{12} 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.

STRUCTURAL FACTORS IN DETERMINING THE EFFICIENCY OF NATURAL AND SYNTHETIC CLAYS IN BINDING BIOLOGICAL TOXINS

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Natural and synthetical clay-sized materials have been increasingly explored for uses as alternatives of antibiotics, as toxin binders, and as drug or gene carriers for their delivery. Often a question arises which clay has the highest efficiency and selectivity in binding the targeted biological molecules. This presentation will summarize recent advances in finding the determinative crystal structural factors that control the interactions of clay minerals and the biological toxins. Despite the very different functions of the biological toxins and drugs, they do share many common O- and N-containing functional groups and therefore, most of the toxin or drug-clay reactions can be understood by studying the reactions of these O- or N-containing functional groups with the clays, but molecular size, polarity, geometry, stereo distribution of functional groups, charge species and charge responses to pH change should be considered. As water is often the medium in which the reactions occur, both the reaction of the clays with water and the reaction of the biological compounds with water are important in determining the binding strength between the targeted compounds and the clays. Recent findings on the efficiency and selectivity of natural smectite, sepiolite, palygorskite, and synthetic layered double hydroxides in binding toxins produced by fungi and bacteria will be presented. The biological toxins include aflatoxin, fumonisin B1, zearalenone, and pyocyanin. Both spectroscopic data and molecular simulations results have been used to reveal the determinative roles of nano-meter size domains of the surface, charge density, and the type of exchange cation, the size and polarity of the tunnels of the minerals in regulating the interactions of the toxins with the minerals. Based on the reaction mechanisms reveals, clay selection or modification can be made to enhance the selectivity of the clay minerals in binding the toxins.

INSIGHTS INTO THE BONDING MECHANISMS OF PYOCYANIN AND MONTMORILLONITE

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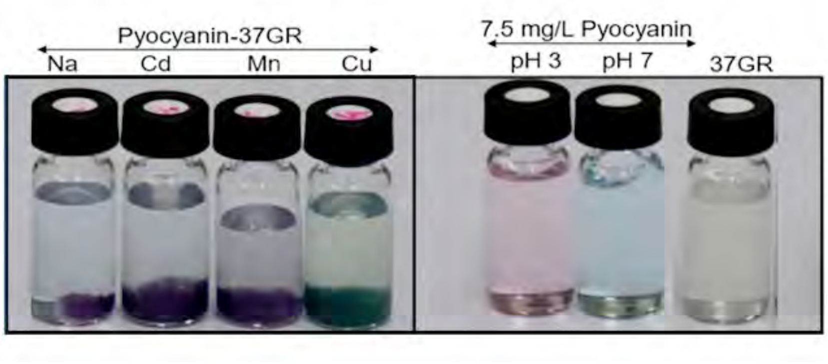
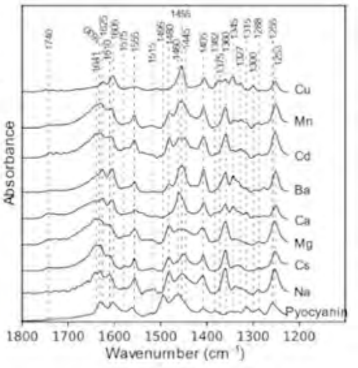
Pyocyanin ($C_{13}H_{10}N_2O$) is an important virulence factor in the pathogenicity and the recalcitrancy of *Pseudomonas aeruginosa*. It was earlier demonstrated that smectites can adsorb both protonated ($PYOH^+$) and neutral forms (PYO) of pyocyanin, therefore smectite might be able to disarm the pathogen by inactivating the virulence factor. The adsorption mechanism of pyocyanin on smectites was later shown to be primarily determined by the type of interlayer cation. Herein, using variable humidity infrared spectroscopy, we investigated the bonding mechanism of the PYO–montmorillonite and $PYOH^+$–montmorillonite complexes. In $PYOH^+$–montmorillonite complexes, the major bonding mechanisms are (I) ionic bonding between $PYOH^+$ and 2:1 layer and (II) water bridge interaction (i.e., inner sphere complexation) between $PYOH^+$ and residual interlayer cations. In PYO–montmorillonite complexes, the major interaction (i.e., mechanism III) is an outer-sphere complexation between interlayer cations and neutral pyocyanin irrespective of moisture condition as evident by the lack of response of the C—O bond and C—N vibration to changes in moisture (moist to dry). Comparing both interaction mechanisms, the mechanism III is more stable as evident by the stronger C—O bond (1625 vs 1645 cm^{-1}), stronger C—N bond (1455 vs 1480 cm^{-1}), and stability of the bonds under varying moisture regimes. Mechanism I & II were dominant in Na^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Mn^{2+}, and Cd^{2+}-montmorillonite while mechanism III in Cu^{2+}-montmorillonite. Both Ca^{2+} and Ba^{2+}-montmorillonite also exhibited traces of the mechanism III.





EFFECT OF MONO-AND POLYSACCHARIDE ON PYOCYANIN ADSORPTION BY SMECTITE AND SEPIOLITE

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Smectite and sepiolite are effective in removing pyocyanin, a virulence factor produced by *Pseudomonas aeruginosa,* by adsorbing and holding it in their interlayer/tunnel, suggesting possible alternative approaches of antibiotics in disarming the pathogen. When employing clay to immobilize and inactive pyocyanin, competition arises with the biological compounds in biofilm, such as eDNA, poly-, and monosaccharides, and proteins. The objective of this current study is 1) to investigate the interference of mono- and polysaccharide on pyocyanin adsorption by smectite and sepiolite, 2) to find out the selectivity of the clay with pyocyanin at the presence of saccharides, 3) evaluating and assessing the smectite and sepiolite as possible pyocyanin adsorbent at biofilm.

Types of exchange cations on smectite dictate the bonding mechanism between pyocyanin and smectite. Pyocyanin is bound with Na-Smectite through ion exchange process and Cu-Smectite through coordination. Due to the contrasting bonding mechanism between pyocyanin and these two cations, Na and Cu-saturated smectite are used in this study. Although pyocyanin can access the tunnel of sepiolite, some large compounds, such as polysaccharides, can potentially block the tunnel for pyocyanin and may not be an effective pyocyanin remover in biofilm.

For this research, clay particles less than 2 μm were separated from bulk samples through size fractionation, and Na-smectite was subsequently saturated with copper. Pyocyanin adsorption was measured by UV-visible spectrophotometer. The interlayer and the tunnel access of pyocyanin and saccharide were analyzed by XRD and FTIR. Some preliminary data suggested that, although glucose and dextran can enter the interlayer of smectite, they have minimal effect on pyocyanin adsorption. Ongoing experiments will reveal more information on the bonding strength, stability, and configuration of adsorbed pyocyanin in the clay minerals when the competing biological compounds are present.

ANTIBACTERIAL CAPACITIES OF REDUCED SMECTITE-ILLITE CLAY MINERALS

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Ferruginous clay minerals are proposed as antibiotic alternatives to traditional medicines because of their antimicrobial capabilities on multidrug-resistant pathogens. Recently, reduced nontronite (NAu-2) have been shown to inactivate *E. coli* cells under circumneutral pH condition. However, various smectite-illite (S-I) minerals are prevalent and more common in nature, but their bactericidal activity has not been fully investigated. Clay minerals in S-I series share a 2:1 layered structure, but differ in iron content, layer expandability and specific surface area. Therefore, we investigated the antibacterial activities of more common smectite-illite (S-I) clays (with structural Fe reduced) towards *E. coli* cells, including montmorillonite SWy-3, illite IMt-2, 50-50 S-I rectorite RAr-1, and 30-70 S-I ISCz-1.

The antibacterial activity of reduced S-I clays exhibited the following order: rRAr-1 > rSWy-3 >> rIMt-2 ≥ rISCz-1, though all clay suspensions did not eliminate *E. coli* cells within the tested Fe(II) concentration range. The strongest antibacterial activity of rRAr-1 was contributed to both •OH and Fe(IV) generated from the oxidation of structural Fe(II) and dissolved Fe^{2+}, respectively. The •OH produced from structural Fe(II) oxidation was the primary factor responsible for the bactericidal capacity of rSWy-3. The antibacterial activity of other S-I clays depended on layer expandability, with expandable smectite being the most antibacterial and non-expandable illite the least. Cells with rRAr-1 exhibited both polar and longitudinal membrane damages. This work showed that reduced smectite-illite (S-I) minerals hold extraordinary abilities to kill pathogen *E. coli*, which provides new insights into the antibacterial mechanisms and design of clay mineral-based bactericidal regents.

CONTROLLED MOLECULAR ARRANGEMENT OF CINNAMIC ACID IN LAYERED DOUBLE HYDROXIDE THROUGH PI-PI INTERACTION FOR CONTROLLED RELEASE

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Cinnamic acid (CA) was successfully incorporated into the Zn-Al layered double hydroxide (LDH) through coprecipitation. The CA moiety was stabilized in the interlayer space through not only electrostatic interaction but also intermolecular pi-pi interaction. It was noteworthy that the CA arrangement was fairly independent to the charge density of LDH, showing the important role of layer-CA and CA-CA interaction in the molecular stabilization. Computer simulations using Monte Carlo method as well as analytical approaches including infrared, UV-vis spectroscopy and differential scanning calorimetry showed the existence of intermolecular interaction. In order to reinforce the molecular stabilization, a neutral derivative of CA, cinnamaldehyde (CAD) was additionally incorporated into LDH. It was clearly shown that the CAD took a role in pi-pi inter-action mediator to enhance the stabilization of CA. The time-dependent release of CA from LDH was first governed by the layer charge density of LDH; however, the existence of CAD provided additional stabilization to CA arrangement to retard the release kinetics.

INTRODUCTION OF DEFECT SITE IN LAYERED DOUBLE HYDROXIDE AND ITS MODIFIED MAGNETIC PROPERTY

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Layered double hydroxide (LDH) has long been utilized as drug delivery carrier or scavengers for aqueous pollutant due to its high affinity to anionic moiety. In order to increase applicability of LDH in biomedical and environmental application, we tried to endow magnetic property to LDH which intrinsically has antiferromagnetic coupling among transition metals through ligand mediated super-exchange. Two types of pristine MgFe-LDHs with different crystallinity were prepared by hydrothermal method (hLDH) or coprecipitation method (cLDH). The reaction was designed to introduce oxygen defect by the treatment of reductant, sodium borohydride. According to X-ray diffraction, the crystalline phase and global crystallinity of both LDHs were determined to be preserved before and after sodium borohydride treatment. Electron microscopy also exhibited that there was no significant change in morphology upon reaction. However, X-ray photoelectron spectroscopy demonstrated that a certain portion of oxygen vacancies were generated upon the reaction and the degree was larger in cLDH than in hLDH. We could observe the peak shift in UV-Vis diffuse reflectance spectroscopy of defected LDH due to the enhanced ligand-to-metal charge transfer. The X-ray absorption near edge structure on Fe K-edge showed an apparent change in pre-edge and white line intensity after reductant treatment, illustrating the development of oxygen vacancy around Fe. Furthermore, the defect induced cLDH was determined to have paramagnetism with coercivity of 182.5 Oe at low temperature, while the pristine cLDH was still diamagnetic at the same condition.

NATURAL TO SYNTHETIC: HOW ANTIBACTERIAL CLAYS CAN HELP FIGHT ANTIBIOTIC RESISTANCE

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The discovery of antibiotics changed the world and ushered in a new era of human prosperity that has been capitalized on for the last 100 years. However, microorganisms have continually evolved resistance to these antibiotic compounds and with the stalled development of new antibiotics, we have entered the antibiotic resistance era. Certain naturally occurring clay mineral deposits were found to have antibacterial properties against the deadliest antibiotic resistant strains of bacteria. While the study of these natural clay deposits proved fruitful, the application of the natural deposits was hindered by sample heterogeneity, variable antibacterial activity, and the risk of toxic metal impurities. Our team was able to successfully synthesize antibacterial mineral formulations that mimicked the natural clay deposits, while eliminating unwanted impurities and controlling the dose of metal release and reactive oxygen species (ROS) generation. The synthetic antibacterial mineral formulations consisted of smectite clay minerals and micro-particle iron sulfides (pyrite) that establish a redox cycle that can be tuned to release varying amounts of ferrous iron and hydrogen peroxide over hours, days or weeks depending on the mixture and chemistry. These synthetic formulations were found to effectively kill the ESKAPE pathogens (*Enterococcus sp., Staphylococcus aureus, Klebsiella pneumoniae, Acinetobacter sp., Pseudomonas aeruginosa* and *Enterobacter sp.*) when tested in vitro. However, in vivo testing with antibiotic resistant infected animals is required to prove that these synthetic analogues are safe an effective for human health applications. Our team also tested the efficacy of synthetic antibacterial clays in a topical MRSA (*methicillin resistant staphylococcus aureus*) biofilm infections using a scalpel scrape mouse model. The results revealed that the synthetic minerals successfully eliminated the MRSA biofilm infections while promoting wound closure. These findings represent a breakthrough in our understanding of antibacterial clays and reveal that natural geochemical processes can be utilized for human health applications. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

THERANOSTIC ANIONIC CLAYS THROUGH TOPOTACTIC LATTICE ENGINEERING AND DRUG INTERCALATION

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Layered double hydroxide (LDH), also known as anionic clay, has potential as drug delivery carrier due to its low toxicity and high drug accommodation property. We have topotactically introduced both drug and imaging moiety into LDH for theranostic application. The interlayer space of LDH was loaded with anticancer drug molecule, methotrexate (MTX), and the lattice framework was partially modified with radioisotope Co-57 moiety. In order to convince the Co-57 incorporation in MgAl-LDH, non-radioisotope Co was utilized and isomorphous substitution reaction was carried out under hydrothermal condition. Time dependent quantification revealed that the incorporation of Co into an LDH was highly dependent on the dissolution of Mg from LDH framework, suggesting the one-to-one substitution between framework Mg and external Co. It was notable that the size (~250nm) and hexagonal plate-like morphology of LDHs did not change significantly upon Co substitution. Transmission electron microscopy-energy dispersive spectroscopy (TEM-EDS) exhibited homogeneous distribution of Co in the LDH particles, suggesting the isomorphous substitution of Co into LDH framework. The substitution reaction was extended to radioisotope Co-57 upon either MgAl-LDH and MTX intercalated LDH (MTX-LDH). It was confirmed that the substituted Co-57 retained 80% of its radioactivity until 24 h in human serum, corroborating stable radio-labeling. In vitro cellular uptake test resulted in ~45ID% high radioactivity delivering efficiency. In vivo biodistribution showed time-dependent tumor accumulation of Co-57 by LDH showing high tumor-to-organ ratios.

HYDROTALCITE-NICLOSAMIDE NANOHYBRIDS AS AN ORAL FORMULATION FOR SARS-COV-2: A NOVEL THERAPEUTIC APPROACH

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COVID-19 has been affecting millions of individuals worldwide and, thus far, there is no accurate therapeutic strategy. This critical situation necessitates novel formulations for already existing, FDA approved, but poorly absorbable drug candidates, such as niclosamide (NIC), which is of great relevance. In this context, we have rationally designed NIC-loaded hydrotalcite composite nanohybrids, which were further coated with Tween 60 or hydroxypropyl methyl cellulose (HPMC), and characterized them in vitro. The optimized nanohybrids showed particle sizes <300 nm and were orally administrated to rats to determine whether they could retain an optimum plasma therapeutic concentration of NIC that would be effective for treating COVID-19. The pharmacokinetic (PK) results clearly indicated that hydrotalcite-based NIC formulations could be highly potential options for treating the ongoing pandemic and we are on our way to understanding the *in vivo* anti-viral efficacy sooner. It is worth mentioning that hydrotalcite–NIC nanohybrids maintained a therapeutic NIC level, even above the required IC_{50} value, after just a single administration in 8–12 h. In conclusion, we were very successfully able to develop a NIC oral formulation by immobilizing with hydrotalcite nanoparticles, which were further coated with Tween 60 or HPMC, in order to enhance their emulsification in the gastrointestinal tract.

HIGHLY ENHANCED BIOCOMPATIBILITY OF DEXAMETHASONE WITH CLAY-BASED DRUG DELIVERY SYSTEM

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Dexamethasone (DEX) is a glucocorticoid with anti-inflammatory effects. It can be used for various diseases such as autoimmune diseases, allergies, cancer, ophthalmic diseases and COVID-19, etc. However, its efficacy is hindered by poor water solubility, necessitating higher dosages that may lead to adverse effects, including hypertension, peptic ulcers, hyperglycemia, and Cushing's syndrome. To overcome these limitations, we focused on developing a drug delivery system using clay nano-vector, layered double hydroxide (LDH), as a carrier to enhance the therapeutic efficacy of DEX. Employing co-precipitation, ion-exchange, and exfoliation and reassembling methods, we successfully intercalated DEX into the interlayer spaces of LDH. X-ray diffraction, molecular spectroscopy, and thermogravimetry analyses revealed the stabilization of DEX molecules within LDH interlayer spaces through electrostatic interactions, preserving their functionality and structural integrity. SEM and DLS results showed that the DEX-LDH particles were evenly dispersed with uniform size. Sustained release properties of DEX under various pH conditions were explored for potential application in the tumor microenvironment. Furthermore, biocompatibility and efficacy of the nanohybrids were evaluated through MTT assays using mouse fibroblast cells and breast cancer cells, respectively, demonstrating their suitability for medical applications. In conclusion, the DEX-LDH nanohybrid exhibited superior efficacy and improved distribution compared to DEX alone and has the potential to enhance therapeutic efficacy.

CLAYS FOR COMBINED PELOTHERAPY AND ELECTROTHERAPY

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Pelotherapy and electrotherapy are therapeutic methodologies with proven success in physical medicine and rehabilitation and dermatology fields. The main purpose of these therapeutic modalities is to reduce pain, accelerate wound healing, alleviate muscle spasms, and improve mobility and muscle tone. Their main challenge is in the passage of some ionic species through the skin barrier. The dermal absorption values are an integral part of the risk assessment process for peloids. This work explores the quality assessment of clays to be used on these two transdermal drug delivery systems (TDDS) and the presentation of methodologies to achieve peloid safety compliance, especially concerning the potential and degree of toxicity arising from ion exchange and trace elements. TDDS of pelotherapy is enhanced by temperature and electrically by iontophoresis. The low voltage of iontophoresis and sweat phenomena with pore dilation driven by pelotherapy allows the use of the same pathways: hair follicles and sweat pore. The therapeutic integration of iontophoresis and pelotherapy focused on patient benefits and low safety-related risk may contribute to the outstanding physiological performance of pelotherapy, specifically, in the way the essential elements and exchange cations pass through the skin barrier.

Clays are naturally ionized and it is possible to change their polarization using electrolytic solutions or blending them with specific medicinal-mineral water (maturation process). The transdermal delivery activation by electrokinetic forces should be studied considering experimental factors such as current strength (0.5 mA/cm2), temperature (40–45 °C) of application, time of application (15–20 min) and electrode materials selection. This is possible by developing an electronic device and a skin electrode specifically to store and heat the peloid, to be approved for clinical use.

The validation of an innovative iontophoretic systems applied to pelotherapy can also promote future challenges in the obtaining of the ideal therapeutic control of peloids and the clinical validation of results with physiological efficacy recognition.

CONCENTRATED COLLOIDAL NANOCRYSTALS OF METAL HYDROXIDES FOR BIOMEDICAL CONTRASTING AGENTS

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Layered metal hydroxides (LMH) are recognized as promising green materials due to their synthesis feasibility in aqueous media under moderate/ambient conditions. Their functionalities are available in aqueous media free from poisoning. 2D layered metal hydroxides composed of low-valence metal cations exhibit additional highlighted properties, such as reversible intercalation/deintercalation and anisotropic ion transfer.

To date, we have reported LMH nanoparticles with a size < 10 nm, demonstrating a high dispersion stability in solvents under a concentrated state at as high as 40 wt%.[1] This unique dispersion system can be used for developing sol-gel systems for monoliths, nanofibers, thin films, and spheres.

This presentation introduces sol-gel systems, based on these colloidal dispersions, for biomedical applications. [2, 3,4] One example is for imaging purposes. LMH nanoparticles acts as a nanofiller and alkaline catalyst to form a silica/LMH monolithic material with homogeneity at the nanoscale. LMH nanoparticles contribute to the strong enhancement of the X-ray attenuation. Imaging and quantification of blood vasculature both in human and animal tissues and organs have been successfully demonstrated. This contrast agent is readily prepared and used and therefore provides a promising option for imaging, allowing high contrast, which has the potential to offer deeper insights into vascular pathology.

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CLAYS AND ZEOLITES AS ROBUST FRAMEWORK FOR PHOTODYNAMIC REACTION: BIOLOGICAL APPLICATIONS OF LIGHT SENSITIZING MATERIALS

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Layered clays or porous minerals has high potential to immobilize and stabilize organic molecules. In this work, we immobilized photosensitizer molecules such as protopophyrin and chlorophyll into clays – illite and layered double hydroxide – and zeolites both in powder and consolidated ball type. According to the adsorption isotherm analyses, it was confirmed that the most of the photosensitizing organic molecules are attached on the mineral surface through Langmuir type adsorption. Even though the single layer adsorption of Langmuir could not guarantee high loading capacity, the strong surface interaction between organic moiety and minerals would enable stabilization of photosensitzers. In order to check the photodynamic property of mineral immobilized phosotsensitzers, we select chlorophyl incorporated zeolite ball as the model material and carried out photocatalyst reaction using radical reagent, 1,3-diphenylisobenzofuran (DPBF). The results exhibited that the chlorophyll incorporated zeolite under light irradiation ball removed most of the DPBF radical within a few minutes, while the DPBF alone maintained 80% of its intact moiety under light irradiation. Then the photosensitizing ball was produced in kilogram scale to check the industrial availability. Approximately 5 kg of photosensitizing balls were filled in a simulating tester with water flow and light irradiation and then the numbers of bacterial colonies in the water were counted. It was confirmed that the colony formation of various bacteria including *Y. Enterocolitica* and *S. Aureus* were dramatically suppressed under the photodynamic actions of photosentizing balls.

NANO-SPECIFIC AFFINITIES: SELECTIVE ADSORPTION OF DEOXYRIBONULEIC ACID STRANDS ON LAYERED DOUBLE HYDROXIDE NANOMATERIALS THROUGH DIMENSIONAL SIMILARITY

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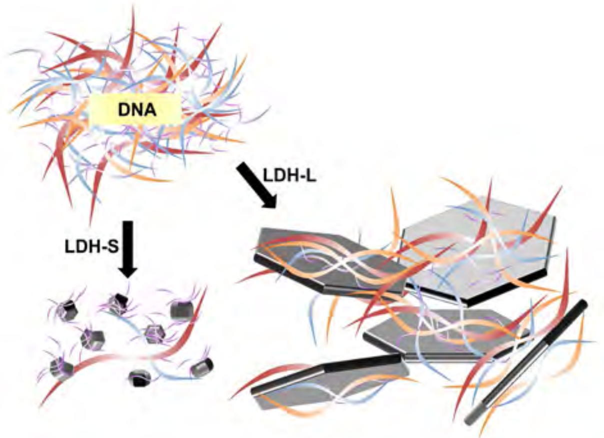
Layered double hydroxides (LDHs) with different particle diameters were synthesized, and their adsorption behavior toward deoxyribonucleic acid (DNA) was examined with respect to the strand length of DNA. Small-sized LDH (LDH-S) was synthesized by conventional coprecipitation, while large particles (LDH-L) were prepared by the urea hydrolysis method. The X-ray diffraction patterns indicated the LDH-L with a higher crystallinity than the LDH-S; LDH-S and LDH-L with average particle sizes of 20 nm and 2500 nm were proved by scanning electron microscopy. Adsorption isotherm revealed that LDH-S had a good agreement with the Freundlich model (multilayered-adsorption), while LDH-L followed Sips (a combination of single-layer and multilayer adsorption). The electrophoresis of ladder DNA after adsorption discovered that DNA with less than 800 bp length was more adsorbed by LDH-S than LDH-L; on the contrary, long-stranded DNA (>800 bp) was more effectively adsorbed by LDH-L than LDH-S. Picogreen assay showed that the amount of adsorbed DNA increased with LDH/DNA ratio. The large particle size of LDH tended to adsorb a longer length of DNA (>800 bp), and the small particle size of LDH was more inclined to adsorb a shorter length of DNA (<800 bp) shown in the Scheme 1.



Scheme 1. Illustration of DNA adsorbed on LDHs with two particle sizes

PH-RESPONSIVE NICOTINIC ACID-LAYERED DOUBLE HYDROXIDE FOR CONTROLLED DRUG DELIVERY

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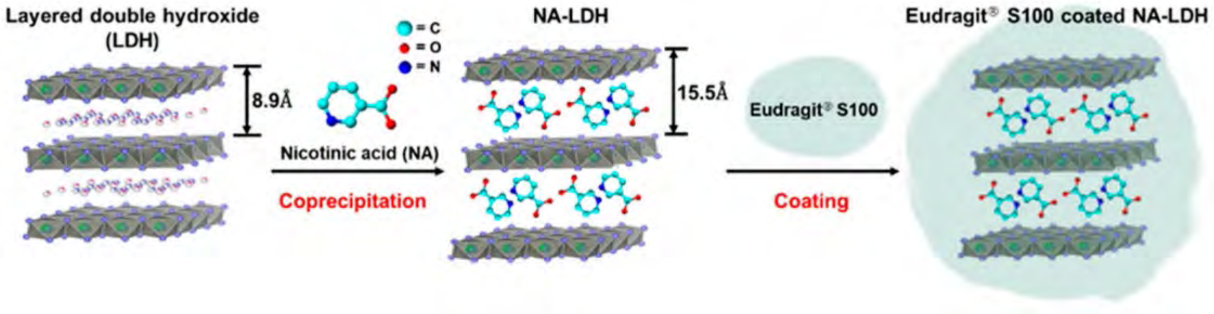
Although nicotinic acid (NA) has several clinical benefits, its potency cannot be fully utilized due to several undesirable side effects, including cutaneous flushing, GIT-associated symptoms, etc. To overcome such issues and improve the NA efficacy, a new inorganic–organic nanohybrids system was rationally designed. For making such a hybrid system, NA was intercalated into LDH through a coprecipitation technique and then coated with Eudragit® S100 to make the final drug delivery system called Eudragit® S100-coated NA-LDH. The as-made drug delivery system not only improved the NA release profile but also exhibited good bio-compatibility as tested on L929 cells. Such an inorganic–organic nanohybrid drug delivery agent is expected to reduce the undesirable side effects associated with NA and hopefully improve the pharmacological effects without inducing any undesirable toxicity.



NONIONIC POLYMER-COATED NICLOSAMIDE-MONTMORILLONITE HYBRIDS: A STRATEGY FOR ENHANCED BIOAVAILABILITY IN COVID-19 TREATMENT

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Niclosamide (NIC), a conventional anthelmintic agent, is emerging as a repurposed drug for COVID-19 treatment. However, the clinical efficacy is very limited due to its low oral bioavailability resulting from its poor aqueous solubility. In the present study, a new hybrid drug delivery system made of NIC, montmorillonite (MMT), and Tween 60 is proposed to overcome this obstacle. At first, NIC molecules were immobilized into the interlayer space of cationic clay, MMT, to form NIC–MMT hybrids, which could enhance the solubility of NIC, and then the polymer surfactant, Tween 60, was further coated on the external surface of NIC–MMT to improve the release rate and the solubility of NIC and eventually the bioavailability under gastrointestinal condition when orally administered. Finally, we have performed an in vivo pharmacokinetic study to compare the oral bioavailability of NIC for the Tween 60-coated NIC–MMT hybrid with Yomesan®, which is a commercially available NIC. Exceptionally, the Tween 60-coated NIC–MMT hybrid showed higher systemic exposure of NIC than Yomesan®. Therefore, the present NIC–MMT–Tween 60 hybrid can be a potent NIC drug formulation with enhanced solubility and bioavailability in vivo for treating Covid-19.

FACTORS INFLUENCING THE GROWTH OF LAYERED DOUBLE HYDROXIDE LAYERS ON ZN ALLOY FOR SMART CORROSION PROTECTION

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Recently, much attention has been paid to magnesium and zinc alloys as temporary biodegradable implants, due to their biocompatibility, nontoxicity, and positive effects on the growth of new bone tissue. Although the density and Young's modulus of Mg alloys are closer to that of human bone compared to other metallic materials used as implants, Zn plays a significant role in bone tissue development. Zinc stimulates cell differentiation, proliferation, and mineralization in osteoblasts, thereby promoting bone formation. Generally, as a structural element of ossein, Zn is important for bone growth and bone quality. The main obstacle to the application of Mg/Zn alloys as a temporary, biodegradable implant is their fast biodegradation rate. Therefore, protective coatings must be used to control the degradation profile and readily improve the functional properties. Implementation of coatings with layered double hydroxides (LDHs) structure will allow the creation of smart biodegradable materials with enhanced corrosion resistance, biocompatibility, and controllable degradation. In this study, we focus on the development of LDH films, directly grown on a Zn surface using the substrate alloy as an internal source of Zn cations to form naturally adherent coatings, supported by the incorporation of corrosion inhibitors and further covered by chitosan film as a natural biopolymer with good biocompatibility, and antibacterial activity. A series of ZnAl-NO_3 LDH coatings were obtained in situ on the surface of Zn alloys under the control of pH. The degree of alloy substrate polishing, the time of growth, and the thickness of LDH structure coatings formation were comparatively investigated towards the formation of a dense LDH surface layer.

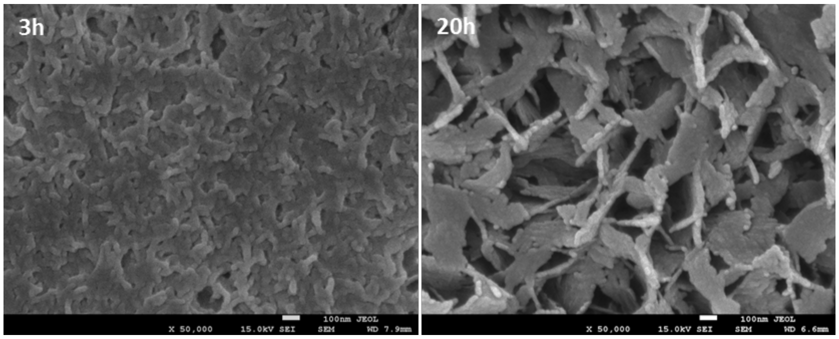

Fig.1. SEM images of ZnAl-NO3 LDHs coatings on Zn alloy after 3 h and 20 h of aging.

The correlation between the structural aspects of the formed LDH coatings, adhesion of the obtained layer to the substrate, and corrosion performance before and after introducing the corrosion inhibitors and top chitosan layers was established. The effects of synthesis conditions on the structure, composition, and mechanical properties were gauged with the use of SEM-EDS, XRD, XPS, and FTIR methods. Corrosion properties were evaluated by electrochemical impedance spectroscopy, potentiodynamic polarization, and hydrogen release measurements.

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Session 13

Nanosized or nanostructured tubular and fibrous clay minerals for versatile functionalization and application

Conveners: YuanPeng (Guangdong University of Technology, China), Pilar Aranda (Materials Science Institute of Madrid of the Spanish National Research Council, Spain), Giuseppe Lazzara (Department of Physics and Chemistry, University of Palermo, Italy); Antoine Thill (CEA Saclay, France), Lala Setti Belaroui (Université Oran 1 - Ahmed Ben Bella, France), Wei Yanfu (Macau University of Science and Technology, China), Pooria Pasbakhsh (School of Engineering, Monash University, Malaysia)

LIGNIN-SEPIOLITE BIONANOCOMPOSITE FOAMS: PREPARATION AND USE IN REMOVAL OF POLLUTANTS IN WATER

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Lignin is a natural biopolymer coming as by-product from diverse industrial process involving lignocellulose biomass. In this study, we evaluate various approaches for producing higher value products from lignin involving its combination with clays. In particular, we explore the preparation of bionanocomposite foams combining either the so-called black liquor (BL) (the residual liquid fraction obtained after kraft pulping, containing solubilized lignin, residual chemical products and some solubilized carbohydrate) or the Kraft lignin (Lig) (isolated from this black liquor by acid precipitation), in combination with sepiolite (Sep). BL/Sep bionanocomposites were synthesized by emulsion tempering, the mechanical agitation of the emulsion favoring the formation of bubbles. The resulting foams show a closed cell structure with macropores of various sizes and specific area between 19 and 35 m^2/g. Lig/Sep bionanocomposites were prepared by freeze-drying water dispersions of the two components, resulting in stable and rigid macroporous foams that present an open cell morphology with surface areas between 1 and 4 m^2/g. The presence of sepiolite in both types of bionanocomposite foams improved their stiffness, with Young's moduli ranging from 0.21 to 9.6 MPa. The resulting foams were tested as adsorbents of metals, drugs and dyes exhibiting adsorption capacities similar to those described for lignin but with the advantage of being easily removed from the water. Moreover, the presence of sepiolite significantly enhanced the adsorption of Cu(II), Cd(II), paracetamol and methylene blue (MB) on BL/Sep bionanocomposites. Meanwhile, Lig/Sep bionanocomposites demonstrated superior adsorption capacities for Cr(VI) anion and aromatic ring compounds, including acetaminophen and MB.

COMPOSITE MATERIALS BASED ON HALLOYSITE CLAY NANOTUBES: FROM MARINE WASTE TO ADVANCED FILMS AND GEOPOLYMERS

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This work presents the development of novel sustainable composite materials employing halloysite nanotubes (HNTs) as natural nanoclays. In the initial stage of this study, we focused on the fabrication of hybrid films using halloysite nanotubes and cellulose extracted from Posidonia Oceanica sea balls (*Egagropoli*), which are marine wastes accumulating along the Mediterranean beaches. Varying the HNTs content from 30 to 80 wt%, composite films with properties similar to pristine cellulose were achieved, even with high amount of clay. Furthermore, the addition of halloysite determined relevant improvements of the thermal stability of cellulose and influenced the films microstructure and wettability. The obtained films displayed competitive elasticity and mechanical resistance, showcasing the potential for packaging applications. Additionally, these films were converted into geopolymeric materials via alkaline activation, resulting in a significant enhancement of the tensile performances, suggesting their suitability in the construction field. In this regard, we also propose another approach for preparing composite halloysite-based geopolymers by filling with beeswax microparticles derived from Pickering emulsions. The homogeneous dispersion of microwax particles within the geopolymeric network was proved together with the enhancement of the mechanical properties and heat storage capacity. These innovative approaches denote a significant step towards developing sustainable composite materials, offering promising ways for both packaging and building applications while addressing environmental concerns through the valorization of natural resources and wastes.

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SEPIOLITE: A POWERFUL CLAY FILLER FOR THE ADVANCED MATERIALS

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Sepiolite (Sep) is a powerful and promising filler, alternative to the. synthetic shape-controlled silica filler for many industrial applications. It possesses unusual structure, producing a "checkerboard" type pattern, where the sheets are covalently bonded, so they cannot be exfoliated.

For this, the breaking down of Sep fibres aggregate is still a challenge to take advantage of the peculiar sepiolite shape for designing nanostructured materials.

In this context, soft-chemistry methods, and the use of functionalizing molecules, often enables the generation of tailored inorganic-organic hybrid interfaces, making Sep fibres exploitable as active component in many formulation products with unique properties.

In the last decade, we are focused on the different possibility to modulate sepiolite bulk properties including surface chemistry and morphology, particle size, shape, and porosity, to design systems employed in several applications, such as polymer nanocomposites (NCs), catalysis, photoresponsive materials and biomedical products.1

The talk will present some examples of the modification and applications of Sep based materials, with some more hints on those which have now reached a quite mature stage of development and for which marketable solutions are currently or shortly available, such as the "SmartNET ™ Technology"2 and the "next generation double function fillers",3 industrially developed in Pirelli Tyre laboratories.

Limits and perspectives will be addressed, especially in the light of the challenging opportunity to control and tuning hybrid interfaces of Sep clay filler with organic species and macromolecular matrix.

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2. PCT Int. Appl. WO 2016174629;
3. PCT Int. Appl. WO 2020110023.

HALLOYSITE CLAY NANOTUBES AS A MULTIFACETED MATERIAL FOR BIOLOGICALLY SELF-HEALING CONCRETE

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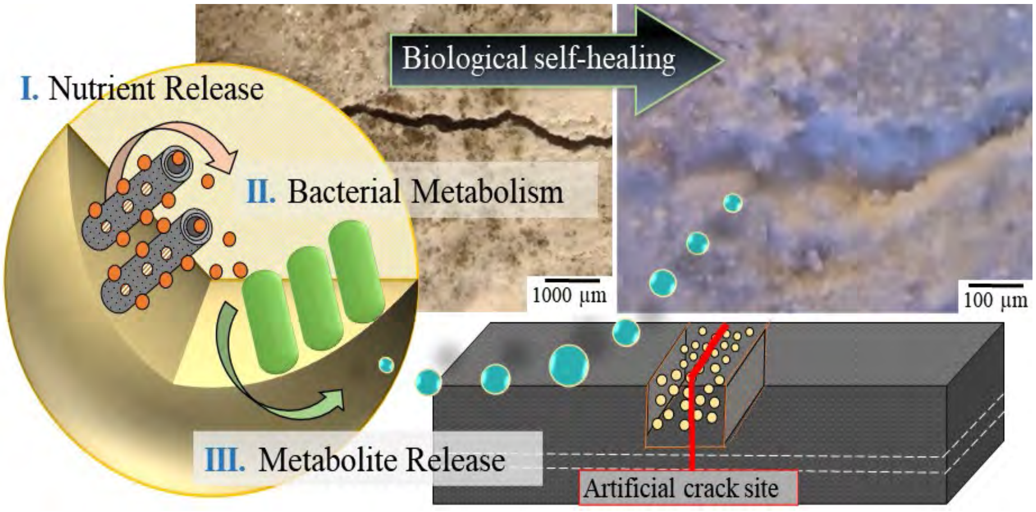
Our research group utilized the hollow, tubular, and porous structure of halloysite clay nanotubes (HNTs) in a biologically self-healing concrete system to address short-term functionality and nutrient loss issues. HNTs could effectively carry bacterial nutrients, support bacterial growth and biomineralization in concrete, improve the organic carrier-cement interface by pozzolanic reaction with the cement matrix, and enhance the resistance of the carrier to the cement environment. Encapsulated nutrient-loaded HNTs exposed to the cement pore solution successfully retained the nutrients and supported intracapsular biomineralization. Encapsulated HNTs mitigated the loss of early flexural strength observed in concrete samples with basic hydrogel microcapsules. The self-healing system successfully healed 300 μm-wide concrete cracks, restoring the crack water tightness by 95% with 75% more flexural strength regain than control samples. While the self-healing system can have various alternative applications, we demonstrated that the self-healing system and metakaolin are suitable for artificial coral reef restoration, being able to replace 25 wt% of cement without impacting coral health while possibly encouraging coral attachment.



ION PAIRING OF CA^{2+}, ZN^{2+}, AND LA^{3+} TO ACETATE IN SILICA NANOPORE

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This study investigated the influence of nanoscale confinement on the ion pairing involving Ca^{2+}, Zn^{2+}, and La^{3+} with CH_3COO^- anions. By modeling the Raman spectra of several concentrations of the cation–acetate, the free (unbound) CH_3COO^- and bound CH_3COO^- in the contact cation–acetate ion pair was quantified for aqueous solutions and on the same solutions confined within 4 nm silica nanopores. Except for Ca^{2+}–CH_3COO^-, the population of the contact ion pair was enhanced in silica nanopores by a factor of 1.80 and 1.10 for Zn^{2+}–, and La^{3+}– CH_3COO^-, respectively. The binding constant increased by ~1.05, 1.30, and ~1.16 for Ca^{2+}–, Zn^{2+}–, and La^{3+}– CH_3COO^-, respectively. The free energy of formation of contact ion pairs in confinement was reduced by 0.11, 0.77, and 0.40 kJ/mol compared to solution phase. The observed shift towards the formation of 1:1 contact ion pair is attributed to the lower desolvation cost in the silica nanopore compared to aqueous solution.

INFLUENCE OF HALLOYSITE FROM DIFFERENT DEPOSITS ON ORGANIC MOLECULES DEGRADATION

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In this work, a catalytic system was investigated using halloysite nanotubes (HNTs) sourced from different deposits. Halloysite nanotubes find application in different fields including drug delivery, enzyme immobilization, polymer technology, catalysts design, removal of pollutants and cultural heritage. HNTs are characterized by mineral impurities that influence the physical and chemical properties of this material. Despite the possibility of using HNTs as support for catalytic purposes, HNTs could have an intrinsic catalytic activity that alter the final experimental results. The purpose of this research is to highlight this aspect through the degradation of ascorbic acid and the photocatalysis of ibuprofen employing four different types of halloysite, as shown in Figure 1. In particular, we observed a correlation between the presence of impurities in the chemical composition and the efficiency of a catalyst. Specifically, we examined how the presence of zinc and manganese in the composition could influence the degradation.

This investigation opens up new perspectives of research for accurately selecting halloysite over other nanoclays options.

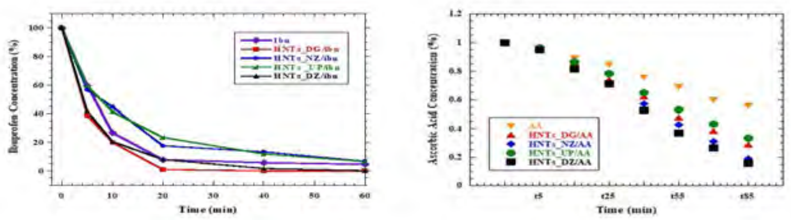

Figure 1. On the left photodegradation of ibuprofen, on the right degradation of ascorbic acid.

HALLOYSITE-BASED ADSORPTION MATERIAL WITH ULTRAHIGH LEAD ION ADSORPTION CAPACITY AND STABILITY

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Natural halloysite nanotubes (Hal) have been widely used in the fields of adsorption and environment applications due to their unique hollow tubular structures and abundant surface hydroxyl groups. However, the adsorption capacity and selective adsorption ability of Hal towards heavy metals are still far from satisfaction.

In this study, a novel halloysite-based adsorption material is synthesized by grafting titanium hydroxyl groups on acid leached halloysite nanotubes (Hal-A-Ti), which exhibited ultrahigh Pb(II) ion adsorption capacity (~1000 mg/g), selectivity (>98 %), fast adsorption equilibrium speed (~2 min), and excellent regeneration performance (>98 % after 5 circles). The well dispersion of the $Ti(OH)_4$ groups on inner/outer wall of halloysite nanotubes and the replacing of SiOH groups by TiOH groups on Hal surface are confirmed by TEM and oxygen K-edge X-ray absorption spectra. The long term stability of the synthesized Hal-A-Ti materials at acid conditions (pH~4) promised a sustainable clay-based nanomaterial for the removal of Pb^{2+} ions from acid wastewater or acid soils.

THE STABILITY, LOCAL BONDING AND ELECTRONIC PROPERTIES OF SINGLE-WALLED HNTS WITH THEIR INNER DIAMETER UPTO 20 NM

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Halloysite nanotubes (HNTs), with unique microstructure and properties, have been widely used in the fields of adsorption, catalysis, drug loading and environment applications. However, the fundamental knowledge on the structure-property relationships of HNTs is still in its infancy at atomic level, due to the large nanotube size of HNTs (inner diameter ranges from about 5 to 50 nm).

In this study, we perform a systematic study on the stability, local bonding and electronic properties of single-walled HNTs with their inner diameter upto 20 nm by several theoretical calculation methods. The formation energies of HNT are compared by using classical mechanical (General Utility Lattice Program, GULP), Density Functional based Tight Binding (DFTB) and Density Functional Theory (DFT) methods. The initial HNT structures were produced using two curling directions (armchair and zigzag) with two typical prototype structures of kaolinite.

It is found that the strain energy of HNTs is influenced by curling direction and initial lattice parameters as well as the detailed optimization procedures. Notably, the strain energy of HNTs decreased exponentially with diameter of HNTs and converge at around 4 nm, agreed well with the natural occurrence of HNTs. For most stable structures at different calculations levels, the evolution of the strain energy, bond length, angle, density of states, band gap and Mulliken charge of HNTs with their diameters were systematically analyzed.

HALLOYSITE-BASED CATALYSTS: COMPUTATIONAL AND EXPERIMENTAL INVESTIGATIONS INTO BIOMASS CONVERSION

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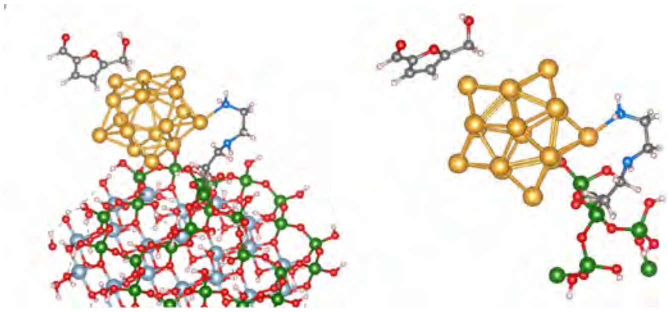
Halloysite is a natural clay mineral with a hollow tubular structure, applicable as a component of biocompatible nanosystems with specific functionalities. Its particular morphology can be exploited to obtain various organic-inorganic composites that can be used for different types of applications such as nanoreactors for various types of chemical processes. In the last decades the selective oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) has become one of the most important reactions that involves the use of biomass and its derivatives. FDCA is one of the most requested chemical compounds: it should in fact be used for the production of polyethylene furanoate, a bioplastic that could replace PET. This study involves the modification of halloysite nanotubes outer surface with an organosilanic compounds, like AEAPTMS. These modifications aim to facilitate the binding of gold nanoparticles on the nanotube surface. Subsequently, the modified nanotubes are explored as heterogeneous catalysts in the oxidation of HMF to FDCA. Both computational and experimental methods are employed to investigate the reaction pathway. The computational analysis focused on analyzing the first steps of the reaction with H_2O_2 as oxidizing agent and then going into a more in-depth analysis of the gold cluster growth. The experimental part consisted in the optimization of a synthesis strategy of the gold nanoparticles and then their linking to the beforehand modified halloysite surface as the starting catalyst for the biomass conversion.



INFLUENCE OF INDIGO-HYDROXYL INTERACTIONS ON THE PROPERTIES OF SEPIOLITE-BASED MAYA BLUE PIGMENT

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Maya blue is a greenish-blue and stable pigment which was widely used in the ancient Mayan area. Now it is known as a hybrid pigment of indigo and palygorskite or sepiolite. However, the color causing and stabilization mechanism of Maya blue are still unclear.

In this study, the interactions between different hydroxyl groups of sepiolite and indigo and their effects on the color and stability of Maya blue pigments were investigated. Sepiolite materials were heated at 160, 360, 610, and 880°C to remove zeolitic water, the first coordinated water, the second coordinated water, and structural hydroxyls. A series of Maya blue simulants were prepared by heating the mixture of indigo and sepiolite materials at 180°C. Reflectance spectroscopy and CIE 1976 color space were employed to characterize color properties and color differences of hybrid pigments. Chemical resistance to concentrated HNO_3 and dimethyl sulfoxide (DMSO), and photostability under visible light were evaluated. Microporous analysis and Fourier transform infrared spectroscopy were applied to study the indigo-sepiolite interaction.

Coordinated water was essential for the greenish-blue color and outstanding stability of Maya blue, while zeolitic water and structural hydroxyls did not affect pigments' properties. Indigo molecules were confirmed to be inserted into sepiolite channels and formed hydrogen bonds with coordinated water at one side. Structural hydroxyls were insignificant for the formation of Maya blue.

CHARACTERIZATION OF SYNTHETIC IMOGOLITE AND GERMANIUM SUBSTITUTED IMOGOLITE BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Nuclear magnetic resonance (NMR) is a very powerful analytical tool for studying the local structure of an atom in liquid or solid state materials. Recently, imogolite which has a unique tubular structure or a germanium substituted imogolite have drawn new attention as new nano-materials. We have already synthesised a germanium analog of imogolite from sodium orthogermanate solution [1]. However, their structure and formation processes are not well understood. Therefore, we analysed them by multinuclear NMR.

Imogolite and germanium substituted imogolite were prepared using mixture of ortoshilicate solution and ortogermanate solution with x (= Ge/(Si+Ge) atomic ratio) = 0, 0.25, 0.5, 0.75, 0.85 and 1. Synthetic methods followed previously reported literature [1]. All solid samples were characteried by XRD, FT-IR, XRF and solid state NMR. Liquid state ^{27}Al NMR was used to further analyse the tube formation process.

In the solid state ^{29}Si NMRspectrum, one peak was observed at -78.5 ppm for x = 0 and 0.25, the same as in natural imogolites, and at -78.0 ppm for x above 0.5. On the other hand, the width at half maximum of the ^{29}Si NMR peak became wider and the broden solid state ^{27}Al NMR signal shifted towards the high frequency side as the Ge content increased. We conclude that the change in the Si-O distance due to the increase in the tube system affected the chemical shift of ^{29}Si NMR.

On the other hand, two signals were observed around 1 ppm and 8 ppm in the liquid ^{27}Al spectrum for the solution during tube formation by heating. The peak of 1 ppm was shifted to lower frequency and became narrowing with increasing heating time. The broader 8 ppm signal shifted towards higher frequencies with increasing heating time and disappeared after 20 days. We have assigned that of 1 ppm as tubular aluminogermanate and that of 8 ppm as by-product in 480h aged solution from these results.

DIAMETER AND CHIRALITY OF NATURAL AND SYNTHETIC IMOGOLITES

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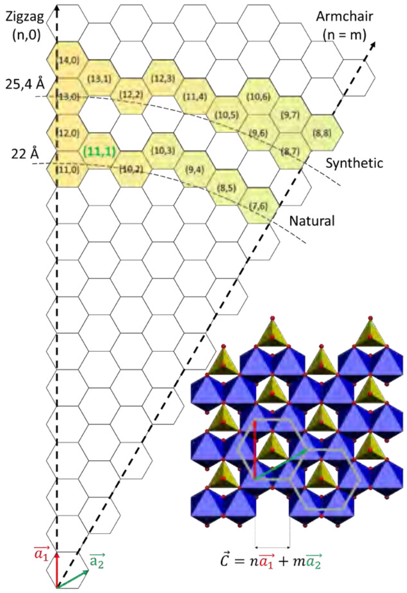

Figure: Possible chiralities for natural and synthetic imogolites.

Imogolite is a natural tubular nanoclay first identified in 1962, whose structure was first described in 1972. As the aluminum atoms are positioned on a hexagonal lattice, it is possible to use the same formalism as for carbon nanotubes to describe imogolites. The chirality vector defined by C*(n, m)* links atoms on the network that will be joined upon rolling (see Figure). In the 1972 study, a zigzag chirality (n, 0) was proposed. Later, Molecular Dynamics (MD) simulations confirmed that it is energetically more favorable compared to armchair configurations[1]. There is however no consensus on the exact value of *n* (10, 11 or 12), which corresponds to the number of Si in the circumference. In 1977, Farmer et *al.* described a protocol to produce synthetic imogolite[2a]. The synthetic nanotube is larger than the natural one and studies obtained some tunability on the diameter[3b]. Recently, D'Angelo et *al.* showed by MD simulations and X-ray diffraction measurements on dispersions and powders that synthetic imogolite is not monodisperse and proposed a 50/50 mixture of (13,0) and (14,0)[3].We have experimentally characterized natural and synthetic imogolite by several techniques (DRX, SAXS, IR, NMR and cryo-TEM) on powders and dispersions. We have also used MD simulations on all possible chiralities. Our results show that a synthetic imogolite sample contains larger and more polydisperse nanotubes than a natural one. In the case of synthetic imogolite, the average diameter measured lies between the one of (13,0) and (14,0) chiralities. We do not obtain the exact same proportion obtained by D'Angelo et *al.* nor rule out the possibility of the presence of other chiralities than zigzag and armchair. For the natural one, the average diameter lies between the diameter of (11,0) and (12,0) chiralities. Analysis of the WAXS does not allow us to draw any definitive conclusions, nor does it rules out non-zigzag and armchair configurations. Surprisingly, the (11,1) chirality is the closest to experimental measurements. Theoretical discussions are conducted to understand the implications of this slight polydispersity in the formation mechanism of imogolite nanotubes.

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ACTIVATION OF NANOSIZED CLAY MINERAL VIA CO-CALCINATION AND MAGNETITE VIA SUBSTITUTION FOR EFFICIENT PHOSPHATE ADSORPTION AND RECYCLING

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The efficient scavenging of phosphate from aqueous media remains a global challenge for aquatic environmental protection and phosphate recovery from wastewater. Here, we demonstrate that this challenge could be tackled by activating nanosized clay minerals (halloysite, kaolinite, palygorskite, chrysotile) and magnetite through co-calcination and isomorphous substitution with La-based precursors, repectively. For clay minerals, this activation involves their initially inert Al/Mg, creating new Al/Mg-based nanoparticles, while enabling La-doped nanoparticles to uniformly coat clay mineral surfaces. Regarding magnetite, low contents of ferrous ions were substituted with lanthanum ions during the creation of La-based magnetite via a hydrothermal reaction, generating reactive La adsorptive sites on the outer layer of magnetite nanoparticles. The activated clay minerals and magnetite exhibited excellent phosphate uptake capacity, strong regeneration ability, and wide applicability regarding the coexistence of competitive anions and broad pH conditions. Efficient phosphate removal using real water samples from sewage effluent was successfully demonstrated. Spectroscopic and microscopic analyses together revealed the scavenging of phosphate by the La-based and Al/Mg-based adsorptive sites, along with multiple capture mechanisms involved, including precipitation, surface complexation, and ion exchange. The materials developed here utilize modified clay minerals and magnetite for their unique capture mechanisms, holding great promise for effective pollution removal in a variety of real-world applications.

CLAY MINERALS MEET NATURAL PLANTS: VALUE CREATION FOR NATURAL RESOURCE UTILIZATION AND SUSTAINABLE DEVELOPMENT

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The rich variety of plants and clay minerals allows researchers to design experiments flexibly for the green preparation of functional materials using clay minerals and plants, which will undoubtedly take the concept of green chemistry and sustainable development one step further, alleviating environmental pollution, energy consumption and resource waste.

Based on the theme of “plant meets mineral”, our group recently has carried out a series of studies on green construction of functional materials combining with plant extracts and clay minerals, especially attapulgite (APT). Generally, plant extracts containing rich active molecules like polyphenols, polysaccharides and proteins have been used as reducing and stabilizing agents to fabricate various functional nanocomposites, such as Pal supported Ag NPs, ZnO NPs and Se NPs. Incorporation of clay minerals could effectively regulate the nucleation and growth of metal-based NPs on the surface and nanochannels of APT, preventing from the aggregation and increase in size of NPs. The obtained nanocomposites containing low doses of metallic substances exhibited low biotoxicity, high antibacterial and antioxidant activity (Figure 1).

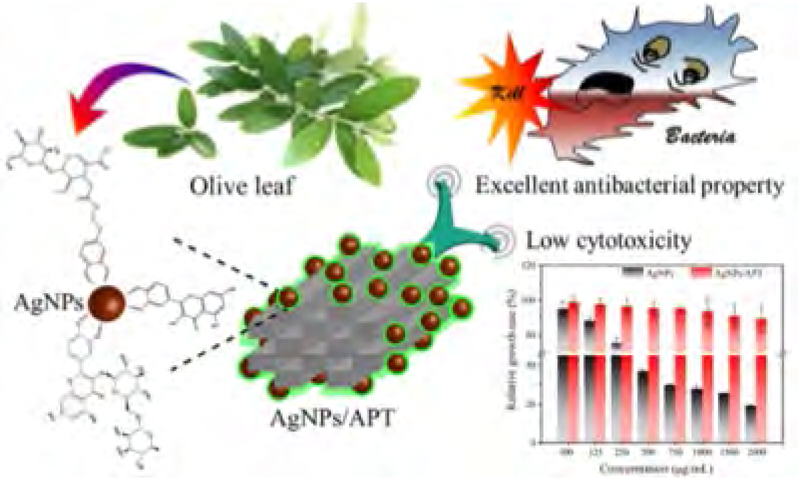

Figure 1. Schematic diagram of preparation of Ag/APT nanocomposites using olive leaf extract

RESEARCH ON THE APPLICATION OF HALLOYSITE IN LOW CARBON-FOOTPRINT BUILDING MATERIALS: GEOPOLYMER AND LIMESTONE CALCINED CLAY CEMENT

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Clay minerals have been used in building materials to improve properties and reduce carbon footprint. Halloysite is a clay mineral with a typical nanoscale tubular morphology and a high pozzolanic activity, indicating that it has a lot of potential for use in the production of building materials. The preparation of innovative halloysite-based binders such as blended cements and geopolymers was investigated in this work. Calcinating halloysite at appropriate temperatures (650°C-850°C) does not affect tubular morphology or mesoporosity, but significantly affects its microstructure and improves reactivity. This pretreatment endows halloysite with large amounts of silica and alumina dissolved in alkaline/acidic solutions, allowing their re-solidification to form high-performance cementitious materials via geopolymerization. The halloysite-based geopolymer exhibited a dense and compact microstructure with a compressive strength over 50 MPa when cured at ambient temperature and moist conditions with a Si/Al ratio of 3.0. At similar calcination temperatures, halloysite can also be used to make limestone calcined clay cement (LC^3) that has excellent mechanical and heat resistance properties. The reaction between halloysite and cement/limestone occurred simultaneously in the inner and outer lumens of calcined halloysite nanotube. Thus, more hydration products of calcium aluminate silicate hydrate gel, hemicarboaluminate, and monocarboaluminate were produced in the as-obtained LC^3. The findings contribute to a better understanding of the hydration mechanism of geopolymer/LC^3 derived from calcined halloysite and highlight a new application for tubular halloysite.

GEOPOLYMEREIZATION OF ION-ADSORPTION TYPE RARE EARTH TAILINGS FOR HEAVY METALS IMMOBILIZATION AND ITS MECHANISM

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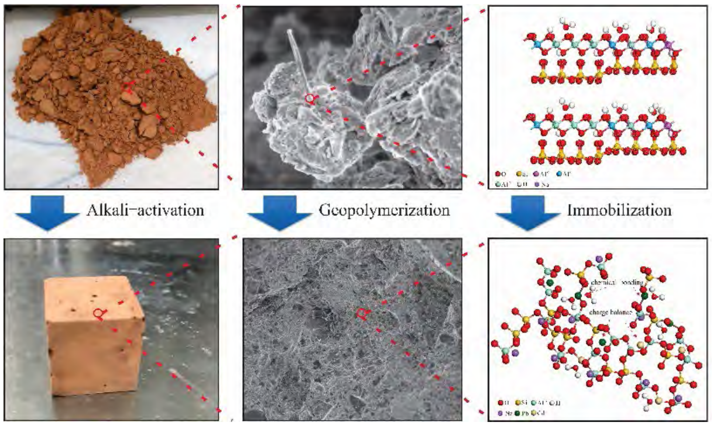
Ion-adsorption type rare earth (IRE) ores form the most important heavy rare earth resource, which provides most of the heavy rare earths consumed annually worldwide. The rare earths in these deposits mainly occur as (hydrated) cations adsorbed on the surface of clay minerals (e.g., kaolinite, halloysite, and illite). However, owing to their low grade, considerable rare earth tailings (RET) are produced after the extraction process. As a type of solid waste that contains clay minerals, RET were used as a starting material to prepare alkali-based geopolymer, a kind of green building material. The effects on the compressive strength of RET-based geopolymer, including the modulus and concentration of the alkaline activator, curing temperature, and liquid/solid ratio, were investigated. Pb^{2+} and Cd^{2+} were added during the preparation of the RET-based geopolymer for evaluating the immobilization capacity of heavy metals in the as-obtained geopolymer. The results showed that geopolymer with a compact and dense microstructure was obtained through the optimization of the above factors, with the highest compressive strength being 28.5 MPa. The leaching test indicated that the RET-based geopolymer possessed a desirable capacity for immobilizing heavy metals, where the immobilization efficiency of Pb^{2+} was above 99% and that of Cd^{2+} ranged from 92% to 96%. Heavy metals were immobilized in the RET-based geopolymer matrix through the formation of chemical bonds (T (Si, Al)–O–M (Pb, Cd)) or through an electrostatic attraction between the metal cations and negatively charged $[AlO_4]^-$. The above results provide a basis for the disposal and resource utilization of RET using geopolymerization technology.



ENGINEERING DRUG-LOADED HALLOYSITE NANOTUBE AND ITS DRAWBACKS IN THE INTRACENOUS ADMINISTRATION ROUTE

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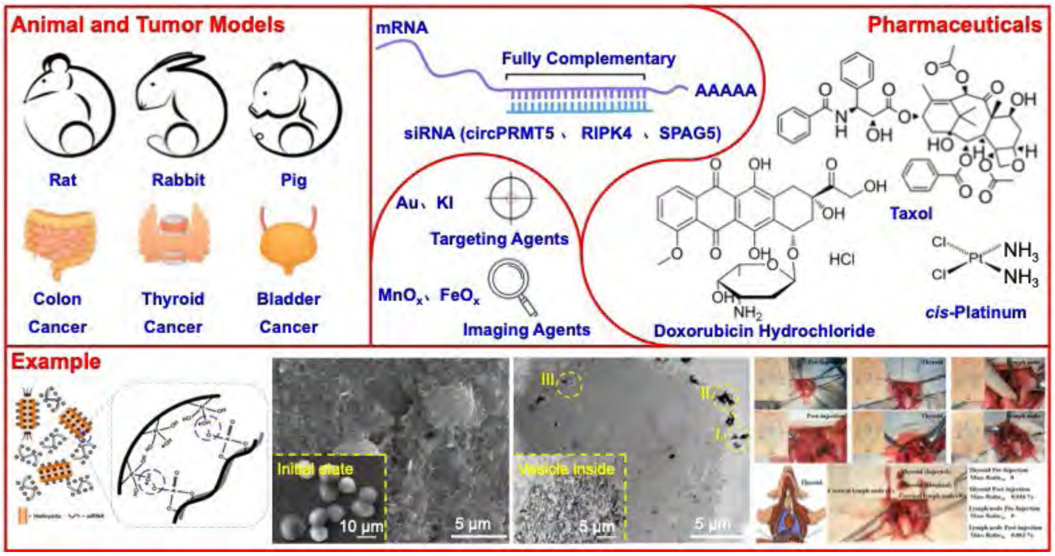
Various basic research works about engineering drug-loaded halloysite nanotube toward human disease treatment. The authors team's research interests focuses on biomedical oriented mineral materials construction, e.g., obtained homogeneous and length-controllable halloysite nanotube through ultrasonic treatment and differential centrifugation, toxicological evaluation toward refined halloysite nanotube with human disease associated cell lines, delivered bio-molecules and drugs toward disease treatment using natural halloysite nanotube in various biological models, etc. Based on research results, engineering drug-loaded halloysite nanotube toward disease treatment still have some unresolved issues, such as, tailoring halloysite nanotube in suitable size range toward different medical use, designing halloysite nanotube toward different organ targeted treatment, elaborating the halloysite nanotube - biological interaction toward different tissue barriers, etc. In this forum, the authors team will be illustrating results on engineering drug-loaded halloysite nanotube and its drawbacks in the intravenous administration route.



PALYGORSKITE-SUPPORTED RUTHENIUM CATALYSTS FOR THE SELECTIVE OXIDATION OF 5-HYDROXYMETHYLFURFURAL TO 2, 5-DIFORMYLFURAN

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The oxidation of 5-hydroxymethylfurfural (HMF) to 2, 5-diformylfuran (DFF) is an important reaction for the synthesis of value-added chemicals from renewable biomass; however, the high selectivity of DFF remains a challenge. Palygorskite is a 2:1 chain-layered clay mineral with fibrous morphology, porous structure, surface active groups and large specific surface area, as well as low cost and environmental friendliness, which makes it a promising support material. In this work, palygorskite-supported ruthenium (Ru) catalysts were prepared for the selective oxidation of HMF to DFF. Results indicate Ru nanoparticles with high dispersion were uniformly distributed on the surface of palygorskite. Ru(III)/Pal exhibited high catalytic activity, and 100% HMF conversion, 98% DFF yield and 98% DFF selectivity were obtained at 110°C and 10 bar of O_2 in toluene after 4.5 h of reaction. The dispersion effect of palygorskite on Ru nanoparticles augments the catalytic activity; moreover, palygorskite could facilitate this reaction due to its acidic and basic sites. Ru active component promotes the activation and dehydrogenation of HMF and intermediate, accelerating the formation of DFF; notably, Ru(III)/Pal achieved higher DFF yield and selectivity compared to Ru(0)/Pal, which is because Ru^{3+} species with oxidability have higher catalytic activity than Ru^0 species, and the size of metal particles of Ru(III)/Pal is smaller. Therefore, this study not only develops an efficient catalyst for the oxidation of HMF to DFF but also expands the application of palygorskite in the conversion of biomass.

PALYGORSKITE-INDIGO INTERACTION OF MAYA BLUE PIGMENT

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Maya blue is an ancient hybrid pigment composed of indigo and microporous palygorskite, with a fantastic hue and outstanding stability. Its color-causing and stabilization mechanism are unsolved problems. Previous work implied that water molecules in clay micropores might be related to the formation of Maya blue pigment. However, the influences of different water molecules and micropores on the color and stability of Maya blue have not been clarified.

In this work, palygorskite materials contained different water molecules were obtained by heating at 180, 300 and 570°C. Maya blue-like pigments were prepared from these palygorskite materials and solid indigo by grinding. The microporous structure of palygorskite and the status of inside water molecules were investigated by thermal analysis, X-ray diffraction, Fourier transform infrared and microporous analysis. The color properties, chemical resistance and photostability of pigments were characterized by reflectance spectra, CIE color parameters and color differences after the attack of concentrated nitric acid, dimethyl sulfoxide, and visible light exposure equaling to about 100 years.

It was confirmed that the greenish-blue and stable hybrid pigment could only be prepared when indigo molecules were inserted into the micropores of palygorskite. Zeolitic water molecules inside the micropores should be removed because they hindered the insertion of indigo molecules. The key to immobilizing indigo molecules inside micropores was hydrogen bonds between indigo and coordinated water (C=OH...OH). This study emphasized the important role of micropores and hydrogen bonds in the synthesis of organic-inorganic hybrid pigments.

Session 14

Clay-related low dimensional nanoarchitectonics for enhanced electronical and optical properties

Conveners: Yusuke Ide (National Institute for Materials Science, Japan), Miharu Eguchi (Waseda University, Japan), and Yusuke Yamauchi (The University of Queensland, Australia)

STABILIZATION OF IRON OXO OLIGOMERS IN SMECTITE CLAY-DERIVED SILICA GELS

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Although iron-based compounds, especially iron oxyhydroxides, are abundant in numerous geological and biological systems, how iron oxyhydroxide solid nucleate and grow from aqueous solutions remains an open question. Isolating and stabilizing iron oxo oligomers without any stabilizing ligands, while achieving the control over their size holds a potential means of not only understanding the growth mechanism of iron oxyhydroxides but also discovering their unprecedented properties and applications.[1-3] However, this endeavor still challenging.

Here, we present the successful isolation and stabilization of iron oxy oligomers within the voids of silica gel networks derived from a layered clay mineral.[4] The aqueous solution of $Fe(NO)_3$ was mixed with synthetic saponite (Smecton SA, Kunimine Industries Co., Ltd.) and then concentrated nitric acid. After stirring the mixture (pH—0.13) for 24h, the solid products were recovered, washed repeatedly with water, and dried at room temperature under vacuum to obtain a white-powder product. Comprehensive characterizations such as X-ray diffraction, X-ray adsorption and high-resolution TEM reveal that the white product is composed of silica gel, formed via acid-leaching of Al, Mg cations and Na cation in the framework and interlayer space, respectively, from the clay and small iron oxy oligomers. Solid state ^{29}Si NMR and N_2 adsorption/desorption analyses suggests that the oligomeric species are encapsulated within the silica gel networks without or with weak interactions like hydrogen-bonding ones. In the presentation, we will show you the size control of iron oligomers encapsulated and applications of the products.

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LAYERED INORGANIC–ORGANIC COVALENLY BONDED HYBRID/ RU-BASED METALLO-SUPRAMOLECULAR POLYMER COMPOSITE FOR IMPROVED ELECTROCHROMIC PROPERTIES

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Metallo-supramolecular polymer (MSP) is synthesized by complexation of metal ions and multitopic organic ligands. Higuchi *et al.* have found electrochromism (EC) of MSP. 1) The metal-to-ligand charge transfer (MLCT) is controlled *via* electrochemical redox of metal ions. A few investigations have been previously reported for MSPs-clay nanocomposites.2) Herein, we aim to prepare a composite consisting of Ru(II)-based MSP (polyRu) and a layered hybrid to improve the EC properties.

We synthesized polyRu and a "layered inorganic-imidazoline covalently bonded hybrids (LIIm)" in which the imidazolyl group is located between and covalently bonding with the inorganic layers according to the previous reports.3, 4) LIIm was combined with polyRu to prepare polyRu–LIIm composites. The polyRu–LIIm composites were characterized by the field-emission scanning electron microscopy (SEM) with an energy dispersive X-ray (EDX), ultraviolet-visible spectroscopy (UV-VIS), cyclic voltammetry, *in situ* spectro-electrochemical measurement, and so on.

The polyRu–LIIm composites exhibited strong MLCT absorptions at ~530 nm and reversible EC changes between red and pale green, caused by the redox of Ru(II/III) upon applied potential. 5) Furthermore, the composite thin films exhibited high optical contrasts (D*T*) of >70%, improved coloration efficiencies (CE), and so on.

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EMISSION FROM HIGHER EXCITED STATE OF MONO-CATIONIC DYE ADSORBED ON SURFACE OF SAPONITE NANOSHEET

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Upon molecule in the grand state (S_0) adsorbs a photon of sufficiently high energy, it becomes an electronically higher excited state (S_n, $n \geqq 2$). However, relaxation of higher excited state to lowest excited state (S_1) is much faster than other processes (e.g. radiative process), thus lifetime of higher excited state is basically short and photon emission/ photochemical reactions occurs from S_1 state. In our previous works, we found out that emission from S_2 state of tetra-cationic porphyrins were enhanced and excited lifetime of their S_2 state were extended, when these molecules were adsorbed on the surface of saponite nanosheet (SN). It will be attributed to the suppression of intramolecular motion of porphyrins by adsorption on SN. This effect might work for not only porphyrins but also other chromophores. In this research, we investigated behavior of emission from S_1 and S_2 state of mono-cationic dyes, which is cyanine and triphenylmethane derivatives, adsorbed on the SN.

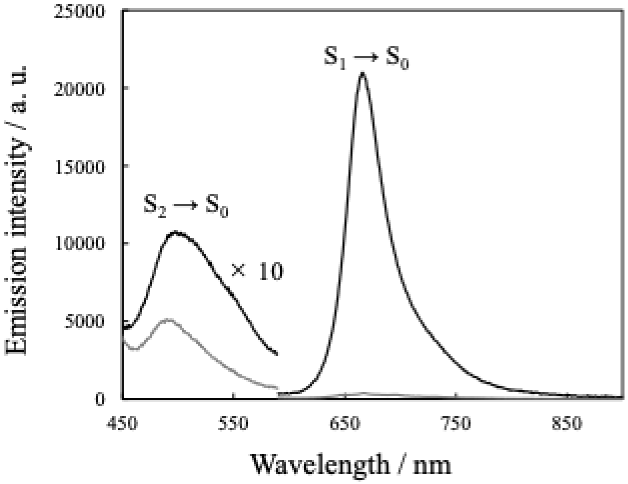

Fig. 1. Emission spectra of MG (gray) and MG/ saponite nanosheet hybrid (black).

The emission spectra of malachite green (MG) aqueous solution and aqueous dispersion of MG/SN hybrid were shown in Fig. 1. The emission band corresponding to S_1®S_0 and S_2®S_0 were observed, and these emission bands were enhanced by adsorption on SN. The magnitude of the S_1®S_0 emission enhancement was larger compared to that of S_2®S_0. Cui and co-workers reported the geometry of MG at S_2/S_1 conical intersection is more planar compared to that at S_1/S_0 conical intersection. Thus S_1®S_0 internal conversion will be effectively suppressed by the steric effect of SN compared to S_2®S_1 internal conversion, and magnitude of S_1®S_0 emission enhancement might be much larger than that of S_2®S_0.

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2D-TO-1D CONVERSION OF LAYERED TITANATES

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Layered titanate is a class of compounds showing, in adiition to semiconducting (photocatalytic) properties, good cation exchange properties which capacity is considerbly higher than that of other ion exchangers including clays. On the other hand, layered titantes are generally composed of two dimensional (2D) micrometer-size crystals, which often limits the diffusion of cations into the entire particles (slow cation exchange rate). Since the successful development of zeolite synthesis-inspired alkali hydrothermal reactions for converting TiO_2-based nanomaterials into other ones by us,[1] we have investigated the 2D-to-1D conversion of layered titanates. As a good example, a most widely studied layered titatnate, $K_{0.8}Ti_{1.73}Li_{0.27}O_4$, was successfully converted into the corresponding 1D nanowire form.[2] Thanks to the accelerated cation exchange rate and enhanced charge separatin efficiency owed by the 1D morphology,[2,3] the $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ nanowire showed ultrafast (< 1 min) adsorption and photoreduction (irreversible immobilization) of Cd ions in water. These results motivfated us to examine the hydrothermal treatment of many other layered titanates.

Herein, we report the sucfessful conversion of $Na_2Ti_3O_7$, which has the *de facto* highest cation excahnge capacity among layered titanates, into the corresponding 1D nanowire form.[4] We will present the excellent cation excahnge properties of the $Na_2Ti_3O_7$ nanowire exceeding the existing inorganic and organic cation exchangers.

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SAPONITE CLAY NANOSHEETS FOR PROTEIN ADSORPTION

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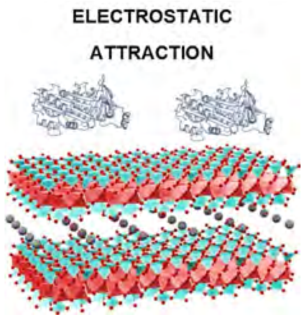

Saponite is a clay mineral possessing large surface area and high cation exchange capacity enable effective adsorption of proteins, enzymes, toxins, and other biomolecules from aqueous solutions. Saponite exhibits selective adsorption capabilities, allowing targeted purification and separation based on the size, charge, and shape of specific biomolecules. Its biocompatibility and non-toxic properties make it suitable for a wide range of biological and biomedical applications, including drug delivery, tissue engineering, and biosensing. Additionally, saponite demonstrates stability under different pH values and temperature conditions, ensuring consistent adsorption performance in diverse biological environments. In biotechnology area, saponite-based adsorbents can enhance the efficiency of downstream processes in biopharmaceutical production and other industrial applications by facilitating protein purification, separation, and immobilization.

In this study, we investigated the adsorption capacity of saponite clay toward ovalbumin protein. At specific H^+ concentrations, saponite exhibits remarkably high adsorption efficiency for proteins, achieving a maximum adsorption capacity of 998.8 mg/g for the standard protein ovalbumin. The adsorption of ovalbumin on saponite clay follows the Langmuir model indicating a monolayer adsorption. Additionally, the adsorption kinetics follows the pseudo-second order more closely, suggesting that the adsorption rate depends on the capacity of the saponite clay adsorbent rather than its concentration. The protein adsorption capacity of saponite is primarily attributed to the electrostatic attraction arising from the negative charge of saponite and the positively charged albumin at the optimum pH of 3. This study lays the groundwork for future medical applications utilizing natural clay materials and affirms the potential of clay materials in medical and biological fields.

END-TO-END PIERCED CARBON NANOSHEETS WITH MESO-HOLES DERIVED FROM MONTMORILLONITE CLAY

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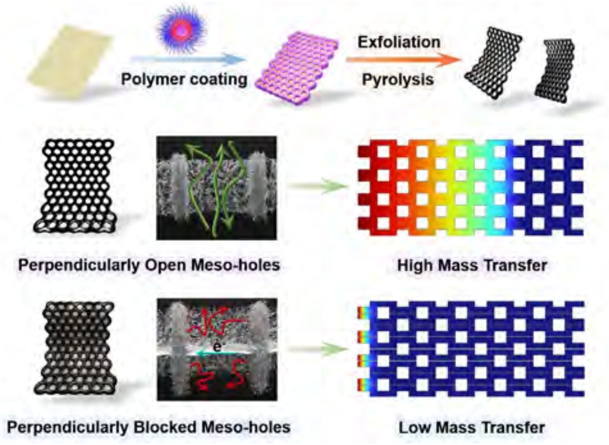
In this study, we present an exfoliation-induced meso-hole opening approach to synthesize 2D carbon nanosheets with end-to-end or perpendicularly open meso-holes (POMC). The key feature of this strategy lies in the use of layered aluminosilicate clay material known as montmorillonite as the sacrificial 2D template for the growth of meso-holey polymeric layers (mPDA), and manipulation of its interlayer space for the effective removal by in situ HF. As a comparison sample, 2D carbon nanosheets with perpendicularly blocked meso-holes are also synthesized using GO as the non-sacrificial 2D template (PBMC).

The openness of meso-holes and microstructure of POMC and PBMC are well-characterized and correlated to the in-depth electrochemical analysis. Comparing POMC to PBMC, we demonstrate a remarkable improvement in mass transfer, with POMC exhibiting up to 32 times faster mass transfer rates. This enhanced mass transfer translates to a significant boost in overall electrocatalytic activity and kinetics for the oxygen reduction reaction (ORR). Interestingly, our findings underscore the crucial role of mass transfer effects over charge transfer effects in determining ORR kinetics. This work highlights the importance of open nanoarchitectures in electrochemical applications and offers valuable insights for leveraging 2D nanomaterials with open meso-holes across various electrocatalytic reactions.



FORMATION OF MOTH-EYE-LIKE STRUCTURES ON SILICON THROUGH IN SITU CRYSTALLIZATION OF HECTORITE-LIKE LAYERED SILICATE

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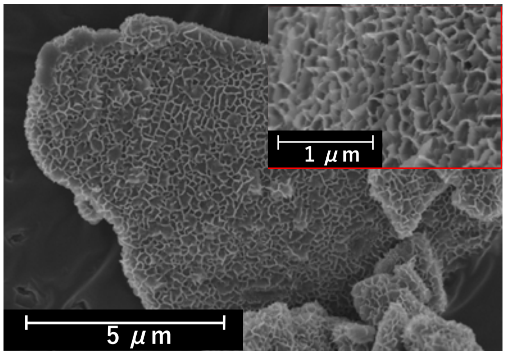

Fig. 1 SEM image of hectorite-like silicate on silicon.

Coating subwavelength-scale pinnacles/thorns on surfaces usually results in antireflection, known as “moth-eye effect.” However, fabrication of such coatings is often complicated and expensive. We have investigated a bottom–up approach for forming a moth-eye-like structure on silicon by directly growing hectorite-like layered silicate (Mg silicate) using a one-step process [1]. When an aqueous solution containing LiF, $MgCl_2$, and urea was heated at 150°C in the presence of silicon particles, fine crystals of the hectorite-like silicate completely covered the silicon surface (Fig. 1). The resulting thorn-like structures reduced the reflectance of silicon in the visible-wavelength range, exhibiting a graded-refractive index profile from air to the silicon substrate. The antireflection feature was observed when the height of the “thorns” was 0.1 μm, which was equivalent to the crystal size of the hectorite-like silicate. The reaction temperature was a dominant factor in determining the reflectance, and the reflectance diminished with increasing temperature from 80°C to 150°C. The aging time at 150°C was crucial for acquiring smooth surfaces without forming light-scattering fine particles. In addition, the heating period is optimized to be 48 h to avoid coprecipitation of light-scattering fine particles, such as amorphous silica and excess quantities of individual hectorite-like silicate crystals. The proposed methodology is feasible for application in the antireflective covering of silicon to enhance power generation in solar panels.

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MXENES *VS.* CLAY MINERALS: 2D SOLIDS FOR THE DEVELOPMENT OF HYBRID MATERIALS AND NANOCOMPOSITES

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A comparative study between clay minerals (silicates) and MXene emerging 2D solids (carbides/nitrides) focusing on the generation of hybrid derivatives and their similarities and differences between structural, physical and chemical characteristics are presented here. Both types of 2D solids share a number of common characteristics, such as colloidal properties, exfoliation/intercalation capacity, hydrophilic character, ion exchange capacity and biocompatibility. However, the main difference between them lies in the excellent electrical conductivity of MXenes, comparable to metals and graphene but unlike clays.

Considering the extensive studies devoted to clay minerals, these solids can be used as models for the future development of new 2D functional MXene materials. Here we discuss selected examples of hybrid and nanocomposite materials derived from clay minerals by assembling with different organic compounds, carbon nanoparticles, polymers and biopolymers, etc., that have been recently applied to MXenes illustrating their behavior as superabsorbents, piezoelectric sensors, antimicrobial & hemostatic materials, among other potential uses.

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CORRELATION BETWEEN SYNTHETIC TEMPERATURE AND CATION-EXCHANGE PROPERTY OF A LAYERED LITHIUM POTASSIUM TITANATE

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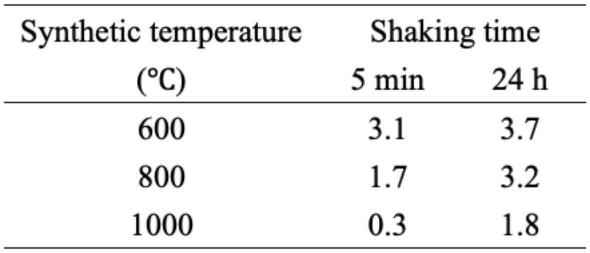
Layered transition metal oxides consisting of transition metal oxide layer and exchangeable cation has been investigated as inorganic ion-exchanger, owing to its high cation-exchange capability and chemical stability [1]. Layered transition metal oxides have typically been synthesized by solid-state reactions. Smaller particle is expected to demonstrate rapid ion-exchange reaction taking a benefit of the larger surface area. Synthesis at lower temperature is a way of directing to smaller particle because of controlled particle growth/inter-particle sintering [2]. The synthetic temperature range of $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ (KTLO), a layered titanate with lepidocrocite structure, is relatively wide (600−1100°C) among layered transition metal oxides. Photocatalytic activity of protonated form of KTLO was correlated with the synthetic temperature of KTLO [3]. In the present study, we examined the effect of the synthetic temperature on cation-exchange property of KTLO against NH_4^+ in water.



Synthetic temperature (°C)	Shaking time 5 min	24 h
600	3.1	3.7
800	1.7	3.2
1000	0.3	1.8

Table 1 Correlation between the synthetic temperature of KTLO and amount of extracted K+ (mmol/1 g of KTLO)

Table 1 shows the amount of K^+ (mmol) extracted from 1 g of KTLO after shaking an aqueous NH_4Cl solution containing KTLO synthesized at varied temperature for different time period. As the lower synthetic temperature was employed, the larger amount of K^+ extracted, reinforcing the importance of the synthetic temperature on design of layered transition metal oxide-based ion-exchangers.

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CATALYST DESIGN USING LAYERED SILICATES HUSS

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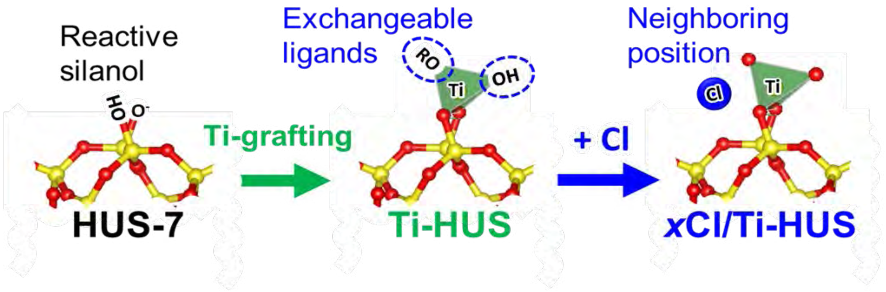
Layered silicates, having reactive neighboring silanol (SiOH and SiO^-) groups regularly located in the interlayer surface, are functionalized by various modifications such as cation exchange, silylation, and pillaring. Therefore, they have attracted interest in many applications such as catalysis and adsorption [1]. The arrangement of neighboring silanol is defined by the crystal structure of the silicate layer and it can act as a ordered connection point for constructing porous or catalytic superstructures. Thus, a novel layered silicate is a source for advanced and innovative material, its synthesis is also crucial. In this presentation, we show the potential of novel layered silicates, Hiroshima University Silicates (HUSs), as the precursor for designing new types of catalyst [2].

The surface silanol group of HUS can be modified with the titanium complex to form isolated tetrahedrally coordinated TiO species [3a,c,d]. Although such isolated transition metal oxide usually exists only the zeolite framework, the complex modification into HUS attained its formation with defined coordination state and high surface density on the silicate layer. The titanosilicate layered catalysts obtained here exhibited promising catalytic performance for several partial oxidation reaction of hydrocarbon. The surface silylation with silane coupling agent with catalytic moiety also provide unique acidic and basic catalytic reaction space in the in the interlayer of HUS [3b, e]. The highly catalytic activity was obtained even in the low specific surface area determined by the N_2 adsorption because the huge surface area of interlayer space enhance the accessibility of reactants into the catalytically active site on the silicate layer.



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Session 15

Clay minerals in building materials

Conveners: Ana Guerrero (Eduardo Torroja Institute for Construction Science (IETcc-CSIC), Spain), Yunfei Xi (Queensland University of Technology (QUT), Australia), Pilar Aranda (Materials Science Institute of Madrid of the CSIC, Spain)

EXPLORING THE USE OF MICA IN TRIBOELECTRIC NANOGENERATORS FOR BUILDING APPLICATIONS

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Capturing energy from the environment has gained appeal as one of the possible solutions to the global energy crisis fueled by human ever-increasing energy demand. Amongst supercapacitors, fuel cells, batteries or solar panels another type of interesting devices are the so-called triboelectric nanogenerators (TENGs) that convert mechanical energy into electricity. A TENG typically consists of a pair of film-shaped, dielectric materials, which generate triboelectric surface charge upon contact between each other. Their relative position in the triboelectric series determines the sign of surface charge on each material. TENGs profit from the phenomena of contact electrification and electrostatic induction, making the production of energy from a variety of environmental sources, such as mechanical motion, vibration and human movements, possible. A particularly interesting source of energy are wind and human motion as they can be used to produce energy in buildings. In this context, natural raw materials such as clays, minerals and biopolymers can be considered sustainable and inexpensive energy materials for the production of TENGs components. Mica is a promising triboelectric material given its position on the far positive side of the triboelectric series. But natural mica is difficult to work with, and obtaining ultrathin films can be expensive and time-consuming. To address this drawback, we have explored the use of crushed mica scales and flakes - residues from mica mining as a more practical and viable alternative to monocrystalline mica sheets. Mica particles of different size and degree of exfoliation were processed with the natural polysaccharide chitosan forming composite films. The electrostatic and triboelectric properties were characterized as well as the microstructural behavior. The preliminary results indicate that the mica particles improved the electricity output of chitosan and may be applicable in energy devices in the future.

LOW EMBODIED CARBON CEMENT BLENDS FROM AUSTRALIAN CLAY MINERAL RESOURCES

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Cement manufacture contributes as much as 9% of global carbon dioxide emissions, and a forecasted 6 billion tons annual production by 2050 means cement and concrete use will continue to increase demands on energy and materials, thereby exacerbating anthropogenic climate change. Given the expected tripling of Australia's current cement production to nearly 30 million tons, shifting to lower clinker-factor cement blends will be important to achieve the Net Zero by 2050 target set by the United Nations. Research in our labs has focused on non-traditional calcined clays as low embodied carbon clinker replacement in cement blends containing gravel wash fines for use in mortars, and calcined bentonite in limestone-calcined clay-cement blends.

On calcination, gravel wash fines contain reactive clay mineral fines as well as non-reactive fine aggregate, and when used to partially replace clinker based on the reactive fines content, exceptional mortar strengths were achieved – equivalent to a reference mortar mix. Depending on the mineralogy of the source fines, resulting mortars had clinker factors as high as 0.5, and up to 45% reduction in embodied carbon. Limestone-calcined bentonite-cement blends, where 50% cement is replaced by 35% calcined bentonite and 15% limestone, resulting in 40% lower embodied carbon, also achieved outstanding performance attributes in terms of mechanical (strength, shrinkage) and durability (chloride ingress, porosity) measures that exceeded reference concrete mixes. Hydration of calcium aluminosilicate hydrates were lower than comparable metakaolin based cement blends. Although water requirement and fresh workability remain two challenges for uptake by industry, our research indicates that cement replacements as high as 70wt% can be achieved, providing good performance low embodied carbon concretes suitable for the majority of construction requirements.

STRENGTH IMPROVEMENT OF STEEL-SLAG DREDGED SOIL MIXTURES BY SOIL ORGANIC MATTER REMOVAL WITH CALCINATION

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Dredged soils are excavated sediments in ports and waterways for safe navigation. Various minerals, including clay minerals, amorphous silica, and soil organic matters (SOM) mainly compose dredged soils. The addition of steel slag improves the strength of dredged soils and enables recycling of the by-products. However, the degree of the strength improvement depends on the soil samples, and some mixtures fall below the required strength for civil engineering constructions. SOM in dredged soils is suggested as one of the inhibitors of strength improvement1). Calcination of clay-rich soils is often conducted to turn clay minerals amorphous, which requires a higher temperature2) than SOM removal. This study aims to understand the effect of SOM removal by calcination, on the strength improvement of steel slag-dredged soil mixtures.

Dredged soils named I and J were used in this study. Soils were calcined at 440 °C for 4 hours, following the SOM quantification method. The crucible's lid was left closed or open to vary the degree of SOM removal, where the names of the resulting soils were labeled with _od and _il, respectively. Mineralogical compositions, soluble Si and Al contents, and total organic carbon (TOC) content were characterized for dredged soils. SOM was characterized with Raman spectroscopy and the emission excitation matrix (EEM). Mixtures were made with the same mixing ratio and curing condition. Uniaxial compressive strength (UCS) and mineralogical phases were determined for the mixtures.

The UCS of the mixtures made with soil I, I_od, and I_il were 39.8, 228, and 589 kPa, respectively. The TOC contents of soil I, I_od, and I_il were 20.3 14.6, and 0.89 mg/g dried soil, respectively. Soil J series followed the same trend. Raman spectra of soil samples suggested that the carbon structure of SOM was conserved in I_od and J_od, but not in I_il and J_il. Whereas soluble Si and Al contents and mineralogical compositions did not change significantly by the calcination. Finally, this study suggests that dredged soils in which SOM plays a role in the inhibition of strength improvement could be utilized as construction materials by calcination at mild temperature for SOM removal.

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LIGHTWEIGHT GYPSUM BOARD WITH CLAY MINERAL AND GLASS FIBRE ADDITION TO ENHANCE FIRE RESISTANCE

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Fire-resistant gypsum board is widely utilized in construction attributed to its ability to retard fire propagation, lightweight nature, and cost-effectiveness. The prevalent method for enhancing the fire resistance of gypsum boards involves the incorporation of glass fibres and porous inorganic additives such as perlite and vermiculite, which reduce thermal conductivity. However, this conventional approach often compromises mechanical strength due to increased porosity, leading to cracks and subsequent failure of the boards above 400 °C, primarily due to gypsum dehydration. This study proposes an innovative approach to fabricating fire-resistant gypsum boards by synergistically combining naturally abundant clay mineral illite (0–30 wt%) and cost-effective glass fibre (1 wt%) as additives.

Illite was selected for its ability to facilitate sintering, attributed to the presence of interlaminar potassium ions acting as fluxing agents, thereby enhancing the mechanical strength of the gypsum boards at elevated temperatures. The inclusion of illite led to a reduction in the number of cracks on the boards when subjected to firing at 600, 800, and 1000 °C. This improvement can be attributed to: 1) the barrier effect of illite hindering the connection of broken gypsum crystals, leading to smaller thermal shrinkage, as evidenced by thermal dilatometric data, and 2) the sintering of illite at high temperatures, densifying the board and enhancing its strength. Moreover, the incorporation of illite led to a decrease in bulk density from 1037 to 666 kg/m^3, rendering the boards lighter and more manageable during transportation. X-ray diffraction analysis revealed the formation of new minerals such as K-feldspar and plagioclase at 1000 °C due to the reaction between illite and gypsum. This research presents a promising avenue for the development of next-generation lightweight fire-resistant composite gypsum boards by leveraging the sintering properties of abundant and environmentally friendly clay minerals.

CRITICAL EFFECTS OF KAOLINITE/ILLITE ON COMPRESSIVE STRENGTH OF FIRED BRICKS

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Clay minerals play a pivotal role in the production of bricks, influencing brick properties through variations in their crystal structure, chemical composition, particle size, and thermal behaviors. Kaolinite and illite are the two most prevalent clay minerals found in brick raw materials, albeit the relationship between these minerals and brick properties remains ambiguous. This study explores the impact of kaolinite/illite in the brick starting materials on the ultimate compressive strength of brick products, exploring a spectrum of clay mineral contents (20-50 wt%) and firing temperatures (900-1200 °C).

The relationship between compressive strength and kaolinite/illite ratios varied at different firing temperatures: an initial increase in compressive strength with kaolinite/illite ratio was observed at 900 °C, followed by a decrease at 1050 and 1200 °C. This divergence is attributed to the shrinkage induced by kaolinite dehydroxylation which effectively reduces the porosity of the brick body post-firing at 900 °C. Concurrently, the dehydroxylation-induced expansion of illite leads to increased porosity and decreased strength at 900 °C. Compared to kaolinite, illite demonstrates superior vitrification at 1050 and 1200 °C, thus better enhancing brick densification and resulting higher compressive strength. In addition, the lower compressive strength with increased clay mineral contents at 900 °C is attributed to the finer particle size and looser packing of clay minerals compared to quartz, feldspar, etc. As the firing temperature rises, clay minerals bring higher strength to bricks due to their vitrification at 1050 and 1200 °C. However, kaolinite alone is insufficient to confer high strength to bricks at 1050 °C; its contribution becomes evident only at 1200 °C. This study illuminates the intricate interplay between clay mineral composition, firing temperature, and brick strength, providing valuable insights for brick production optimization.

Session 16

Clays and clay minerals for carbon dioxide removal in negative emission technologies

Conveners: Tsutomu Sato (Hokkaido University, Japan), Takao Nakagaki (Waseda University, Japan), Yuji Arai (University of Illinois at Urbana-Champaign, USA), and Corey Myers (Lawrence Livermore National Laboratory, USA)

CONSTRAINING THE ROLE OF AUTHIGENIC MAGNESIUM RICH CLAYS ON CARBONATE PRECIPITATION IN ALKALINE LACUSTRINE ENVIRONMENTS

Arizaleta, Maria L.*[1], Raudsepp, Maija J.[1], Zeyen, Nina[2], Kenney, Janice[3], Wilson, Sasha[1]

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Authigenic Al-poor, Mg-rich phyllosilicates (*e.g.,* stevensite, sepiolite, kerolite, talc), are important components of sediments deposited in a wide array of environments, including alkaline lakes and siliceous marine environments. Mg-silicates are often associated with carbonates (*e.g.,* calcite, dolomite, magnesite) in modern and ancient sedimentary settings and it has been hypothesized that they can facilitate the precipitation of carbonate minerals.[1,2] The presence of specific microbial groups and metabolic processes (e.g., oxygenic photosynthesis, heterotrophy) is thought to promote the transformation of Mg-silicates to carbonates by aiding with silica removal, alkalinity generation and increasing cation availability.[3] Mg-silicate minerals may transform into carbonate phases via a process known as carbon mineralization, which involves the dissolution of silicate or hydroxide minerals followed by precipitation of carbonate minerals where dissolved CO_2 binds to free divalent cations, in this case Mg^{2+}.[3]

The purpose of this study is to test the hypothesis that authigenic, 2:1 Mg-silicates can transform into carbonates under alkaline conditions. A series of bench-top batch experiments was undertaken to study the reaction between a synthetic, poorly-crystalline Mg-silicate phase (stevensite-like), microbes and various natural filtered lake waters. Variables tested are aqueous Mg/Si ratio, alkalinity, pH, and the presence or absence of microbes. Results showed the precipitation of a hydrated magnesium carbonate mineral, dypingite, and Mg-rich silicate or hydroxide phases. Results from this study can contribute towards geochemical models of the environments where we observe carbonation of clay minerals, such as alkaline lakes, which can then be utilized for predicting evolution of these natural systems and serve as natural analogues for industrial uses such as in ultramafic mine tailings and consequently help improve industrial Carbon Dioxide Removal projects globally.

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APPLICATION OF ENHANCED ROCK WEATHERING IN ACID MINE DRAINAGE WITH ITS PASSIVE TREATMENT

Htut San Hkaung*[1], Nono Kimotsuki[1], Naito Yamashita[1], Fugo Nakamura[1], Frances Chikanda[2], Ryosuke Kikuchi[2], Yoko Ohtomo[2], Tsubasa Otake[2], Tsutomu Sato[2]

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Deployment of Enhanced Rock Weathering (ERW) onto the cropland by using basaltic powder has the potential for large-scale Carbon Dioxide Removal (CDR) with the co-benefit of food security. However, under stagnant conditions in a neutral environment such as cropland, the rate of dissolution of minerals in rocks is limited. In comparison, ERW may be expected in strongly acidic and flow-through system such as acid mine drainage (AMD). In this context, on-site experiments of ERW using local basalt at AMD (Shojingawa abandoned mine in Japan) was conducted. From the results of on-site experiments, the high dissolution potential components such as glass matrix, olivine, pyroxene, and Ca-feldspar in the basalt dissolved and leached significant amounts of Ca^{2+} and Mg^{2+} ions, and then pH of the AMD increased to 3.2. This pH increasing resulted in the formation of schwertmannite from iron and sulfate dissolved in the AMD, which adsorbed arsenic and reduced the arsenic concentration in the AMD. The results of on-site experiments such as dissolved Ca^{2+}, Mg^{2+} and As^{2-} concentrations, pH and schwertmannite formation after reaction can be reproduced by 1-D reactive transport modeling (1-D RTM) incorporated with mineral dissolution kinetics. Although only one ton of basalt was installed in this time, it is expected that passive treatment can be sustainably achieved along with ERW when the amount of basalt is increased. From the results of parameter studies by the 1-D RTM, it is cleared that the AMD at Shojingawa abandoned mine can dissolved the components with high dissolution potential in about 150t basalt with diameter of 2.5 mm for one year. Based on CDR equation by Beerling et al (2020), around 50 t CO2 can be removed from atmosphere for one year by basalt weathering in the AMD at the Shojingawa abandoned mine and increase pH of the AMD. Consequently, the results of this study indicate that applicability of ERW in AMD and its possibility of obtaining the benefits of both CDR and passive treatment of AMD. This presentation is based on the results obtained from a project JPNP18016, commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

NANO-CONFINEMENT EFFECT ON H_2 AND CO_2 CLUSTER FORMATION

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Molecular clustering of gases within nanopores plays an important role in nanofluidic, gas adsorption/desorption, and geological gas storage. In this study, we employed metadynamic molecular simulations to investigate the aggregation of H_2 and CO_2 molecules within hydrated hydrophobic pyrophyllite and hydrophilic gibbsite nanopores. The results indicate that nanoconfinement enhances gas dimer formation in nanopores, irrespective of surface chemistry. However, surface hydrophilicity prohibits the formation of gas clusters larger than dimers, while large gas clusters form easily in hydrophobic nanopores. Our results also indicate that gas prefers to enter the nanopores as individual molecules but to exit the nanopores as dimers/clusters. This investigation provides fundamental insights into cluster formation under nanoconfinement that are relevant to various applications, including geological gas storage.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

APPLICABILITY OF STEELMAKING SLAGS IN CARBON DIOXIDE REMOVAL FROM ATMOSPHERE BY THEIR ENHANCED WEATHERING

Nono Kimotsuki*[1], Naito Yamashita[1], Htut San Hkaung[1], Ryosuke Kikuchi[1], Yoko Ohtomo[1], Tsubasa Otake[1], Tsutomo Sato[1]

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Enhanced weathering is a carbon sequestration technique that typically involves dispersing ground silicate rocks, such as basalt, across land surface and the dissolution of minerals. Steelmaking slag, an industrial by-product, is a novel material for enhanced weathering, owing to its high reactivity and equilibrium pH facilitated by abundant Portlandite [1]. This study investigated its CO_2 capture potential in acidic (acid mine drainage: AMD) and mildly acidic conditions (rainwater), given the limited study in this area. Column experiments were conducted using steelmaking slag and sulfuric solutions simulating AMD and rainwater to understand their interaction and explore the major factors of the weathering rates. An On-site column experiment was performed at an AMD site in Hokkaido, Japan, to validate the applicability of laboratory findings on a larger scale. Additionally, geochemical reaction transport models were constructed to validate the experimental outcomes and identify mineral dissolution behaviours, successfully reproducing both laboratory and on-site results. Column experiments with varied pH condition revealed minimal differences in pH and Ca concentration in collected output solutions. These results indicated a negligible dependency of the steelmaking slag weathering rate on the variation from dissolution equilibrium of the initial reaction system. Additional models were then constructed to further investigate the impact of reaction conditions on the weathering rate, with a particular focus on solution pH and flow rate. Reactive transport modelling demonstrated that the dissolution of steelmaking slag is significantly accelerated regardless of solution pH, provided that the reaction system is far from dissolution equilibrium due to the rapid flow rate of the reaction solution.

This work was partly funded by the Steel Foundation for Environmental Protection Technology.

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PREDICTION METHOD FOR QUANTIFICATION OF CO_2 MINERALIZATION BY GAS-SOLID CONTACTOR USED AS INDUSTRIAL ENHANCED ROCK WEATHERING

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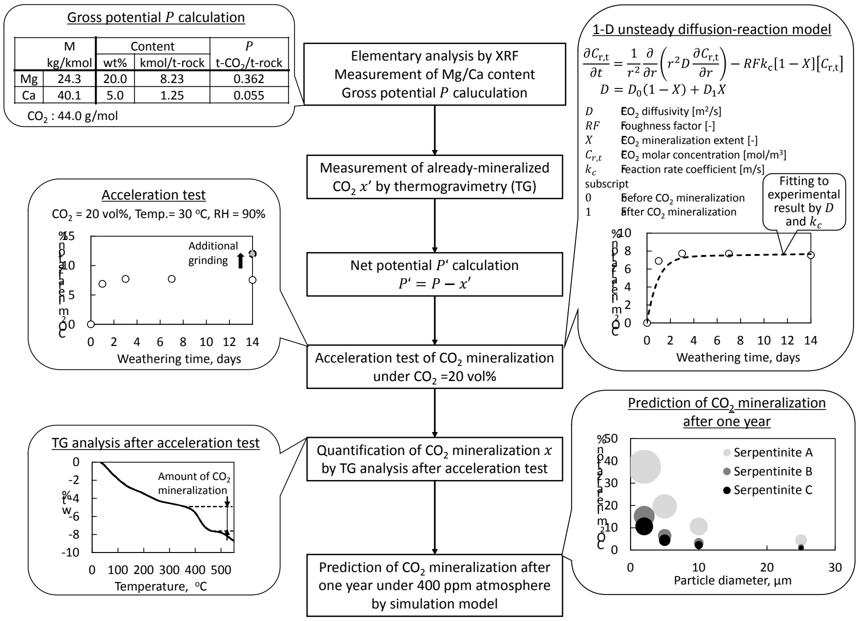
Enhanced rock weathering (ERW) has attracted attention as a feasible negative emission technology that uptakes and sequestrates atmospheric CO_2 into natural mafic and ultramafic rocks as carbonates. A great expectation is found in the famous global reports. However, inaccurate carbon accounting is pointed out as a common problem, including the industrial pretreatment of natural rock, transportation, CO_2 mineralization rate, complex changes in the natural carbon cycle, and so on. The difficulty of carbon accounting of ERW is attributable to accurately quantifying carbonates derived by rock weathering widely scattered on application lands, rivers, and seas. This point is essentially different from biochar which requires a simple carbon accounting by weight of concentrated biochar and survival rate after 100 years, so development of measurement, reporting, and verification (MRV) protocol for ERW technologies is expected to be difficult.



Prediction method for quantification of CO_2 mineralization

The "A-ERW" project is conducted by four parties and ten subcontractors as one of the "Moonshot Goal 4" research and development programs funded by Japan's New Energy and Industrial Technology Development Organization. In this project, considering the properties of mafic rocks easily obtained in Japan, we are developing an industrial ERW technology that aims solely to mineralize CO_2 with finely ground rocks by a simple gas-solid contactor in a greenhouse. The finely ground rock, preferably basic ultramafic rocks such as peridotite and serpentine, is thinly laid on the tiered trays and contacts with humidified air by forced convection of ID fans. The greenhouse covers these facilities and prevents ground rock from leaking outside for accurate measurement and health reasons due to exposure to dust. The prediction method for quantification of CO_2 mineralization should be simplified and the following procedure is proposed in this paper, which can offer an affordable MRV protocol well-balanced easiness and rigor.

THE VITAL ROLE OF CLAYS DURING GEOLOGIC CARBON SEQUESTRATION IN BASALT RESERVOIRS

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Geologic carbon sequestration is a critical carbon-negative strategy to help mitigate climate change impacts due to greenhouse gas emissions. To date, the Wallula Carbon Storage Pilot project remains to be the first and only field-scale injection of supercritical CO_2 in basalt and the only demonstration where sidewall cores containing mineralized products were retrieved post-injection. In this presentation, we highlight the important role played by secondary clay linings within basalt pore spaces that drive subsurface carbon mineralization processes – an aspect that has been largely overlooked so far. By comparing pre- and post-injection basalt samples, we show that these clay pore-linings serve as the primary source for key carbonate forming cations, such as Mn. Additionally, we also find that clay minerals along with zeolites are precipitated simultaneously along with carbonates post CO_2 injection in basalt. Understanding the nature of these precipitated clays, provides a holistic view of mineralization products formed beyond carbonates, and pinpoints the fate of cations present within the pore fluid. Collectively, these insights provide a more meaningful picture of complex subsurface processes during geologic carbon sequestration in reactive reservoirs. Finally, this work provides critical new parameters for predictive reservoir modeling at the field scale for any future carbon sequestration effort worldwide, particularly in older basalts that may host altered clay linings.

CLAY-MEDIATED RAPID CARBON MINERALIZATION DYNAMICS IN BASALTS: INSIGHTS FROM WALLULA PILOT PROJECT

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This study seeks to study the interplay between clay alteration layers and carbon mineralization in basalts, specifically focusing on petrographic observations from Pacific Northwest National Lab's Wallula pilot project, the world's only supercritical CO_2 injection in a subsurface basalt to date. Sidewall cores collected ~ 2 years post-injection revealed that the vesicle pore system is completely lined by clays, mainly zeolite in some zones and predominantly chlorophaeite in other zones (Fig 1). Further, carbon mineralization habits vary drastically with clay type and vesicle connectivity, whereby chemical zonation of large post-injection carbonate nodules is clear in the vesicles lined with chlorophaeite (Fig 2). Supported by results from XRF map, it is hypothesized that clay is a source of cations for this rapid carbon mineralization (Mn^{2+}, Fe^{2+}, Ca^{2+}). Towards understanding this hypothesis, we (1) characterize the nanoporosity of zeolite and chlorophaeite using electron microscopy (e.g., SEM/EDS, FIB-SEM) combined with bulk measurements (gas pycnometry, NMR) and (2) simulate single-phase ion diffusion and multiphase evaporation of water film on the surface of clay using pore-scale Lattice Boltzmann Method (LBM) techniques.

The findings reveal the morphological properties (porosity/connectivity/tortuosity) and structure of the clay pore system. Further, SEM/EDS maps depict the spatial distribution and mineralogy of cation sources in the clay layer. These properties are used to estimate how the 3D geometry of the clay alteration layers controls the in-situ mineralization of CO_2 in a multiphase brine-CO_2 system. Variables probed include thickness of the water film and clay layer, and distance between clay surface to precipitation site. Looking forward, these findings can be compared to clay and carbon mineralization habits in other basalts to identify the ubiquity of clay-carbonate precipitation relationships for future in-situ carbon mineralization projects.

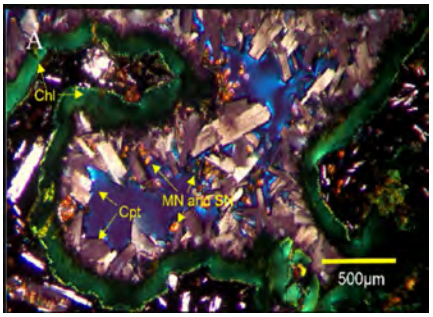

Fig 1. Zeolites and chlorophaeite in basalt

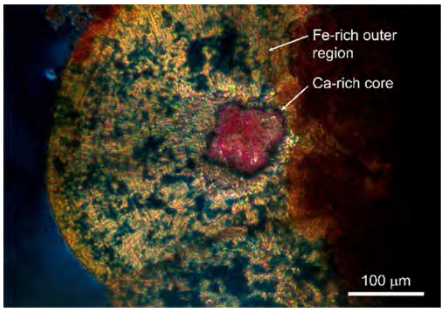

Fig 2. Chemical zonation in carbonate nodules

BASIC STUDY ON ANION EXCHANGE PROPERTIES AND ALGAE GROWTH OF POROUS CONCRETE CONTAINING LAYERED DOUBLE HYDROXIDES IN SEAWATER

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The oceans are a major reservoir of carbon on Earth. It is estimated that 190 ~ 240 million tons of blue carbon are stored annually in marine sediments. Shallow waters are reported to account for about 80% of this. Therefore, blue carbon is expected to reduce carbon dioxide. On the other hand, since blue carbon is disappearing at a rate of 2 ~ 7% per year, efforts are being made to conserve and restore marine ecosystems. In these efforts, the technology of using concrete structures as a substrate for algae growth is effective in restoring marine forest. The purpose of this study is to develop a high-performance concrete that concentrates nutrient elements used for algae growth in seawater and to use it as a substrate for their growth.

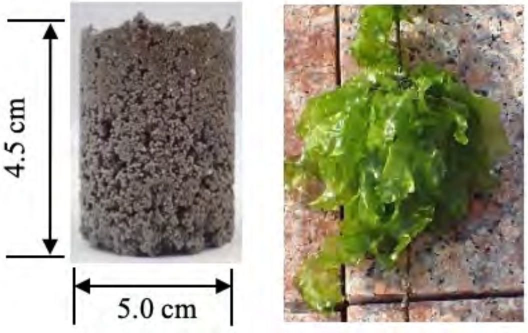

Fig.1 LPOC (left) and LPOC with algae (right)

The test specimen (LPOC) was prepared by mixing porous concrete (POC) with layered double hydroxide (LDH) which can selectively exchange nitrate ions (Fig.1). The LDH used was Mg-Al-Cl LDH with a Mg/Al molar ratio of 5, which contains chloride ions in the interlayer. The theoretical exchange capacity of Mg-Al-Cl LDH is 2.0 mmol g^{-1}. The nitrate ion adsorption of LDH and LPOC in seawater was evaluated using artificial seawater containing 30 mmol L^{-1} $NaNO_3$. The ion concentration in the aqueous solution was determined by ion chromatography. The ion exchange properties of LDH in seawater were evaluated by FT-IR measurement before and after immersion of LDH in seawater for 24 hours. The basic experiment of seaweed growth was carried out in the coast. The specimens were placed vertically at a depth of 50 cm. After 3 months, algae was collected and weighed.

FT-IR spectra of LDH after seawater immersion showed peaks related to nitrate, sulfate, and carbonate ions. In seawater, LPOC adsorbed 0.7 mmol g^{-1} of nitrate ion. These results indicate that LPOC can adsorb nitrate ions from seawater where various anions coexist. In a coastal experiment from June to August, LPOC grew more algae than POC. These results suggest that LPOC may affect the growth of algae.

THE IMPACT OF ONE YEAR BASALT POWDER APPLICATION ON SOYBEAN GROWTH AND SOIL CARBON IN A FIELD IN HOKKAIDO, JAPAN

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Background: The chemical weathering of silicate minerals has the potential to sequester carbon dioxide into the soil as carbonates and bicarbonate ions. Also, minerals provide elements such as calcium and magnesium to the soil in the process of weathering and would improve the soil fertility. In this study, we applied basalt powder on an agricultural land and investigated its effect on soybean growth, and soil carbon on a field scale.

Materials and Methods: Soybean (*Glycine max*) was grown from June 1 to September 23 in 2023 in an experimental field (gray lowland soil, pH = 5.6) on Hokkaido University campus (43.07^o N, 141.34^o E). We had 4 treatments: conventional plot (Control), and basalt 5, 10, 20 wt% (=75, 150, 300 t/ha) application plots (BA5, BA10, BA20, respectively). The mean basalt's particle size was 37.08 μm and it was applied on May 19. Plants were sampled at harvest and measured for yield components. Soil at 0-15 cm depth was sampled from each plot at harvest, air-dried, and measured for soil total carbon, pH with ultrapure water.

Results and Discussion: Regarding plants, the number of pods showed slight difference among the treatments ($P < 0.1$), and its average tended to increase by basalt application. Soil pH at harvest was significantly higher in BA10 and BA20 than in Control. There was a significant positive correlation between soil pH and the number of pods ($r = 0.52$, $P < 0.05$), which indicated the increase of the number of pods could be caused by the increase of soil pH by basalt application. Soil total carbon at harvest showed no significant difference among treatments, which could imply basalt application didn't contribute to the carbon storage at surface layer in only one year cycle of cultivation in this study.

EFFECTS OF BASALT APPLICATION AND THE MINERAL COMPOSITION ON SUGAR BEET GROWTH

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Background: Weathering reactions occur when basalt is applied to soil. Carbon dioxide in the atmosphere can react and remain in the soil. At the same time, some ions in the basalt are dissolved. The produced process of basalts is different and therefore weathering rate also show differences based on the origin, which may affect plant growth. The purpose of this study was to determine the effect of different rock properties and levels of application on plant growth using sugar beet.

Materials and Methods: In the pot experiment, three levels of basalt (28 g = 5%, 56 g = 10%, 112 g = 20%) were applied to 800 g of air-dried andosol by using three different basalt types (basalt A, B, C). The mean basalt's particle size was 37.06 µm. Sugar beet (*Beta vulgaris* L. subsp.*vulgaris*) seedlings were transplanted to the pots with three replicates. Sampling was carried out 91 days after sowing. Shoot and roots were collected, and dry weight and elemental concentrations were measured. In addition, soil was collected, and soil pH was measured.

Results and Discussion: The application of 10% of basalt A and B increased dry weight of whole plant biomass. The results of elemental analysis showed that Ca and Mg concentrations did not increase with the increased application. However, Na concentration in shoot significantly increased with the increased application. A positive correlation was found between dry weight of whole plant and soil pH in the case of basalt A and B application. Since sugar beet is known to grow well in soil with high pH, the increase of pH by basalt could increase its biomass.

MG CARBONATE HYDRATE FORMATION IN ENHANCED WEATHERING EXPERIMENTS USING MGO

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Carbonate mineral formation on the Earth's surface would play a significant role for enhanced weathering, which is a negative emission technology using alkaline materials such as mafic or ultramafic rocks. Since Mg is a main component of these rocks in addition to Ca, this study focuses on the behavior of Mg. Whereas aqueous Ca^{2+} can be consumed by $CaCO_3$ (e.g., calcite) precipitation, aqueous Mg^{2+} may be consumed by some Mg carbonate hydrate phases (e.g., dypingite, hydromagnesite, and nesquehonite) rather than $MgCO_3$ (magnesite) at ambient temperature. This study aims to demonstrate CO_2 mineralization with Mg^{2+} in outdoor experiments and identify the mineral species of the secondary carbonate phase.

MgO (DENMAG®KMA-X, Tateho Chemical Industries, Japan) was used as a starting material. The MgO samples were sieved to a particle size of 1–2 mm (surface area = 3×10^{-2} m^2 g^{-1}). 20 g of MgO has been placed in a reactor (Fig. a) and exposed to outside weather conditions on the rooftop of the AIST Tsukuba office since September 1st, 2022. During the 12 months from the beginning of the experiments, total rainfall was 1534 mm and the average temperature was 17°C.

Water samples (the original rainwater and the water passing through MgO) were collected within a few days after each rain event. Because of the MgO dissolution, aqueous Mg^{2+} concentration (~2 mmol L^{-1}) and pH (~9) increased after passing through MgO, suggesting that CO_2 were additionally dissolved in the alkalized solution and removed from the air. Solid samples (weathered MgO samples) were collected after 1, 3, 6, and 12 months. The surface area increased for 12 months (2×10^{-1} m^2 g^{-1}). Powder X-ray diffraction analysis showed formation of dypingite (Mg carbonate hydrate mineral), and scanning electron microscopy (Fig. b) and Fourier-transform infrared microscopy revealed that dypingite precipitated on the MgO surface. Thermogravimetry suggested that dypingite constituted 5 wt% of the 12-month aged sample. Since unreacted MgO remained after 12 months, further CO_2 mineralization will be observed in experiments with longer-term exposure or finer starting material.

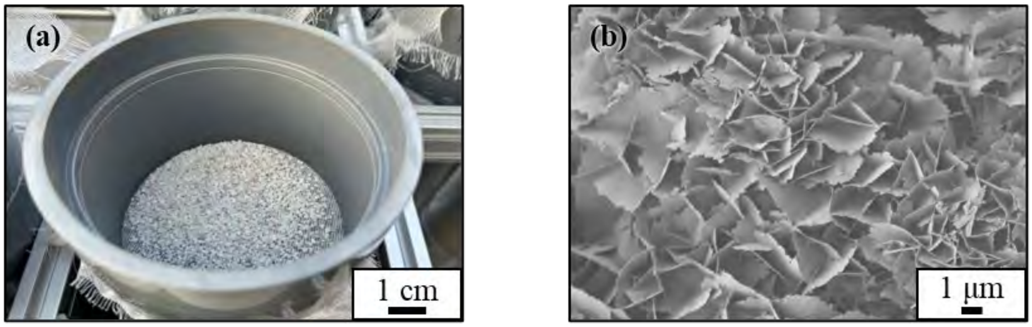

Figure. Photograph of MgO particles in the outdoor experiments (a) and scanning electron microscope image of the secondary phase on the surface of the MgO particle (b).

EFFICIENCY AND FACTORS AFFECTING BASE PROPERTIES OF SMECTITE-DERIVED POROUS COMPOSITES

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Clay minerals from the smectite group like hectorite possess a small basic character resulting from the presence of Mg in its structure. In an acidic environment, protons` attack affects some mobility of magnesium ions and causes their gradual release from the octahedral sheet leading to the collapse of the structure and loss of the original ordering. However, the mobility ability of octahedral ions can be directed by forcing their migration into site-selected localization. This is especially possible when smectite constitutes a structure-forming platform of crystalline-amorphous clay-derived composites with highly developed porosity.

This contribution focused on the determination of the efficiency and factors affecting Mg release from the octahedral sheets of synthetic layered hydrous magnesium silicate (hectorite) introduced into porous silica-clay composites by templating method resulting in the enlargement of the base properties of parent clay mineral. In this approach, we gauged the application of benign proton attack delivered by the use of mechano-chemical impregnation with a slightly acidic salt solution of $Fe(NO_3)_3x9H_2O$ salt, microwave irradiation, and hydrothermal treatment on the formation of the new base centers in the composite.

Our study showed that applied treatments bring about the auto-transformation of the structure of the clay-derived composite. The leached-out Mg cations were captured on the surface of the porous composite grain, confirmed by an increase of the Mg/Si ratio, and constituted the source of cations for nucleation of nanostructured MgO moieties with weak base properties assessed by CO_2 sorption. The increase of the Mg/Si ratio was accompanied by the decline of the (Mg_3OH) absorption bands intensity attributed to synthetic hectorite and discussed regarding the formation of dispersed nanostructured MgO moieties capable of adsorbing CO_2. CO_2-TPD investigation and DFT calculations revealed that the sorption of CO_2 molecules on MgO basic centers is closely related to the coordination of oxygen sites in the MgO lattice while edge and corner O^{2-} sites facilitate the interaction with CO_2 molecules. Treatment of clay-derived composite by $Fe(NO_3)_3x9H_2O$ salt not only triggered the mobility from the octahedral sheets, it also resulted in the nucleation of nanocrystalline α-Fe_2O_3 able to capture CO_2 molecules with the strength and quantity higher than on MgO centers. The differences in their kinetic of the sorption have been revealed by the TG/DSC breakthrough curves. In this work, the mechanisms leading to nucleation and formation of basic centers on the porous clay-derived composite surface are described in detail with the use of advanced XRD, SEM/BSE/EDS, FTIR, XPS, TG/DSC, CO_2-TPD methods and ^{57}Fe Mössbauer spectroscopy supported by DFT calculations. The efficiency and factors affecting base properties as well as the contribution of surface species in the efficient sorption of CO_2 molecules on porous clay-derived composite are discussed.

Session 17

Scientific and engineering aspects of clays in nuclear waste disposal

Conveners: Jeffery Greathouse (Nuclear Waste Disposal Research and Analysis Department, Sandia National Laboratories, USA), Patricia Fox (Climate & Ecosystem Sciences Division, Lawrence Berkeley National Laboratory, USA), Tsutomu Saito (Laboratory of Eco-materials and resources, Hokkaido University, Japan), Satoru Suzuki (Repository Engineering Group, Nuclear Waste Management Organization of Japan, Japan), and Cristophe Tournassat (Institut des Sciences de la Terre d'Orléans, Université d'Orléans, France; Energy Geosciences Division, Lawrence Berkeley National Laboratory, USA)

BENCH-SCALE COLUMN TESTS ON BENTONITE BUFFER AND COUPLED THERMO-HYDRO-CHEMO-MECHANICAL PROCESS FOR GEOLOGIC DISPOSAL OF HIGH-LEVEL RADIOACTIVE WASTE

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Compacted bentonite is often considered as a backfill material for engineered barrier systems (EBS) in a geological repository for high-level radioactive waste (HLW). As most design concepts impose a thermal limit of 100 ºC in bentonite, laboratory and modeling studies on compacted bentonite and THMC processes have been focused on conditions under 100 ºC. Data at high-temperature conditions is therefore limited. Understanding bentonite behavior and coupled THMC processes under higher temperatures could allow for a more economic repository design and would expand the data and knowledge base for more reliable modeling. At LBNL, we are conducting bench-scale laboratory investigations on compacted bentonite at high temperature (up to 200ºC) under HLW repository relevant conditions, providing a laboratory analog of the field experiment to obtain a comprehensive set of characterization data and monitoring measurements. Two sets of column tests have been completed, which aim to understand the impacts of bentonite geometry, compacted density and water content, water chemistry and hydration pressure, etc. In each test set,

a comprehensive monitoring approach was applied, including (1) frequent X-ray CT scanning to gain a detailed understanding of bentonite at a sub-millimeter spatial resolution; (2) emplaced sensors providing point measurements, and (3) detailed post-dismantling characterizations of bentonite samples after the experiments. Two test columns were used — a control column undergoing only hydration, and an experiment column experiencing both heating and hydration. During the experiments run for over 1 year, frequent X-ray CT images provide a 3D visualization of the density distribution and present the spatiotemporal evolution of (1) hydration/dehydration, (2) clay swelling/shrinkage, (3) displacement, and (4) mineral precipitation. A detailed post-dismantling characterization of bentonite samples and embedded metal coupons was carried out for assessing potential corrosion of canister in the repository. These comprehensive characterization data and monitoring measurements will help to better understand and model the coupled processes, especially for the early state of a HLW repository.

TRACKING SUBTLE MINERALOGICAL CHANGES IN THE BUFFER MATERIALS TO MODEL THEIR LONG-TERM ALTERATIONS IN NUCLEAR WASTE REPOSITORIES

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Numerical simulations of potential migration of radioactive compounds within and outward from deep geologic disposals of nuclear waste typically assume that the properties of geoengineered barriers and host rock would not change over time. However, numerous experiments have shown, that bentonites used as buffer analogs undergo alterations when exposed to temperature, brines, and contacts with other materials within the multi-barrier system. Crucial properties such as cation exchange capacity (CEC), swelling pressure, gas permeability, and ion diffusivity are controlled by the structure and contents of clay minerals, which can change over the storage time. As experiments on buffer material can last for years or even decades, it is essential to thoroughly understand their results to extrapolate them over thousands of years. The observed mechanisms of alteration allow for predicting the equilibrium state reached in the system, while the rate of reaction determines its kinetics.

As alterations occurring over short-term experiments are subtle compared to potential changes over millennia, detecting and quantifying these alterations require applying dedicated tools. Here, we present and discuss a series of new tools currently available:

- Apparent layer charge (LC) determination using a new, precise, and fast method provides insight into both structural changes in 2:1 layer and interlayer cation fixation
- Detailed X-ray diffraction analysis, including smectite saturation with various cations and solvents to detect neoformation, minute illitization and LC changes
- CEC analysis using index cations of different properties to address temporary vs. permanent interlayer cation fixation and changes in LC
- The composition of major exchangeable cations, which control numerous petrophysical properties
- Changes in the composition of brine-delivered K^+, Rb^+, Cs^+, $NH4^+$ cations, which can block further fixation of cationic radionuclides
- Hydrogen and oxygen isotope ratios as proxy for the water-clay interaction and mineral neoformation

CHEMICAL AND HYDRATION TIME CONTROLS ON MICROSTRUCTURE AND SWELLING PRESSURE OF COMPACTED MONTMORILLONITE

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Montmorillonite is the major mineral phase of bentonite that has been proposed as a buffer material in engineered barrier systems (EBS) for geological repositories of high-level radioactive waste. Its ability to swell upon being hydrated by groundwater from host rock is important for bentonite to perform its key safety function for the repositories, but swelling is a process that is affected by geochemical and hydraulic changes that can lead to microstructural change. In this study, we applied an μ-oedometer system equipped with X-ray transparent cells (PEEK) holding compacted montmorillonite. This approach allowed us to determine the chemically- and time-resolved swelling pressure, and microstructural changes using small-angle X-ray scattering (SAXS) technique. Our SAXS measurement profiles show the presence of mixed interlayer hydration states (0 – 4 water (w) layers) and osmotic swelling. In general, the interlayer crystalline basal and osmotic swelling spacing increase with decreasing water ionic strength (IS) and varies with cation type (Na^+ vs. K^+). Specifically, we observed: (i) the hydration state is dominated by 2w layer at 5.0 M NaCl, 2w + 3w at 1.0 M NaCl, 3w at 0.1, 0.01 and 0.001 M NaCl; (ii) in contrast, 2w dominates at 1.0, 0.1 and 0.01 M KCl and 3w + 4w at 0.001 M KCl. The dominant 2w + 3w at 1.0 M NaCl vs. 2w at 1.0 M KCl indicates that K^+ leads to lower swelling pressures. Interestingly, we observed a broad osmotic swelling peak with an intermediate spacing of 40.3 Å at 0.001 M NaCl, which decreases to 35.7 Å at 0.01 M NaCl and 34.3 Å at 0.1 M NaCl. We also observed a mixture of 3w and 4w hydration and a strong osmotic peak (45.5 Å) at 0.001 M KCl, which leads to a D001 spacing larger than that observed for 0.001 M NaCl, suggesting hydration time is an important factor given the difference in hydration times (14 days for 0.001 M KCl clay cell versus 7 days for the 0.001 M NaCl). These SAXS results are in good agreement with our chemically- and time-resolved swelling pressure measurements where the swelling pressure continuously increases with decreasing IS, and decreases with increasing K^+/Na^+ ratios. In addition, the chemical effect of swelling is time-dependent and cannot be completely reversed. Long hydration times appear to close the pore space and significantly affect ion diffusion and transport through the compacted montmorillonite. These observations provide an improved understanding of the dynamics of clay swelling under variable chemical and hydration conditions.

LARGE-SCALE MOLECULAR DYNAMICS SIMULATIONS OF CESIUM DIFFUSION IN SYSTEMS WITH CLAY PARTICLES AND WATER MOLECULES

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Understanding the radionuclide diffusion phenomena is crucial for the safe geological disposal of high-level radioactive waste. The diffusion in clay-water systems is particularly important for the performance of the artificial barrier made of bentonite. Numerical simulation is one of the best research methods for understanding the phenomenon at the microscopic level. Recently, large-scale molecular dynamics (MD) simulations of the systems with clay particles and water molecules were realized [1]. In this presentation, we will show numerical simulation results of diffusion of cesium in the large system with MD. Our recent results suggest that cesium is less diffuse than sodium.

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IRON/BENTONITE INTERACTION – WHAT CAN WE LEARN FROM EUDIOMETER TESTS?

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The stability of iron/steel-based canisters containing high-level radioactive waste depends on the reaction with the surrounding material. In the case of crystalline host rock, bentonite will be used as additional barrier in contact with the canister and in some clay based concepts (e.g. France) the canister will be in direct contact with claystone. After a comparably short period of time, anaerobic conditions will prevail because oxic corrosion will consume the entrapped oxygen. Accordingly Fe^{2+} containing corrosion products such as magnetite, Fe-silicate, or siderite are observed. The corrosion mechanism, however, is still under discussion. Therefore, it is important to obtain as much information about the reaction as possible. Particularly the effect of different types of exchangeable cations and the presence or absence of admixtures such as carbonates and reactive silica (opal-A, C, CT) was not investigated systematically yet. Anaerobic conditions lead to the formation of hydrogen – the amount of which forms hence indirectly reflects the mechanism and the extent of corrosion. In a couple of pre-tests, hydrogen was measured by pressure sensors. Measuring the hydrogen pressure, however, turned out to be hardly reproducible which was explained by the small diameter of the hydrogen molecules and the resulting difficulty of sealing the pressurized systems. In the present study, therefore, the hydrogen volume was measured using eudiometers which turned out to be reproducible enough to measure the effect of different solid/liquid ratios, clay types, and admixtures. 5 g of bentonite powder was mixed with 5 g of iron powder (20 – 100 µm). After addition of water (standard 11 mL but also varied) the reaction vessels were connected to the eudiometers. Quasi constant hydrogen volumes were observed after 4 – 6 weeks. Theoretically, 1 g Fe^0 powder could result in about 400 mL of hydrogen. Practically only 10 mL hydrogen was observed in the case of high water contents (solid liquid ratio 0.3). Higher solid liquid ratios led to much less hydrogen formation (e.g. 6 mL hydrogen per g Fe at a solid/liquid ratio of 1). Using Fe^0 powder only (without addition of clay) leds to much less formation of hydrogen compared to the systems containing bentonite (1 mL in case of solid/liquid 0.3 and 0.1 in case of solid/liquid = 1). Different bentonites led to the formation of significantly different amounts of hydrogen. The eudiometer tests are, therefore, believed to allow a comparison of the corrosivity of different types of bentonites. Hence, in the present study different types of bentonite and admixtures were used to investigate their effect on the amount of hydrogen formed.

EVALUATION OF NOVEL MATERIALS FOR ANIONIC SORPTION

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Smectite clays are an ideal material for deployment in the engineered barrier system (EBS) of a deep geologic repository (DGR) for nuclear waste. Often used in bentonite buffer or backfill, smectites possess low permeabilities in which ion transport is dominated by diffusion and they have high sorption capacities for many of the long-lived cations present in nuclear waste. Anionic radionuclides (e.g., I-129) are a significant concern in performance assessment due to the weak interaction between anions and clays, allowing anions to have faster transit in the EBS relative to cationic species. An EBS design that includes materials that provide some degree of sorption for anionic species has the potential to reduce the biosphere radionuclide release, where anionic species dominate the radionuclide dose release to the far-field [1, 2, 3].

Previous work included synthesis of a glycol-exfoliated boehmite "glycoboehmite" [4] and demonstrated nickel functionalized glycoboehmite material is successful in anionic sorption [5]. We will present experimental and modeling studies that aim to understand why nickel outperforms other divalent metals such as magnesium and calcium in anion sorption in functionalized glycoboehmite, including possible mechanisms for these modifications. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525- SAND2024-02212A.

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COMPREHENSIVE SIMULATION AND ASSESSMENT OF SWELLING BEHAVIOR IN KOREAN BENTONITE BUFFER BLOCKS ACROSS DIVERSE INITIAL DRY DENSITY CONDITIONS

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This research employs numerical analysis within COMSOL Multiphysics to evaluate the swelling characteristics of Korean compacted bentonite buffer block. Utilizing a nonlinear elasticity model, the study simulates swelling pressure experiments and validates the outcomes against actual measurements. The analysis incorporates isotropic constraints and water injection pressure to replicate experimental conditions accurately. The model effectively could simulate swelling deformations during saturation, establishing a correlation between higher dry density and increased swelling pressure. Nevertheless, it is required to improve the prediction accuracy of the simulation model by incorporating a nonlinear elasticity model in future studies.

Keywords: *Compacted bentonite, Swelling, Hydro-Mechanical coupled analysis, COMSOL Multiphysics*

PHYSICAL ADSORPTION OF OH^- IONS CAUSES CHARGING AT MINERAL-WATER INTERFACE

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Charging of solid-fluid interface is a ubiquitous phenomenon and plays a central role in numerous natural and lab processes including metal ion adsorption. Chemical adsorption of proton/hydroxide ions is the most common process which can induce interface charging.

In this study, using first-principles molecular dynamics (FPMD) simulation, we investigated the charging mechanism at high pH by taking corundum-(0001) as a model surface. We will show that the surface charge at high pH as experimentally measured do not come from surface OH groups or surface-bound water molecules. Instead, the FPMD simulations suggest that the special interfacial structure effectively trapped the OH^- ions through physical adsorption, that led to negative charges on the surface. This novel charging mechanism also applies to other mineral-water interfaces, including clay minerals and (hydr)oxides minerals. The geochemical and environmental implication of this finding will be discussed.

THE INFLUENCE OF MINERALOGY AND ORGANIC MATTER CONTENT ON ACTINIDE SORPTION IN A CARBONATE DOMINATED REPOSITORY ENVIRONMENT

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The storage of radioactive waste in deep geological repositories is necessary as nuclear materials (from medical or energy production activities) are produced. The storage of this waste normally occurs in deposits with granite, tuff, clay, or salt dome compositions. These rock types exhibit low hydraulic permeability along with minimal fracturing during storage. However, many countries do not have the ideal rock types for deep geologic storage and must rely on regional deposits for storage of radioactive waste. Our team studied a carbonate rock core taken from the vadose zone of the Yamin plain in the Negev desert in Israel. We characterized the mineralogy of the core using quantitative X-ray diffraction. Additionally, the organic matter was characterized using gas-chromatography mass-spectrometry (GC-MS), pyrolysis GC-MS and NMR. A series of sorption experiments with actinides (Np, Pu, Am, Cm) were also conducted to determine the partitioning of radionuclides between the organic-rich rock and groundwater during storage. The XRD results reveal that the majority of the core is dominated by calcite, with minor contributions from kaolinite, quartz, pyrite and apatite. The organic matter (OM) content in these rocks ranged from 2-10 wt. % and was dominated by hydrocarbons. The OM in the aqueous phase was composed of small organic acids and larger macro molecules with a CRAM structure (carboxyl-rich alicyclic molecules). Variations in mineralogy and solution pH appear to be dominant predictors of sorption for the radionuclides tested, with apatite rich rocks sorbing the most actinides. Understanding the sorption behavior of actinides in complex rock materials is important for predicting how radioactive waste will behave on geologic time scales. Future work will investigate hydrothermally altered parent rock material to determine if changes in mineralogy and OM influence actinide sorption. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

FULL PORE SIZE DISTRIBUTION OF SHALE BY COMBINATION OF INNOVATIVE GAS ADSORPTION ISOTHERMS, MERCURY INTRUSION POROSIMETRY AND LABORATORY NANO-X RAY TOMOGRAPHY.

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The pore size distribution of clay rocks and soils is crucial for understanding and modelling cation exchange, gas migration, solute diffusion, and hydro-mechanical behavior. The proportion of bulk water and the water within the double layer at the surface of minerals, as well as capillary and osmotic pressures, are controlled by the pore size. Conventional methods, such as mercury intrusion porosimetry and gas adsorption isotherms, are commonly used to characterise the pore network across a wide range of scales. However, isotherms are applied to crushed powder samples, which is inappropriate for assessing the preserved microstructure, and the two pore size distributions provided never successfully match to our knowledge. For this reason, nitrogen adsorption experiments were conducted on preserved rock blocks using an innovative approach with kinetic control of adsorption equilibrium [1]. Pore size analysis was performed by simulating isotherms with Grand Canonical Monte Carlo kernels. This approach was applied to the Callovo-Oxfordian shale, which is planned to host the French nuclear waste repository. For the first time, this study provides a complete set of comparable data between mercury intrusion porosimetry and gas adsorption isotherms, accurately measuring pore throat and pore body size distributions. However, it is important to note that this coupling only probes pores ranging from the smallest micropores to macropores with a size of 600nm, and therefore a full description of the pore network has not yet been achieved. The largest pores missing were imaged using laboratory nano X-ray tomography on a 1.5 mm wide core of resin impregnated shale with a voxel size of 295 nm. Advanced in-house algorithms were applied to denoise and restore the numerical volume, and to identify the pores. The segmentation of the pores allowed for the estimation of their size distribution, which was used to build a complete balance of the pore network.

To illustrate the impact of the enhanced pore size distributions achieved, a multiscale model implemented in the Code_Aster Finite Element software [2] was used to simulate an experimental swelling pressure curve that was recorded on the Callovo-Oxfordian shale. The results showed a significant improvement in consistency with the experimental data.

[1] Matskova N., Prêt D., Gaboreau S., Cosenza P., Brechon R., Gener I., Fialips C.I., Dubes G., Gelin F. (2017) Towards a Balance of Pore Size Distribution in Non-Conventional Hydrocarbon Reservoirs: a Combination of Bulk Techniques Applied to Comparable Sub-Samples Localized by 3D X-ray µTomography. Proceeding of the Unconventional Resources Technology Conference held in Austin, Texas, USA, 24-26 July 2017. DOI 10.15530-urtec-2017-2689299.

[2] Mhamdi Alaoui H., Giot R., Prêt D., Cosenza P., Hedan S. (2023) Development and numerical implementation of a multiscale constitutive law for double-porosity clayey geomaterials. Computers and Geotechnics, 61, 105612.

TEMPERATURE EFFECTS ON URANIUM ADSORPTION TO MONTMORILLONITE

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The U.S. currently has 85,000 tons of spent nuclear fuel that must be safely disposed in a subsurface nuclear waste repository. In this repository, an engineered barrier system (EBS), consisting of bentonite will encapsulate nuclear waste canisters to minimize underground contamination after canister failure. As uranium is the main component in spent nuclear fuel, and montmorillonite clay in bentonite, it is important to study uranium-montmorillonite adsorption processes. Previous research on uranium-montmorillonite adsorption mostly focused on the effects of pH, contact time, and ionic strength at room temperature conditions. However, temperature effects on uranium adsorption are also important to study, since radioactive decay heat will lead to high temperatures in the EBS during early waste storage. Hence, our goal is to characterize temperature effects on uranium-montmorillonite adsorption behavior and kinetics. For this purpose, a literature review was conducted to evaluate the current knowledge on temperature effects on uranium-montmorillonite adsorption. In addition, uranium-montmorillonite batch adsorption experiments are performed as a function of temperature (up to 90°C) to characterize the impacts of temperature on various uranium adsorption processes.

Our literature review shows that, while only a limited amount of equilibrium and kinetic data are currently available, increased temperatures appear to enhance uranium adsorption onto clay. However, previous studies have often only focused on a few, specific temperature conditions, or involved clay samples representative of the local mineralogy of the researchers. This makes it difficult to draw generalized conclusions, since detailed, mineralogical characterizations of solids are often missing. Finally, temperature effects on uranium solution speciation have been largely ignored during the interpretation of temperature effects on uranium adsorption processes. A summary of our own experimental results will be provided during this poster presentation.

THERMO-HYDRO-MECHANICAL BEHAVIOR OF A CLAY-PELLETS MIXTURE INTENDED FOR BARRIER SYSTEMS

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Deep geological repository is the most favorable option for the safe disposal of high-level nuclear waste (HLW) and spent nuclear fuel (SNF). The design of such a facility relies on the multi-barrier system, encompassing a cylindrical metallic container (encapsulating the HLW/SNF), an engineered barrier system (EBS, around the metallic container); and the host-rock (or natural barrier). The most preferred buffer material to construct the EBS is bentonite clays. They are being considered as potential buffer materials because of their high swelling capacity provides mechanical stability to the metallic canister containing the HLW/SNF; their good thermal conductivity assists to dissipate the heat released by the HLW/SNF; their low permeability delays the flow of water and gas through the system. It is envisaged that EBS will be built using blocks of compacted bentonites or a combination of high-density clay-pellets mixtures and blocks of compacted bentonites (i.e., where the metallic container rests). Clay-pellets mixture is also considered as possible seal materials to fill gaps that characteristics in this type of system, e.g., the gap between the EBS and the surrounding host-rock. Clay-pellets present several advantages, amongst others, they are very suitable for filling (small) technological voids, there is no need for additional in-situ compaction when they are used as a buffer/backfill material, and it is relatively easy to manufacture them. Because of the nuclear waste radioactive decay, the clay barrier will be subjected to high temperatures. Most of the previous research in this area have considered a maximum temperature of 100°C. Recently, it has been an increasing interest in understanding the behavior of clayed materials at higher temperatures, up to 200°C. The main motivation is to optimize the repository footprint. However, the information in this area is scarce. The aim of this paper is to investigate the thermo-hydro-mechanical behavior of clay-pellets mixture when subjected to long term hydration and heating at 200°C.

EFFECT OF CS+ ON TRANSFORMATION OF SMECTITE TO ILLITE (ILLITIZATION)

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Bentonite, mainly comprised of smectite clay, is a material with ideal properties for its use in an engineered barrier system (EBS) of a nuclear waste repository. When exposed to water, smectite generates high swelling pressures, self-sealing capabilities, low hydraulic conductivity, and it has a high sorption capacity; desirable for sorption of potential migrating radionuclides [particularly Cs-137 with a half-life of 30 years (Muslim et al. 2023)]. Illitization occurs when smectite is transformed into illite which weakens the performance of the EBS, reducing its ability to absorb water or cationic radionuclides into the interlayer. The illitization process is well recognized in natural, geologic settings and most prominently occurs due to high temperatures and pressures (at geologic depth) with an external K^+ source.

Wyoming montmorillonite (smectite) SWy-2, acquired from the Clay Minerals Society, was the starting material for our Parr Vessel reaction studies. In previously conducted experiments, the effect of interlayer cation (Na^+ or K^+) was investigated (Mills et. al, 2022). Reaction conditions consisted of: high temperature (200 °C); reactor solutions: 1M KCl or deionized water; reaction times ranging from 7 to 112 days; and liquid to solid mass ratios (L/S) of 100, 500 and 1000. The solid reaction products were collected and re-exchanged with NaCl to determine K^+ fixation within the clay interlayer. Analysis of oriented and glycolated samples by XRD was used to identify differences in swelling capacities, indicating formation of mixed-layer and discrete phases of smectite and illite. Samples were also examined under SEM to determine morphology changes of the clay. Samples were analyzed by ICP-OES for liquid chemistry. From the previous study, L/S of 1000 had the greatest extent of conversion of smectite to illite, where mixed-layer clay occurs after 28 days of reacting under the conditions above. In Recent experiments, Cs-form smectite was reacted under similar conditions as above. Preliminary results presented here indicate Cs^+ in the clay interlayer delays the transformation of smectite to illite when compared to smectite in the Na- and K-form. Understanding the role of cesium in the EBS is important for future predictions of long-term deep geological disposal of nuclear waste. SAND2024-02432A

EFFECT OF PORE FLUIDS, EXCHANGEABLE CATION, AND TEMPERATURE ON THE SWELLING PROPERTIES OF BENTONITE

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Bentonites are considered as a component in an engineered barrier system (EBS) for deep geological storage of high-level radioactive waste. The swelling/shrinking behavior and properties of bentonite-based barriers can be modified by external factors, such as surrounding groundwater from the host rock, dissolved solids in the water, and the heat released by the radioactive waste. The objective of this work is to investigate the swelling behavior of BCV bentonite (Mg/Ca type) under various salinity, temperature, and pressure conditions that the EBS may experience in the underground repositories by using experimental methods (meso-scale swelling pressure measurements and mineralogical analysis) and molecular dynamics (MD) simulations. The adopted methodology for this research included a series of swelling pressure (SP) tests at constant volume that correspond to the macroscopic swelling potential of compacted samples, and the effect of pore fluid concentration on bentonite swelling behavior. In addition, X-ray diffraction analyses identified the effect of the pore fluid on the crystalline swelling of different compacted and powder samples. MD simulations were used to explore the swelling behavior of model montmorillonite layers by considering the effect of interlayer cations (Na/Ca mixtures in the interlayer) and temperature.

Results suggest that high salinity led to a decrease in the SP of the samples. This is caused by cation exchange, reduced double-layer thickness, and the osmosis effect when the samples were exposed to high-salinity pore fluid. The changes in basal d_{001} spacing of the clay minerals in response to ionic strength suggested that the interlayer water potential relative to the fluid played the most important role in causing the measured SP changes. MD simulations showed that the expansion of the interlayer was dependent on both the ratio of monovalent-divalent cations (Na/Ca) and the temperature of the system.

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

SWELLING PRESSURE BEHAVIOR OF COMPACTED BENTONITE UPON WETTING WITH VARIOUS SALINE SOLUTIONS

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Compacted bentonite is being considered in the design of engineered barrier systems (EBS) and seals in the context of deep geological disposals envisaged for the isolation of high-level nuclear waste (HLW) and spent nuclear fuel (SNF). The EBS will be subjected to complex thermo-hydro-mechanical-chemical (THMC) processes triggered by the heat released by the HLW/SNF, the hydration of the clay (due to water from the surrounding rock), increments in stresses induced by the progressive wetting and swelling of the compacted bentonite under highly confined conditions, and chemical interactions. For this reason, this study focuses on the swelling behavior of compacted bentonite samples, with particular attention to the effect of the pore fluids on the swelling pressures (SWP) developed during clay hydration.

The methodology adopted in this research combined experimental and numerical investigations to understand the swelling behavior of compacted clays. SWP experiments on divalent, compacted bentonite were performed in a constant volume cell to examine the effects of osmotic suction on the swelling pressure of samples with an initial dry density of approximately 1.5 Mg/m^3. The osmotic suction was applied by using a different pore fluid, including distilled water and various concentrations of NaCl and $CaCl_2$. An in-house numerical code was adopted to simulate the experimental results. The key component of the analysis was an advanced chemo-mechanical model for unsaturated soils able to account for the two basic structural levels typically found in this type of clay, namely, the macro- and micro-structures. The experimental results revealed that the SWP of the bentonite decreased as the saline (osmotic suction) increased. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

STABILIZING EFFECT OF RADIOACTIVE CESIUM IN INCINERATED FLY ASH AND SOIL MIXED GEOPOLYMER BY CLAY MINERALS

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Radioactive cesium derived from the Fukushima Daiichi Nuclear Power Plant accident in 2011 was concentrated into incineration fly ash (FA) as disaster waste[1]. The geopolymer solidification (GS) method is applied for stabilization of FA accompanied volume reduction. Clay mineral has the stabilizing capability of radioactive materials owing to its layer structure. In this study, we investigated the stabilizing effect of clay minerals in soil for the elution suppression of radioactive cesium by the geopolymer solidification method mixed FA and soil.

The FA sample was collected in Fukushima prefecture in January 2012. Akadama soil (red ball earth) was used for making FA/soil-mixed GS. Crystal phase analyses of each material, which are raw fly ash, akadama soil, and FA/akadama-mixed GS, were performed using X-ray diffractometer (Rigaku, MiniFlex 600) after drying each sample. The elution suppressing effect of radioactive cesium was evaluated by a leaching test.

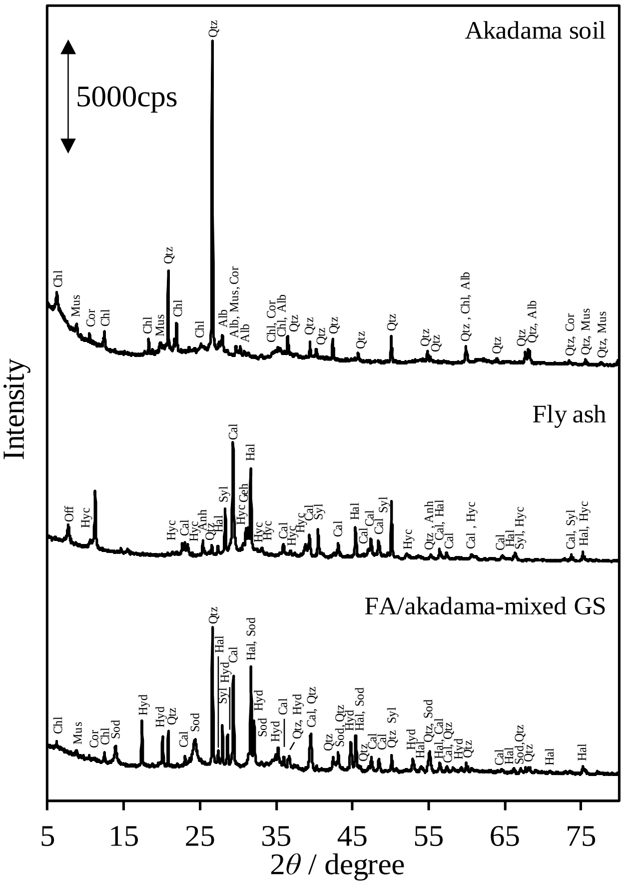

Figure 1. X-ray diffraction patterns of fly ash, Akadama soil, Akadama soil-mixed GS.

Off: offretite (K, Ca, Mg $)_3Al_5Si_{13}O_{36}$ ・ $14H_2O$), Anh: anhydrite ($CaSO_4$), Cal: calcite ($CaCO_3$), Syl: sylvite (KCl) , Geh: gehlenite ($Al_{1.54}Ca_2Mg_{0.21}O_7Si_{1.24}$), Hal: halite (NaCl), Hyc: hydrocalumite ($Ca_2Al(OH)_6Cl(H_2O)_2$) ,Alb : albite ($NaAlSi_3O_8$), Chl: chlorite ($(Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$), Mus: muscovite ($KAl_2AlSi_3O_{10}(OH)_2$), Sod: Sodalite $Na_4Al_3(SiO_4)_3Cl$, Hyd: Hydrogarnet 3CaO Al_2O_3 $6H_2O$.

The identification results of crystalline phases in FA, akadama soil and FA/akadama-mixed GS are shown in figure 1. In this result, muscovite one of clay minerals was identified on the diffraction pattern of akadama soil. In the result of the leaching test, elution suppressing effect of radioactive cesium was shown due to the stabilizing capability of muscovite.

We will investigate the elution suppression mechanism of radioactive cesium by clay minerals using various soils and FA.

1 Oshita, K., Aoki, H., Fukutani, S., Shiota, K., Fujimori, T., Takaoka, M. (2015). *J. Environ. Radioact.*. 143, 1-6.

SWELLING CLAYS AND THE NUCLEAR 137-CS THREAT

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The present study aimed to find out if and if yes which dioctahedral swelling clays belonging to the vermiculite-smectite family could be used in the treatment of radiocesium-contaminated natural waters.

One dioctahedral soil vermiculite (1E), three beidellites (IP2, SbCa, and Sbld), and four montmorillonites (SWy-3, Saz-3, SCa-3, and STx) having the layer charges from 0.44 – 0.76/T_4O_{10} were used in the present study. Adsorption experiments were performed for drinking waters and artificial sea waters containing ~1000 ppm, ~100 ppm, ~10 ppm, ~1 ppm, and ~0.1 ppm of ^{133}Cs. Cs concentrations in obtained solutions were measured using the ICP-MS method.

In the case of drinking waters, the adsorption efficiency (AE) (calculated as a percentage of Cs adsorbed) of low-charge smectites was 50%->90% depending on Cs-concentration, whereas the AE of high-charge clays reached values between 95% and >99%. In the case of sea-waters AE was 30%-50% for low-charge clays and 60-86% for high-charge clays. This indicated that all of the studied clays adsorbed Cs selectively from fresh waters and likely could be used for the treatment of Cs-contaminated drinking waters. In the case of marine waters, only high-charge clays showed selectivity for Cs-adsorption.

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STUDY OF MICROBIAL VIABILITY IN KUNIGEL V1® BENTONITE AND IMPACT ON THE METAL CORROSION

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Bentonite buffer is a key engineered barrier for the retardation of radionuclide migrationin the geological disposal of the high-level radioactive waste (HLW) in Japan. Additionally, the suppression of microbial activity within the bentonite buffer is necessary to prevent microbially induced corrosion (MIC) of metal containers for HLW over a period of 1,000 years. This study investigated the effects of dry density, temperature, and irradiation on microbes within bentonite. The viability of microbes in Kunigel® V1 (KV1) bentonite decreased as dry densities increase from 1,000 to 1,800 kg/m³, becoming negligibly small at densities exceeding 1,400 kg/m³. When subjected to temperatures of 80°C or 120°C for 6 months under anaerobic conditions, microbial viability in KV1 decreases than those at 30 °C but is not fully suppressed. An increase in gamma absorbed dose rate from 1 to 100 Gy/h resulted in a significant decrease in microbial viability in KV1 after 3 months at room temperature under anaerobic conditions. However, the calculated dose rate at the surface of an overpack was 11 mGy/h, lower than the experimental conditions mentioned above, suggesting a negligible impact of irradiation. Furthermore, while the corrosion of carbon steel coupons embedded in the bentonite specimens may not be influenced by microbial activities, pitting holes were discovered in a few coupons after cultivation at the lowest density of bentonite. These findings indicate that the dry density of KV1 plays a crucial role in preventing microbial activities, more so than temperature and irradiation. Although corrosion is not accelerated by MIC, maintaining high densities is necessary to avoid pitting corrosion.

THE ROLE OF MINERAL IMPURITIES FOR THE ADSORPTION OF URANIUM(VI) ONTO BENTONITE

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Most future nuclear waste repositories will include engineered bentonite barriers to minimize the release of uranium (U) and other radioactive contaminants into the natural environment. Bentonite predominantly consists of montmorillonite clay, which will largely control uranium(VI) adsorption and transport processes in engineered barriers. In addition, bentonite also contains small fractions of mineral impurities (e.g., plagioclase, quartz, calcite), which may directly or indirectly affect U(VI) adsorption. First, mineral impurities can provide additional surfaces for U(VI) binding, with potentially lower adsorption affinities or a different pH dependence for U(VI) adsorption processes. Furthermore, dissolution products from mineral impurities could lead to an increase in ionic strength, the presence of cations competing with UO_2^{2+} for montmorillonite ion exchange sites, and/or changes in U(VI) solution speciation, e.g. due to the formation of ternary U-Ca/Mg-carbonate solution complexes. These effects may be further enhanced at elevated temperatures caused by the radioactive decay heat of spent nuclear fuel in the EBS, which could lead to higher mineral dissolution, mineral transformations, and the formation of new solid phases with different surface characteristics. The goal of this study is to characterize and decouple these parameters and processes based on lab-scale U(VI) adsorption experiments involving solids of different complexities, and before and after heat-treatments. We will present experimental data for U(VI) adsorption onto purified montmorillonite, a well-characterized solid mixture of montmorillonite and calcite, and FEBEX bentonite impurity fractions, after solid exposure to various temperatures. Our data interpretation is supported by a detailed characterization of solution and solid phases.

MICROSTRUCTURAL EVOLUTION OF BINARY BENTONITE BARRIERS DURING SATURATION

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The nuclear waste disposal concept based on the horizontal placement of canisters on a rigid support made of highly compacted bentonite blocks and the filling of the reminder of the gallery with granular bentonite material (GBM, i.e. pellets) has been tested in large-scale tests such as the EB and FE carried out at the Mont Terri URL (NAGRA 2019). These binary barriers are a source of bentonite heterogeneity, since the initial dry density and structure of the two components noticeably differ. A series of tests in cells (10x10 cm) were carried out to obtain information about the evolution, at laboratory scale, of initially inhomogeneous bentonite samples (pellets/blocks) upon hydration under isothermal conditions (Villar et al. 2021). The materials used were the same as in the EB in situ test (García-Siñeriz et al. 2015): FEBEX bentonite compacted at dry density 1.6-1.7 g/cm^3 with water content 14% and GBM with dry density 1.3 g/cm^3 and water content 4%.

Bentonite water content and dry density gradients were observed at the end of the laboratory tests (maximum duration ~1 year). Although they attenuated over time, they persisted even after full saturation was reached. In the in situ test, which was fully saturated after 10 years of operation, the level of homogenization reached in terms of water content and dry density was significant (i.e. the dry density of the blocks part decreased and that of the GBM increased). However, the microstructure of the bentonite in the two components was different even after full saturation and long testing periods and, unlike with water content or dry density, there was not a smooth change between the microstructural parameters of GBM and block. Notwithstanding, the separation between macro and mesopores could be set at 200 nm in both cases. The most notable change in the GBM upon saturation was the overall drastic decrease in size and volume of macropores, whereas the volume and mean size of the pores smaller than 200 nm increased with respect to the original values. To a lesser extent the increase in volume and size of mesopores also occurred in the blocks, but the volume of macropores increased in them (because of the dry density decrease). Nevertheless, the volume and size of macropores continued to be higher in the GBM than in the block parts. The increase in the volume of mesopores was related to the increase in basal spacing as a result of the hydration of the interlayer cations, although for a given water content the block samples tended to have lower basal spacings than the GBM. The change from the 2-layer to the 3-layer hydration state took place for water contents between 32 and 38%.

These trends were common to the lab and the EB samples and mostly related to their dry density (and hence to their water content, because they were fully saturated), which would indicate that no further microstructural changes are expected in the barrier once full saturation is achieved.

García-Siñeriz et al. https://doi.org/10.1016/j.enggeo.2015.04.002
NAGRA Technical Report NTB 15-02.
Villar et al. https://doi.org/10.1016/j.enggeo.2021.106272

EXPERIMENTAL DETERMINATION OF PR(III) SORPTION ONTO SAPONITE AND CA-RICH MONTMORILLONITE TO 70^{O}C

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A buffer material is a key component of a multi-component engineered barrier system in a high-level nuclear waste (HLW) deep geological repository. The first function of a buffer material is to prevent the percolation of groundwater onto waste packages owing to its swelling properties. The second function is to retard the movement of radionuclides from a waste package to the surrounding environment via the sorption capability of the material, should the waste package becomes breached. In our previous study, we have found that saponite, a tri-octahedral smectite with an ideal formula of $Mg_3(Si, Al)_4O_{10}(OH)_2{\bullet}4H_2O$ and a swelling property similar to montmorillonite, is a good candidate buffer material in harsh environments such as high pH and high temperatures, because of its chemical stability under those conditions [1].

In this presentation, we report our experimental studies regarding sorption of Pr(III) onto saponite. We use Pr(III) as an analogue to Pu(III) and other trivalent actinides. We use NaCl solutions as ionic strength supporting media. The ionic strengths in our experiments range from 0.001 $mol{\bullet}kg^{-1}$ to 0.1 $mol{\bullet}kg^{-1}$. We investigate the sorption of Pr(III) onto saponite as functions of ionic strengths, pH and temperatures. The experiments were performed at 25°C, 40°C, 50°C, 60°C, and 70°C. The pH values range from pH~4 to pH~12. For comparison, we also conduct the parallel sorption experiments with Ca-montmorillonite from Gonzales County, Texas, from the Source of Clay Repository, Clay Minerals Society.

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RESEARCH STATUS ON DEVELOPMENT OF HIGH-PERFORMANCE BENTONITE BUFFER MATERIALS

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The bentonite buffer material is a crucial component for disposing of high-level radioactive waste (HLW). This study introduces the research status on the development of high-performance bentonite buffer materials such as additive mixtures to reduce disposal area. First of all, this paper evaluates the thermal conductivity of mixtures involving bentonite-silica sand and bentonite-graphite considering various dry density and water content values. The thermal conductivity for bentonite additive mixtures is shown to be 10-30% higher than that of pure bentonite, with a significant increase observed in the high water content range. Furthermore, saturated hydraulic conductivity, swelling pressure, and equilibrium distribution coefficient for Cesium are evaluated for several additive-bentonite mixtures. In short, this paper aims to evaluate the overall thermal-hydraulic-mechanical-chemical (THMC) properties to meet the performance targets of the buffer material.

Keywords: *High-performance buffer, bentonite-additive mixture, grade improvement*

ADSORPTION OF IODINE ANIONS BY CHRYSOTILE AND HALLOYSITE: THE EFFECT OF NANOPORE STRUCTURE

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With the development of nuclear energy, large amounts of radionuclides are produced and inevitably released into the environment, threatening human health. Among them, radioactive iodine is one of the greatest concerns because of its low adsorption tendency/high mobility and potential toxicity. Iodine exists primarily as anions (IO_3^- and I^-) depending on redox and pH conditions, both of which are repulsed from the negatively charged surface of most sediments and minerals. Therefore, the efficient adsorption of radioactive iodine anions is of great importance.

In this work, the adsorption of iodine anions by nanotubular chrysotile and halloysite was carried out by batch adsorption experiment and spectral analysis. The results show that chrysotile bundles (Chry-B) exhibited strong adsorption to iodide and the distribution coefficient (K_d) to iodide was 179.24 mL/g, which is two orders of magnitude higher than those for previously reported clay minerals. The wedge-shaped nanopores among the neighboring nanotubes in Chry-B were inferred to be the primary adsorption sites for the iodine anions. The nanotubular halloysite exhibited strong adsorption to IO_3^-, with a K_d value of 131.6 ± 14.6 mL/g, which is more than 30 times higher than that of flaky kaolinite. It was proposed that the strong adsorption is due to the curved octahedral sheet causing a geometry match between three oxygen atoms in iodate and three OH above the vacant sites of the octahedral sheet. These results indicated that chrysotile and halloysite could be efficient adsorbents for iodine anions and that the nanopore structure played a crucial role in the adsorption. Our findings also provided new insight into the potential application of nanoporous minerals in nuclear waste disposal.

STUDY THE EVOLUTION OF BENTONITE BUFFER UNDER HIGH TEMPERATURE HEATING USING LARGE SCALE FIELD TEST AND THE CORRESPONDING MODELING

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Deep geological repositories for high-level radioactive waste consist of a host rock and an engineered barrier system (EBS) which includes the waste canister and the buffer material. Bentonite is typically chosen as a buffer material due to its low hydraulic conductivity, high swelling capacity and retardation ability. The bentonite is subjected to heating from radioactive decay of the waste and hydration from the host rock, which leads to chemical and mechanical alterations. Numerous studies have been conducted to study the evolution of bentonite buffer under simultaneous heating and hydration, but most of them focused on heating under 100 °C because the prevailed concept was that the thermal limit in bentonite buffer has to be kept under 100 °C. However, understanding the evolution of bentonite under hydration and high temperature heating opens the possibility of having a higher thermal limit which can significantly decrease the cost of repository. Field tests and the associated modeling work will be the ultimate measure for such a purpose.

This study presents the HotBENT field test at the Grimsel Test Site in Switzerland. The test consists of 4 heaters compartmentalized in two sectors and emplaced in a granite tunnel with granulated Wyoming (Heaters 1-3) and BCV (Heater 4) type bentonite filling the space between heater and tunnel wall. Heating started in September 2021 and heaters reached the target temperatures of 175 °C and 200 °C in May 2022. Monitoring data were collected since heating started and dismantling of one of the sectors is planned 5 years after the heating. Meanwhile, coupled THM/THC models were developed to interpret the observed data and make predictions of the state of the bentonite after 5 years. A 2-D cross-section surrounding heater 1 (200 °C) was modeled considering vertical symmetry about the axis of the gallery where the radial flow was assumed for hydration and heat transfer. A time-dependent Dirichlet temperature boundary condition is prescribed to the heater. The numerical model was calibrated with field test data for temperature and relative humidity. The model shows reasonable agreement with temperature data but measured relative humidity data are too scattered to draw clear trends. Model showed strong desaturation near the heater and evaporation/condensation leads to high ion concentration at areas near the heater.

PHYSICAL DEFORMATION OF ROCHESTER SHALE AND OPALINUS CLAY – IMPACTS ON ISOTOPIC SIGNATURES OF CLAY MINERALS

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Clay rocks have been investigated as nuclear waste repository host rock due to their favourable isolation properties enabling effective nuclear waste storage over long geological time periods (Grambow, 2016, Yardley et al., 2016). This study follows up on physical deformation experiments of Silurian Rochester Shale (Brett 1983) by Zwingmann et al. (2019). In addition, the Jurassic Opalinus clay, Switzerland, which has a distinctly different clay mineralogy is included in the follow-up study (Zwingmann et al., 2017). The Rochester shale is illite rich (~60%), contains minor kaolinite (~9%) and about 23% quartz, whereas the Opalinus clay samples contain a lower amount of ~30% illite, ~ 35% kaolinite, 11% chlorite, ~ 6 % of carbonates and a lower amount of quartz with 13%. The Opalinus clay samples were included in this study because of the potential radioactive waste disposal in Switzerland and originate from the Mont Terri underground research laboratory (Bossart et al., 2017). Detrital clay minerals are abundant in clay rocks and have been investigated using Ar dating as bulk sediment provenance proxies (van Laningham and Mark, 2011). Authigenic illite occurs in fault gouges and isotope dating of the radiogenic noble gases they contain may be used to constrain timing of deformation. The potential influence of deformation or fault slip and ambient temperature on the isotope signature of authigenic clay minerals, however, remains largely unknown (Zwingmann et al., 2019). Existing studies mainly focus on the influence of thermal events to understand isotope data in clay minerals. The effect of physical deformation processes like: shearing and grinding of clay minerals, including the possibility of porewater release, and its impact on the isotopic signatures and, therefore reliable isotopic ages, remain widely unknown and poorly understood. The present study investigates the influence of physical deformation via mechanical comminution, (grinding) and its influence on the isotope signatures of clay minerals, in a set of well-defined laboratory experiments using the above introduced Rochester shale and Opalinus clay. The samples are suitable for testing physical deformation as its maximum burial temperature was low, as shown by the maximum burial temperature of ~85°C (Mazurek et al., 2006) for the location.

Deformation experiments were carried out using different milling equipment, grinding force (ball mill and McCrone mill), time (5 to 60 min) and temperature conditions (room temperature to 300 ºC). The integrated data obtained decipher physical deformation and temperature effects on Argon retention in clay minerals. In the Rochester shale study the milling data were compared with rotary shear experiment data. The latter revealing a loss of 55 to 84% radiogenic Ar related with increasing temperature (Zwingmann et al., 2019). For comparison, the ball mill experiment reduce radiogenic Ar only from 15 to 56% without external heating, but increasing milling time. A similar increasing radiogenic Ar loss trend of 32 to 80% could be observed in the McCrone mill experiments with increasing milling time.

In the Opalinus study the milling experiment data indicate a larger loss of radiogenic Ar using the ball mill; ranging from 9 to 48 %, and a lower loss of 2 to 14% using the McCrone mill. In addition to the effect of temperature, the amount of strain and the mineralogy influence the Ar loss. We interpret the different radiogenic Ar loss ranges between the Rochester shale and Opalinus clay caused by different amounts of quartz and feldspar and different clay mineralogy of the starting materials. The shape and the hardness of the quartz/feldspar will influence the deformation of the clay particles inside the mill.

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Session 18

Electron Microscopy on Clay Sciences – Featuring a Special Session Honoring Dr. Toshihiro Kogure

Conveners: Ryosuke Kikuchi (Hokkaido University, Japan), and Yuji Arai (University of Illinois at Urbana-Champaign, USA)

FORMATION MECHANISM OF FE-RICH CHLORITE FROM HYDROTHERMAL DEPOSIT IN JAPAN REVEALED BY HIGH RESOLUTION SCANNING TRANSMISSION ELECTRON MICROSCOPY

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Fe-rich chlorites and Fe- and Al-rich serpentine group minerals are closely related to each other from the viewpoints of crystallochemistry. When Fe content of chlorite is high (Fe/(Fe+Mg)>0.6), the 7 Å – 14 Å interstratified structure is ubiquitously occurred. The crystallochemical relationships between component layers in the interstratified mineral and chlorite and serpentine group mineral are still unclear. High resolution (scanning) transmission electron microscopy (HR(S)TEM) is the most powerful technique to characterize the 7 Å – 14 Å interstratified minerals. In this study, the 7 Å – 14 Å interstratified mineral which was the product of direct precipitation were characterized by HR(S)TEM technique.

The studied sample was obtained from Yatani mine, Yamagata Prefecture, Japan. The chlorites were found in the spherulite-like amygdules. The amygdule consists of Fe-rich outer part and Fe-poor inner part. The outer part was composed of packets of Fe-rich 7Å-14Å interstratified minerals (Fe/(Fe+Mg)> 0.8). The inner part was a mixture of low-crystallinity phase with Fe-poor chlorite chemical composition (Fe/(Fe+Mg) < 0.6) and microcrystals of Fe-rich 7Å-14Å interstratified mineral (Fe/(Fe+Mg)> 0.8). In comparison with the hydrothermal events at Yatani, the inner low-crystallinity phase was first formed. Then, the Fe-rich 7Å-14Å interstratified minerals were formed. In addition to the direct observations of its stacking structure, the Fe content and $Fe^{3+}/\Sigma Fe$ was investigated at nanoscale. The evolution of chlorite, 7Å-14Å interstratified mineral and serpentine group mineral will be discussed in terms of oxidation states of iron.

QUANTITATIVE ANALYSIS OF PETROGRAPHIC TEXTURES OF BENTONITE ORES BY IMAGE PROCESSING

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Quantitative mineralogy using electron microscopy has been a vital technique in various geological fields such as ore deposits and petroleum reservoirs. While recent techniques, such as QEMSCAN and TIMA, have proven to be strong tools, it is also necessary to quantitatively evaluate petographic textures including fine particles to understand the physical properties of earth materials. For instance, in the context of geological disposal of high-level radioactive wastes, a few microns of silica adhering to the edge of montmorillonite may degrade the swelling property of bentonite (JAEA & RWMC, 2019). However, these techniques often limit usability due to their high costs, and struggle to capture the contours of fine particles due to the limitation of spatial resolution. This study aimed to address these challenges by developing a quantitative method using the conventional electron probe micro analyzer (EPMA) and an open-sourced image processing library OpenCV, employing bentonite ores as materials.

Six bentonite ores were collected from Tsukinuno bentonite deposit in Yamagata prefecture, Japan. Thin sections were prepared by dry polish technique without using any water and oil (Owada et al., 2013). Scanning electron microscopy (SEM) observation demonstrated a few microns of silica widely distributed on the matrix of montmorillonite with variations in their amounts, sizes and other accessory minerals. To quantitatively compare the characteristics of petorographic textures, an image processing technique was developed combining back scattered electron (BSE) image obtatined by SEM and elemental maps obtained by EPMA. BSE images provided high spatial resolution, clearly capturing the contours of micro silica with binary. Meanwhile, elemental maps provided chemical compositions to distinguish identical minerals and gave a hint for thresholds of brightness in BSE imges. These images were integrated into "mineral map", which could visually illustrate the distributions of individual mineral grains and provide some parameters related to petrographic texture such as grain sizes, perimeters, distance between centroid of grains, etc. This mineral map may provide a means to quantitatively investigate the correlation between petrographic characteristics and some physical properties of bentonite buffer such as swelling pressure and permeability in the nuclear waste disposal facility. Furthermore, this approach may be applicable for predicting physical properties of other earth materials where fine grains are of interest, such as shales and soils.

NI-BEARING SMECTITE-SERPENTINE FROM THE TAGAUNG TAUNG NI-LATERITE DEPOSIT (MYANMAR): MINERALOGY AND NANOTEXTURES BY FIB-TEM

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Analysis of Earth's surface materials, including clays and soils, requires micro- and macro-analysis at various scales. In recent years, in addition to bulk analysis, focused ion beam (FIB) – transmission electron microscopy (TEM) technique has become a common approach for pinpoint analysis of complex ore samples. Here, we report on the application of FIB-TEM to Ni laterite ores, important sources of Ni.

Samples from Ni laterite at the Tagaung Taung, Myanmar were examined. The laterite consists of three layers: laterite, saprolite, and serpentinized harzburgite bedrock. The previous report suggested that smectite formation in saprolite layer is a key mechanism of Ni concentration [1]. In addition to smectite, a low-crystalline mineral with a composition intermediate between smectite and serpentine was also found as a Ni-host, and thus, FIB-(S)TEM was used to characterize it. In the Ni enriched areas in the lower saprolite, fine mixture consisting of serpentine with widths of several hundred nm and smectite exfoliating from them were observed. Ni was especially enriched in the packets of this mixture as finer packets with widths of several tens of nm, containing up to 36 wt% of Ni. No sign of Ni-bearing hydroxide formation was observed. Toward the upper saprolite from the lower one, heterogeneous Ni distribution became more homogeneous, and smectite was found the main host mineral rather than the serpentine-smectite fine mixture.

We are currently analyzing Ni laterite ores from Petea, Indonesia in the same manner for comparison. Preliminary results indicated that besides serpentine-smectite mixture, fine-grained iron hydroxide is also present as Ni host minerals, suggesting that climatic and topographic conditions in the two regions influenced the type of host minerals.

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TRANSMISSION ELECTRON MICROSCOPY STUDY OF SMECTITE-TO-ILLITE REACTION

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Naturally occurring microbially induced smectite-to-illite (Sm-I) reaction is of great interest to understand the control for the conventional Sm-I transformation, the source of bioavailable iron (Fe) in sediments, and the evolution of the microbial community in the deep biosphere. Transmission electron microscopy (TEM) has been majorly used to understand the crystal structures and chemistry of two distinct clay phase in the Sm-I reaction, regardless of biotic or diagenetic process. Nano-scale TEM measurement of illitization in the organic matter (OM)-rich claystone in contrast with those of coeval OM-poor claystone (2163 m–2217 m below sea floor) buried at Nankai Trough (Integrated Ocean Discovery Program Site C0002) will be presented through electron energy loss spectroscopy and HR-TEM technique. In particular, factors that control the Sm-I reaction will be discussed.

ABERRATION CORRECTED SCANNING TRANSMISSION ELECTRON MICROSCOPY AND THE NATURE OF NANOPARTICLE SURFACES

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Aberration-corrected scanning transmission electron microscopy (ACSTEM) is now capable of imaging individual atoms and identifying their molecular entities through energy-dispersive X-ray spectroscopy or electron energy-loss spectroscopy. Resolution of STEMs now reaches down to a half angstrom. Applications in clay mineralogy are relatively scarce, but have found a place in nanoparticle (NP) characterization. Two unique studies have focused on studying the surface roughness of two common minerals rutile (α-TiO_2) and goethite (α-FeOOH). The studies hypothesized that increasing roughness of nanoparticle surfaces could increase the number of different types of sites available for adsorption of either cations or organic molecules. ACSTEM was employed to image the last atoms on the surface of the NPs (Ti in rutile and Fe in goethite) and track the structure of the surface.

In the case of rutile, calculated loadings of amino acids (L-glutamate) titrated into batch adsorption experiments were higher than expected. It was hypothesized that surface roughness could be the reason for high loadings. ACSTEM observations of rutile showed that the rutile prism faces contained significant roughness, enough to account for the increase in glutamate adsorption.

Goethite is known to increase its adsorption capacity significantly with decreasing specific surface area – smaller crystals adsorb less than large crystals (surface normalized). ACSTEM was used to investigate the possible effects of crystal size, habit, surface roughness, and oriented attachment in solution and upon drying. Electron tomography revealed that both large and small crystals contain {210} tips and {101} faces with little {001} present. The large crystals appeared to be comprised of smaller crystals, possibly growing by an oriented attachment process. Small crystals were composed of two sets of {101} faces, one set much larger than the other creating a tablet habit. ACSTEM showed that the samples differ mainly in their surface roughness. Larger crystals had greater surface roughness than smaller and the roughness scaled with the size of crystals. These roughness features explain the differences in adsorption capacity between goethite NP size populations.

ATOMIC RESOLUSION OBSERVATIONS FOR BEAM-SENSITIVE MINERAL SAMPLES USING LOW-DOSE SCANNING TRANSMISSION ELECTRON MICROSCOPY

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The development and progress of aberration corrected technologies have significantly improved the spatial resolution of Transmission Electron Microscopy (TEM) and Scanning TEM (STEM). The latest STEM image resolution has been achieved up to 40.5 pm [1] and the atomic resolution imaging for many materials has become common with the correctors. Furthermore, atomic resolution chemical analysis has been realized with an Energy Dispersive X-ray Spectroscopy (EDS) and/or an Electron Energy Loss Spectrometry (EELS), owing to the correctors. Thus, aberration corrected S/TEM has been utilized for many applications of state-of-the-art industrial materials such as semiconductor materials and so on.

The atomic resolution observations and analysis with an aberration corrected S/TEM also have been performed for natural materials such as rock and mineral [e.g., 2-4]. For instance, Kogure and Okunishi [2] have visualized and distinguished each cation site (Mg, Fe, Ca and Si) in two kinds of silicate mineral using High Angle Annular Dark Field (HAADF) method by aberration corrected STEM. However, the method normally requires a high electron dose so that it has been restricted for only the minerals having relatively high resistance to intense electron radiation.

On the other hand, recently optimum bright field STEM (OBF-STEM) has been developed as a low-dose atomic-resolution imaging method by using an aberration corrected STEM with a segmental detector [5]. It can observe beam-sensitive materials such as zeolites and visualize not only the cation site (Si and Al) but also anion (O) site for zeolite with a high signal-to-noise ratio [6]. The method has possibility of direct observations in atomic level for more highly beam-sensitive mineral samples, including phyllosilicate and clay minerals.

Here I applied OBF-STEM to beam sensitive OH-bearing mineral samples and obtained their atomic resolution images by using an aberration corrected 300 kV microscope (JEM-ARM300F) with a segmental STEM detector under low electron dose conditions. In this presentation, I will share the details of results as well as introduction of the aberration corrected technologies and related imaging methods such as HAADF-, OBF-STEM and so on.

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CRYSTAL CHEMISTRY DURING SAPONITE GROWTH: A STUDY BASED ON FTIR AND HAADF-STEM ANALYSIS

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Smectites play a crucial role in various fields due to their abundance on both Earth and Mars. Despite their significance, the crystal growth processes of smectites remain poorly understood. This study investigated the crystal chemistry processes during smectite crystal growth through experiments based on hydrothermal synthesis, focusing on tri-octahedral Mg–Ni-saponites. The Mg–Ni-saponite system was chosen because of the similar ionic radii of Ni^{2+} (0.70 Å) and Mg^{2+} (0.72 Å), and the different atomic masses of Mg (24.3) and Ni (58.7), which are valuable when performing crystal-chemistry analyses such as FTIR spectroscopy and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The Mg–Ni-saponites were synthesized using the mixture of different precursors (end-members Mg-saponite and Ni-saponite) prepared under varying conditions. The crystal chemistry and morphology were analyzed using FTIR and HAADF-STEM. The key points from this study are summarized as follows: (1) The formation of Mg–Ni-saponite solid solutions is facilitated when the precursors are small particles. In contrast, large-particle precursors limit their own dissolution, resulting in the absence of Mg–Ni-saponite solid solutions. (2) Mg–Ni-saponite solid solutions are more likely to form in a system composed of quasi-amorphous Ni-saponite and well-crystallized Mg-saponite precursors. This preference arises because Ni^{2+} exhibits a greater stability within saponite structure compared to Mg^{2+}, so that Ni^{2+} can substitute for Mg^{2+} in well-crystallized Mg-saponite. (3) The crystal chemistry during saponite growth can be obtained via the combination of FTIR and HAADF-STEM, and used for estimating the growth mechanisms of saponite solid solutions.

CHARACTERIZATION OF SUBMICRON-THICK LAYERED STRUCTURE IN HYDROGENETIC FERROMANGANESE NODULE

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Ferromanganese nodules and crusts have been the focus of extensive research, due to their potential as resources for many critical and base metals, their important role in the chemical sedimentology and geochemical processes of oceans, and their ability to record the history of oceanic and climatic conditions. However, nanoscale characterization of the nodule is scarce and seems incomplete. Here we attempted to elucidate mineral phases in the local areas of a hydrogenetic ferromanganese nodule (D535 with a few centimeters in diameter from the Central Pacific Ocean) and their relationship with composition and valence state, using various analytical techniques.

Visual and SEM observation of the thin section identified a micronodule-dominant region around the core, a crust near the surface with Mn- and Fe-rich layers, and stromatolite-like textures between them. These micro-textures are composed of distinct and indistinct submicron-micron layers (SMLs) parallel to their growth front. µXRD indicated that the mineral in indistinct layers is Fe-vernadite, while 10 and 7Å phyllomanganate is present in the distinct layers, besides Fe-vernadite. Although the distinct and indistinct SMLs have different mineral phases, the transmission electron microscopy revealed that these layered structures are actually interstratification of SMLs with different crystal sizes of foliated phyllomanganates. Large crystals contain higher Mn oxidation states than small crystals. Such variations of Mn oxidation state with different crystal sizes along the growth direction imply the short-term regular fluctuation in the redox condition of the Lower Circumpolar Deep Water.

Session 19

Molecular Simulation of Clay Minerals and Related Phases

Conveners: Ian C. Bourg (Princeton University, USA), Xiandong Liu (Nanjing University, China), Kideok D. Kwon (Kangwon U.), and Christophe Tournassat (University of Orléans, France)

DISJOINING PRESSURE IN ADSORBED WATER FILMS ON SMECTITE CLAY PARTICLES

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The stability of thin water films on mineral surfaces is a fundamental question with implications in soil science, geochemistry, and atmospheric studies. Extant characterizations of mineral-water interactions present considerable discrepancies, both in theoretical formulations and in experimental determinations of water film thickness (h) at specific relative humidities (RH). This challenge is compounded when considering clay mineral nanoparticles, as water can adsorb simultaneously on external surfaces and within interlayer nanopores. To address this issue, we present a novel molecular dynamics (MD) simulation approach that yields the disjoining pressure Π (a measure of RH) in adsorbed water films with precision of ± 1 MPa, a marked improvement over the ± 10 MPa precision of prior MD simulation studies. We leverage this approach to reveal the dependence of water and ion distribution near clay particles on water content and aqueous chemistry; discern the difference in hydroscopic properties between Na- and K-smectite clay; and establish the relationship between Π and h for phyllosilicates over a relatively wide range of water film thicknesses, up to ~20 Å. Our results reveal that the relationship between disjoining pressure and water film thickness follows a double exponential decay with decay length scales of ~2.3 Å and ~7.5 Å that predominate at h smaller or larger than 14 Å, respectively. The two length scales are associated with hydration repulsion and osmotic uptake of water in the adsorbed film, respectively.

MOLECULAR DYNAMICS STUDY ON NANOCRYSTALLINE VERNADITE STRUCTURE

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Vernadite, a ubiquitous turbostratic nanocrystalline phyllomanganate, plays a vital role in the (bio) geochemical processes of trace metals. This study employs molecular dynamics (MD) simulations for the first time to investigate the long-range structure of vernadite, using Zn^{2+} as the sorptive ion probe. Simulations in both vacuum and aqueous phase were conducted for vernadite nanoparticles with diameters of 3 and 6 nm, containing varying numbers of stacked Mn octahedral sheets. The MD simulations reveal non-uniformly curved Mn octahedral sheets, contrasting the often postulated flat or uniformly curved sheets. The degree of sheet curvature depends on lateral size and the number of stacked sheets. The stability of vernadite's structure in an aqueous phase is contingent on a minimum Mn^{4+} vacancy content of 4.9 to 6.5%, emphasizing the significant role of octahedral vacancies adsorbed with cations. Zn cations at the Mn vacancy sites on the exposed basal planes were tetrahedral in vacuum but octahedral in an aqueous phase. At the lateral edge surfaces, the coordination and speciation of Zn cations were influenced by the presence or absence of surrounding water. These simulation results aid in interpreting experimental analyses of vernadite and vernadite-like phases, such as δ-MnO_2, providing insights for experimental investigations into vernadite's chemical reactivity, which is crucial for deciphering the geochemical cycling of trace metals in the environment.

EFFECT OF LAYER BENDING ON MONTMORILLONITE HYDRATION AND STRUCTURE FROM MOLECULAR SIMULATION

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The hydration and dehydration properties of swelling clays is an important consideration in the performance of clay-containing phases such as engineered barriers or host rock for deep geological repositories of spent nuclear fuel. Conceptual models of smectite clays such as montmorillonite (MMT) consist of parallel aluminosilicate layers separated by zero (0W), one (1W), two (2W), and three (3W) water layers. Such models are used in molecular simulations of hydrated MMT. However, recent theoretical studies have evaluated the energetic and mechanical properties of clay layer bending during transitions between hydration states (Honorio et al., 2017; Honorio et al., 2018). Such bending would enable a more gradual transition involving fewer water molecules at a given time rather than abrupt changes in *d*(001) spacing and water content. Recent X-ray diffraction (XRD) profile modeling studies use interstratified hydration states to account for multiple *d*(001) spacings (Chaaya et al., 2023, Ferrage 2016). In this study we used molecular dynamics (MD) and grand canonical Monte Carlo (GCMC) simulations to evaluate the hydration and structural properties of MMT in interstratified hydration states (*e.g.,* 0W-1W) consisting of clay layers in either bent or planar configurations. Results include water adsorption isotherms from GCMC simulations using small periodic models (nm dimension) with either monovalent (Na^+) or divalent (Ca^{2+}) interlayer cations. Results also include large-scale MD simulations and simulated XRD patterns using models with multiple hydration regions in the same interlayer. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

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ANGLING FOR A NEW (CLAY-)MINERAL FORCEFIELD

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Classical Molecular dynamics (MD) and Monte-Carlo (MC) simulations of clay minerals can ideally provide detailed insights into the atomistic structure, thermodynamics and dynamics of hydrated clay-based systems [1]. The predictive power of such simulations relies however on the accuracy of pre-defined and generalized mechanistic forcefields. This research presents an entirely new forcefield called MINFF, which incorporates (covalent) angle constraints to maintain accurate bonding distances, angles and overall unit cell metrics. The development of this new forcefield was motivated by the need to improve structural and vibrational data between experiments and simulations using existing forcefields such as CLAYFF and the INTERFACE FF [1,2], as revealed from the analysis of vibrational properties, Bond Valence Sum (BVS) data and comparison of experimental/theoretical XRD diffractograms. Moreover, this new forcefield introduces new atomtypes that enable the simulation of a wider range of clay minerals than is currently possible.

The forcefield optimization was performed via iterative MD simulations in Gromacs controlled by a Levenberg–Marquardt routine and the *atom* toolbox in MATLAB [3]. All simulations used a single type of angular constraint for all M-O sites (M being Al, Mg, Si, Fe, Ca), fixed partial charges and starting C6 dispersion coefficients from the programs Chargemol and DFT-D3, respectively [4,5]. Optimization was made synchronously for multiple clay and oxide minerals and targeted the Lennard-Jones parameters (*i.e.* the *VdW* interactions) by minimizing the weighted residuals from differences in bonds, angles and unit cell metrics. Although the results from this study applying new angle constraints to both CLAYFF and MINFF forcefields show significant improvement in the unit cell metrics and atomic positions of many types of common layered and non-layered (hydr)oxides minerals, it also questions the actual benefit of using generalized forcefields versus mineral specific and tailor-made forcefields.

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INTERLAYER WATER STRUCTURES AND FRICTIONAL PROPERTIES OF SUPER-HYDRATED KAOLINITE AND TALC

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Clay minerals are often postulated as major contributors to aseismic displacement within the rock fault zone due to their inherently low frictional coefficients associated with the mineral-water interface. Although kaolinite and talc are typically non-expandable clay minerals at ambient conditions, they can intercalate water under high pressure conditions. These "super-hydrated" phases of kaolinite and talc may influence the deformation dynamics and seismic characteristics at deep depths, such as the water-containing cold subduction zone. However, the interlayer water structure and frictional properties of hydrated kaolinite and talc remain largely unknown. In this presentation, we report grand canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulation results that explore the hydrated phases of kaolinite and talc at high pressure and temperature. Our MC simulations identified three hydrated phases of talc with the basal *d*-spacings of 10, 12 and 15 Å. MD simulations of the 10 Å phase revealed that interlayer water, forming strong H-bonds with the hydroxyls of Si tetrahedral sheets, reduces the frictional force compared to dehydrated talc. In kaolinite simulations, periodic friction force changes observed in the dehydrated phase, commensurate with the lattice parameters, were not found in hydrated kaolinite in which frictional weakening occurs by interlayer water molecules. Notably, interlayer water in kaolinite under pressures exceeding 1 GPa exhibited an ice-like water structure. These findings offer insights into the roles of hydrated clay minerals under extreme conditions, contributing to our understanding of geological processes and seismic phenomena in deep Earth environments.

MACHINE LEARNING MOLECULAR DYNAMICS STUDY OF HYDRATED KAOLINITE UNDER HIGH PRESSURE

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Kaolinite is a layered substance primarily made of aluminum oxide and silica, with the chemical composition $Al_2Si_2O_5(OH)_4$. It is one of the most basic clay minerals and is used in a variety of applications, including ceramics, paper, and as an adsorbent for hazardous substances. Although kaolinite has a relatively simple structure among clay minerals, recent research has reported that it reveals structural phase transitions under high pressure [1] and stabilizes in hydrated forms $Al_2Si_2O_5(OH)_4 \cdot 3(H_2O)$ under high-pressure conditions [2]. It is considered that molecular dynamics simulation is useful for obtaining detailed physical properties of kaolinite under high pressure. In this presentation, we report the results of simulations on hydrated kaolinite under high pressure using machine learning molecular dynamics (MLMD) and classical molecular dynamics (CMD). Using MLMD and CMD, we calculated changes in lattice constants, XRD data, vibrational modes of hydroxyl groups, etc., under various pressures, and these calculations were compared with reported experimental data. We found that experimental data such as XRD and IR spectra of kaolinite under high pressure were well reproduced by MLMD.

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MOLECULAR DYNAMICS STUDY OF ICE IN/ON KAOLINITE UNDER EXTREME CONDITIONS

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Ice is a ubiquitous material on Earth and in space. It is known that ice requires a nucleus to form, and clay minerals are thought to play an essential role as nuclei for ice formation. For example, kaolinite is a candidate for ice formation nuclei. In addition to these normal environments, ice in extreme conditions has attracted much attention recently.

Recently, the pressure-induced hydration state of nakhlite (a polymorph of kaolinite) was observed [1]. The interlayer water configuration was similar to that of ice Ih, suggesting that some “ice” is being formed. Although previous studies have explored the water molecule arrangements, there have yet to be studies of the observed IR spectra. We interpreted the experimental results by analyzing the vibrational spectra of the OH groups of nacrite using machine-learning molecular dynamics, which has been shown to reproduce the experimentally observed vibrational spectra of kaolinite under normal conditions with high accuracy [2].

In the extreme conditions of interstellar dust in space, amorphous ice is thought to play an essential role in forming organic molecules. Interstellar dust consists of a silicate core and an amorphous ice mantle. The structure and physical properties of the amorphous ice are currently being investigated intensively. We considered kaolinite as an idealized model of the interstellar dust core and performed molecular dynamics simulations of ice formation on its surface.

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FACET-DEPENDENT DISPERSION AND AGGREGATION OF AQUEOUS HEMATITE NANOPARTICLES

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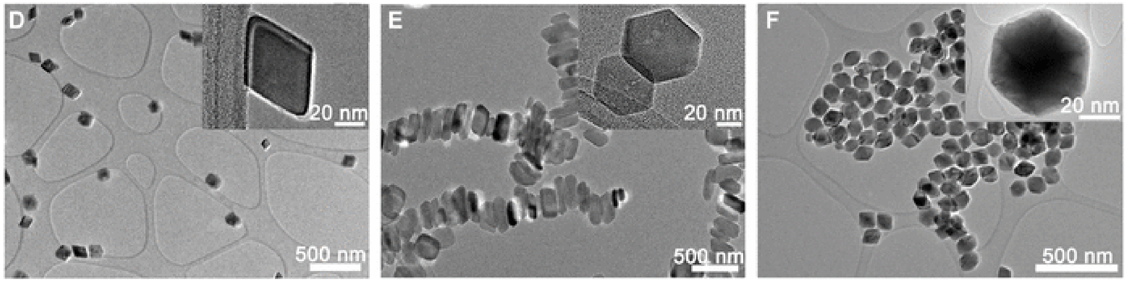
Nanoparticle aggregation in solution controls surface reactivity and function. Complete dispersion often requires additive sorbents to impart a net repulsive interaction between particles. Facet engineering of nanocrystals offers an alternative approach to produce monodisperse suspensions based simply on facet-specific interaction with solvent molecules. Here, we measure the dispersion/aggregation of three morphologies of hematite (α-Fe_2O_3) nanoparticles in varied aqueous solutions using ex situ electron microscopy and in situ small-angle x-ray scattering. We demonstrate a unique tendency of (104) hematite nanoparticles to maintain a monodisperse state across a wide range of solution conditions not observed with (001)- and (116)-dominated particles. Density functional theory calculations reveal an inert, densely hydrogen-bonded first water layer on the (104) facet that favors interparticle dispersion. Results validate the notion that nanoparticle dispersions can be controlled through morphology for specific solvents, which may help in the development of various nanoparticle applications that rely on their interfacial area to be highly accessible in stable suspensions.

Transmission electron microscopy images of synthetic ~50 nm hematite nanoparticles bearing distinct morphologies dominated by (D) the (104) facet, (E) the (001) facet, and (F) the (116) facet.



QUANTIFYING THERMO-OSMOTIC FLOW MECHANISMS IN NA-MONTMORILLONITE NANOPORES USING MOLECULAR DYNAMICS SIMULATIONS

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Thermo-osmosis is interfacial fluid flow induced by a temperature gradient. Remarkably, under certain conditions the flow direction opposes the temperature gradient, contrary to convection-driven flow. As an interfacial phenomenon, thermo-osmosis becomes a dominant flow mechanism in nanoscale pore structures such as those found in clayey soils. Therefore, thermo-osmosis should be considered as a heat transfer mechanism in clays, with applications for radioactive waste repositories and underground power lines[1]. Historically, thermo-osmosis has been defined using the principles of non-equilibrium thermodynamics. Flow is driven by deviation of specific enthalpy of the interfacial fluid $h(z)$ from the specific enthalpy of the bulk fluid h_B. The fundamental molecular-scale mechanisms of thermo-osmosis remain uncertain due to insufficient experimental means to observe interfacial properties directly. This study utilizes molecular dynamics (MD) simulations to assess the molecular mechanisms of thermo-osmosis in sodium montmorillonite (Na-Mt), which is the dominant mineral in bentonite mixtures used in the lining of landfills and waste repositories.

The model uses two Arizona Na-Mt layers of the formula $Na^+_xAl_{2-x}Mg_xSi_4O_{10}(OH)_2$, where x is the ion defect ratio. The mineral layers are separated at various d_{001}-values with water molecules inserted into the interlayer space. Mineral layers are periodic in x and y directions but are not constrained in the z direction so that stable d_{001}-values are obtained during equilibration. Previous studies have shown thermo-osmosis to be locally mechanically equivalent to mechano-caloric flow which is less computationally expensive to simulate[2]. In a mechano-caloric simulation, rather than positioning the system between thermal reservoirs of different temperatures, interlayer water molecules and sodium ions have a force applied to them at an average temperature. The simulations explored the effects of several independent variables, including d_{001}-value, average temperature, x (ion defect ratio), mean pressure, and applied force. Then, internal energy, pressure, and density were calculated with respect to distance perpendicular to the Na-Mt surface to quantify enthalpy deviation from the bulk value, $\Delta h(z)$. Simulations were performed with the GROMACS 2016.3 simulation package, compatible with the GROMACS-LS[3] (Local Stress) patch. Interatomic interactions were defined with Interface Force Field (IFF) and the TIP4P water model. The nanomaterial modeler of CHARMM-GUI was used to obtain the mineral structure of Na-Mt and necessary simulation input files. The resulting $\Delta h(z)$ values were numerically integrated over the interlayer width b, yielding an average enthalpy difference ΔH. Therefore, these simulations develop ΔH as a function of interlayer spacing, temperature, ion defect ratio, mean pressure, and flow rate. This provides a way for upscaling to macroscopic modeling, such as finite element.

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MOLECULAR DYNAMICS STUDY OF STABILITY OF CS IN INTERLAYER SPACE

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Cesium is a large ion, that can be very selectively adsorbed within the interlayer space of smectites, especially high-charge ones. This study aims to address this effect and concentrates on a detailed evaluation of mechanisms behind the possible irreversibility of this fixation. The hypothesis tested was that dioctahedral structures can exhibit stronger retention for Cs relative to their trioctahedral counterparts.

In this study, molecular dynamics was used to evaluate the effect of opening of interlayer space of various swelling clays. Structures of phlogopite, montmorillonite, and beidellite with layer charges: of 0.3, 0.5, and 0.7 per T_4O_{10} were taken into account. Increasing stress was applied to the clay layers to expand them. The evolution of total energy and zz-strain was monitored during the expansion. Completely dry and a structure with one layer of water were tested.

The results show higher differences in total energy and zz-strain for higher charge clays. The received values of cleavage energies are practically linear with charge for all the studied models. The effect of the location of layer charge is less visible, although montmorillonites have generally higher differences of energy and zz-strain than beidellites and phlogopites. Cesium as a large ion does not enter ditrigonal cavities in tetrahedral sheets and for dry beidellite/montmorillonite, the distance between the hydrogen of an octahedral sheet and Cs^+ is 4.5 Å, while for phlogopite it is 3.5 Å. These differences affect also the distance between Cs^+ and aluminum substitution in tetrahedral sheet (~0.1 Å), as well as basal spacing (~0.4 Å). Thus it can be concluded that in nature trioctahedral clays should possess lower Cs^+ retention than dioctahedral ones.

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CHARGING THE MINERAL/WATER INTERFACE: MOLECULAR DYNAMICS SIMULATIONS OF THE ELECTRIC DOUBLE LAYER UNDER APPLIED ELECTRIC FIELDS.

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Spectral Induced Polarization (SIP) spectroscopy is a burgeoning geophysical technique that applies a low-frequency electric field (<MHz) to a soil or rock sample to collect complex impedance spectra. It is a nondestructive method that can be applied, in principle, to ascertain the mineralogical composition, water content, and pore-water chemistry of a sample.

Yet, despite its promise, the resultant spectra are often difficult to deconvolute in terms of various physically meaningful processes due, in part, to insufficient information about the different responses of specific mineral/water interfaces during polarization and relaxation.

In the present study, we utilize equilibrium and non-equilibrium classical molecular dynamics simulations to understand the effect of an applied electric field upon the reordering and subsequent relaxation of various model electric double layer/mineral interfaces in slit-pore geometries. This understanding is achieved as a function of pore-width and pore-water chemistry for the (104) calcite and (001) montmorillonite surfaces, which turn out to differ substantially in most cases due to the impact of permanent layer charges on electrical double layer structure and dynamics in the latter.

Session 20

Investigation of Phyllosilicates on Mars through Remote Sensing, Rover Instruments, and Analog Studies

Conveners: Janice Bishop (SETI institute & NASA Ames research center, USA) and Joseph Michalski (University of Hong Kong, China)

SEARCH FOR POSSIBLE AMMONIUM-SMECTITES, IMPLICATIONS FROM CURIOSITY ROVER ON MARS

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Nitrogen is one of the essential elements of life as we know it, due to its incorporation into both amino acids, the building blocks of proteins, and nucleobases, the foundation of DNA and RNA. Nitrogen on present-day Mars has been detected both in the atmosphere and in surface soils in the form of nitrates indicating that nitrogen fixation processes occurred in early Martian history. But little is known about other possible nitrogen reservoirs on Mars, including smectites that may contain reduced NH_4^+ in the interlayer space. The presence of reduced N in the form of NH_4^+ in clay mineral exchange sites would have important implications for the development of a nitrogen cycle on Mars, and therefore Mars' past habitability.

In this work we prepared smectites with NH_4 cations in the interlayer space, namely NH_4-montmorillonite (SWy-2) and NH_4-nontronite (NAu-2). NH_4-smectites were analyzed by X-ray diffraction (XRD), evolved gas analysis mass spectrometry (EGA-MS), pyrolysis gas chromatography/mass spectrometry (GC-MS) and the data were compared with data from instruments onboard the Curiosity rover.

COMPLEX PHYLLOSILICATE - SULFATE ASSEMBLAGES AT MAWRTH VALLIS AS INDICATORS OF THE ANCIENT CLIMATE ON MARS

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Assemblages of phyllosilicates and sulfates at the Mawrth Vallis region of Mars document changing environmental conditions during the ancient Noachian period. Identification and characterization of these minerals is performed through analysis of CRISM hyperspectral images. Fe/Mg-smectite is the most abundant mineral in the Mawrth Vallis region and is frequently observed across Mars. Montmorillonite and allophane are also common at Mawrth Vallis at the top of the clay stratigraphy. We are employing new image calibration and machine learning mineral mapping methods that enable characterization of smaller deposits and weaker spectral signatures. Numerous outcrops containing alunite+halloysite, bassanite, gypsum+opal, jarosite, and polyhydrated sulfates (PHS) are observed at the tens of meters scale (or larger), often in between the transition from Fe/Mg-smectite to Al-rich phyllosilicates. The hydrated sulfates may have formed as evaporites in the channel or by brine percolating through the horizons, whereas the alunite and jarosite likely formed in acidic waters. Alunite occurs commonly together with halloysite and gypsum with opal or hydrated silica.

Smectites typically form in wet/dry cycling environments where water ponds. The smaller outcrops of polyhydrated sulfate (similar to starkeyite) may indicate acidic waters and evaporitic conditions while the smaller outcrops of halloysite may indicate intense wet periods and well-drained systems.

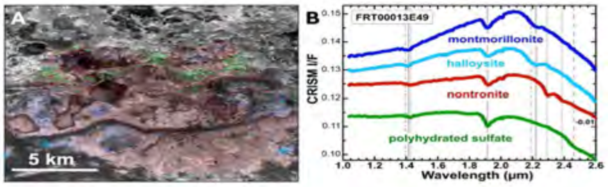

Figure 1. A) CRISM mineral parameters over CTX on an HRSC DTM. Layered units containing nontronite in red, montmorillonite in dark blue, halloysite in light blue, and polyhydrated sulfate in green. B) CRISM I/F spectra of mapped units.

ALTERATION OF SUBAERIAL VOLCANICLASTICS COMPRISING BASALTIC LITHICS AND DACITIC ASH IN SUBAQUEOUS ENVIRONMENTS IN THE SOUTHERN WASHINGTON STATE

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The widespread distribution of various phyllosilicates on the martian surface indicates complex aqueous environments on Mars [1-4]. Understanding how these phyllosilicates formed is key to interpret the early history of Mars, and characterizing terrestrial compositional analogs can assist in providing working hypotheses. In light of the dominance of basaltic deposits on the martian surface [5-6] and the prevalence of Fe/Mg-smectites in phyllosilicate-bearing terrains [1-2], previous analog studies have investigated basaltic materials in various terrestrial environments, including the Columbia River basalts, Hawaiian and Icelandic ones [7-9]. However, evolved volcanic rocks have been detected by orbital studies in the past decades [10-15], and silica-rich volcanic rocks have been found at the Gale Crater by the *Curiosity* rover [16-17]. Recently, diverse volcanism associated with both mafic and felsic volcanic compositions has been discovered around the ~3.5–4-billion-year-old Eridania basin [18], highlighting the need for additional analog studies in a similar context.

The Wildcat Creek beds (WCB), which are in the continental basins adjacent to the Ancestral Cascades Arc in the southern Washington State, record a succession of volcaniclastic facies from various volcanic sources [19]. Detailed lithofacies analyses interpreted that WCB samples are the products of subaerial eruptions (pyroclastic fall or density currents) and subsequently deposited in subaqueous environments [19-20]. The geochemical composition revealed by XRF analysis suggested that the lithics are basaltic to basaltic-andesitic whereas the pumice and ash are dacitic in WCB samples. Preliminary XRD and SWIR analyses revealed the smectite-illite assemblage in subaerial altered products and the chlorite-illite assemblage in subaqueous altered products. The recently discovered suite of diverse volcanic rock is dated to the early-Hesperian to Noachian period [18], during which explosive pyroclastic eruptions were the primary volcanic activity [21 and references therein], and most martian paleolakes were active [22-23]. Therefore, WCB volcaniclastics provide an ideal scenario to conduct analog studies that could shed light on alteration observed on Mars where diverse pyroclastics have likely been deposited in ancient lakes and seas.

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HYDROLYSIS PRODUCTS OF FE(III)-SI SYSTEMS WITH DIFFERENT SI/(SI+FE) MOLAR RATIOS: IMPLICATIONS TO DETECTION OF FERRIHYDRITE ON MARS

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Ferrihydrite, a nanocrystalline iron (oxyhydr)oxide mineral, is widely distributed in soils and sediments on Earth and is probably an important component and/or precursor of widespread nanophase iron minerals on Mars. Terrestrial ferrihydrite often co-occurs with amorphous silica and/or contains a certain amount of Si in its structure. However, it remains ambiguous how environmental Si concentration affects the formation-evolution and structure-spectral features of ferrihydrite in the Fe-Si systems. To this end, hydrolysis experiments were carried out for Fe-Si systems at an unprecedentedly wide range of initial Si/(Fe+Si) molar ratios (0~0.8), followed by characterizing the products detailly. X-ray diffraction, Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, Mössbauer spectroscopy, and transmission electron microscopy results showed that at Si/(Fe+Si) molar ratios ≤ 0.3, the main phase of the products was ferrihydrite, of which the unit cells enlarged, the crystallinity decreased, and the existing state of Fe changed with increased Si contents; at Si/(Fe+Si) molar ratios ≥ 0.4, ferrihydrite was no longer formed and a novel amorphous Fe-O-Si phase was instead obtained, with the excess Si forming amorphous silica. The visible and near-infrared spectroscopy, the most powerful tool to detect hydrous minerals on the surface of Mars at global or regional scales, showed weakness in identifying ferrihydrite-like materials obtained in the Fe-Si systems. Raman spectroscopy can identify ferrihydrite and Si-containing ferrihydrite but cannot differentiate between them. Mössbauer spectroscopy showed great potential in both identifying and differentiating between ferrihydrite and Si-containing ferrihydrite, and thus can be used to characterize the poorly-ordered iron (oxyhydr)oxides on Mars.

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Keywords: ferrihydrite, iron (oxyhydr)oxide, Si, Si-ferrihydrite, spectroscopy, Mars

STRUCTURE DETERMINATION OF SMECTITE

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Smectite is the most abundant group of clay minerals in the Earth's near-surface environment, as well as on the surface of Mars. It plays a crucial role in geological processes such as the enrichment and migration of elements and organics. As a type of natural 2D nanomaterial, it has wide applications in industry.

The weak interlayer bonding of smectite results in complete random layer translations and rotations (known as turbostratically disordered layers), which appear as extremely asymmetric broadened diffraction peaks near the *hk0* positions (e.g., *02l*) in XRD patterns. Traditional methods are unable to accurately quantify and determine their crystal structure.

We used X-ray total scattering technique and pair distribution function (PDF) method, which effectively characterize both long-range and short-range structures, to analyze the local structure of the intralayer. The results show that it consists of coherent crystalline domains with a size of ~24 Å, which closely matches the talc model with triclinic symmetry (Rw=0.037). Furthermore, the interlayer cations and structural -OH of smectite were reconstructed using Material Studio software, followed by density functional theory (DFT) optimization of its crystal structure. Our results reveal that smectite exhibits triclinic symmetry and P-1 space group, with cell parameters: a=5.294 Å, b=9.162 Å, c=12.800 Å, α=90.788°, β=98.345°, and γ=90.399°.

This study provides theoretical support for the quantitative analysis and structural determination of smectite in samples returned from future Mars and asteroid exploration missions.

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MARS LABORATORY ANALOG SEDIMENT FLOWS: INVESTIGATING THE EFFECTS OF PRESSURE AND WATER-ROCK RATIO

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Introduction: Decades of Mars orbital and rover-based observations have provided strong evidence of past transport of sediments by liquid surface water. Most liquid water activity persisted billions of years ago during the Noachian and Hesperian epochs when surface pressures were at a minimum of 100mbar. However, punctuated water events also occurred into the cold and arid Amazonian when surface pressures were decreasing to the ~7 mbar average of today. Previous experimental studies show that < 7 mbar, sediment-water flows (bentonite composition over warm surface) with highwater to rock ratios have processes (e.g., boiling, levitation, grain sputtering) that affect deposit run-out and morphology[1]. Further experimental studies are needed to constrain if these processes are significant for early Mars pressures or sediment-water flows with lower water to rock ratios. This information is important as deposit properties are commonly used to interpret past surface processes and the hydrological history on Mars.

Methods: Our work builds upon previous studies by performing sediment transport experiments of basaltic sediments with varying water-rock ratios at Mars relevant pressures and temperatures. Experiments were run in a pressure chamber at Open University, U.K. where sediment-water mixtures (blended inside chamber) were poured over a 10° inclined test bed of either warm unconsolidated sand or frozen sand to simulate different martian surface conditions. We also varied the chamber pressure (5mbar, 14 mbar, 20 mbar, 500 mbar, 1014 mbar) and temperature (247 K, 293 K), and water-rock ratios (ranging from 30:70 to 80:20). For each run, videos were taken of the flows from a top-down, front-facing, and 45° side-view angle to document their morphological evolution down the test bed. Final deposit morphologies were documented with a DSLR (Digital single-lens reflex) camera, and these images were used to make surface models using the Agisoft Metashape photogrammetry software. The surface models are used to determine deposit morphologies such as volume, slope, and surface roughness.

Results: In this study I note six significant results. In the first result, I obtained similar bubbling and levitation results as Brož et al. 2020a, despite the change in composition to simplified basaltic sediments, that removed the complexity of swelling clays and salts. For the second, both warm and cold bed experiments, there is longer run-out distances for higher water rock ratios. The third result looked at how lower water-rock ratios exhibit thicker deposit morphology. Furthermore, the thickness is more pronounced in cold bed experiments. In the fourth result we see that the boiling process produces bubbling and levitation behavior that only occurs in experiments with pressures of 14-mbars or lower. The fifth result relates to how increasing pressures exhibit a bimodal distribution for length-width ratio values, and the sixth result shows that at lower pressures the quantity of lobes increases.

In conclusion, results from this study provide a framework for characterizing martian sedimentary deposits and landforms that formed under varying pressure and temperature conditions. This framework is necessary for constraining Mars' paleohydrology, climate, and the potential for habitability.

1 P. Brož et al., "Experimental evidence for lava-like mud flows under Martian surface conditions," Nat. Geosci., vol. 13, no. 6, pp. 403–407, Jun. 2020, doi: 10.1038/s41561-020-0577-2.

LAVA-BAKED CHEMICAL WEATHERING OF PYROCLASTICS DEPOSITS IN TENGCHONG VOLCANIC FIELD, SOUTHWEST CHINA – IMPLICATIONS TO MARS EXPLORATION

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Remote sensing exploration of Mars has reveals thousands of clay deposits on its ancient surface, indicating past aqueous activity. Ubiquitous clay minerals was capped by dark mafic unit. The mafic cap unit shows rugged and massive appearance, with meter-scale boulders, which might support the volcanic origin. The interactions between hot lava flow and hydrated clay minerals remain enigmatic. Such scenarios are likely to frequently occur on early Mars. There are several key questions: (1) How does it alter the mineral and chemical composition? (2) How does this transformation affect our interpretation of the climate of early Mars? (3) How deeply does the thermal "baking" effect of hot lava penetrate into the wet, cold saprolites, which is particular crucial when searching for biosignatures on Mars. Here, we investigate the mineralogy, spectroscopy and geochemistry of 2 m thick lava-baked chemical weathering pyroclastic deposits in Tengchong, southwestern China to understand the mineralogical and chemical transition from top to the bottom, the timing and the duration of clay formation.

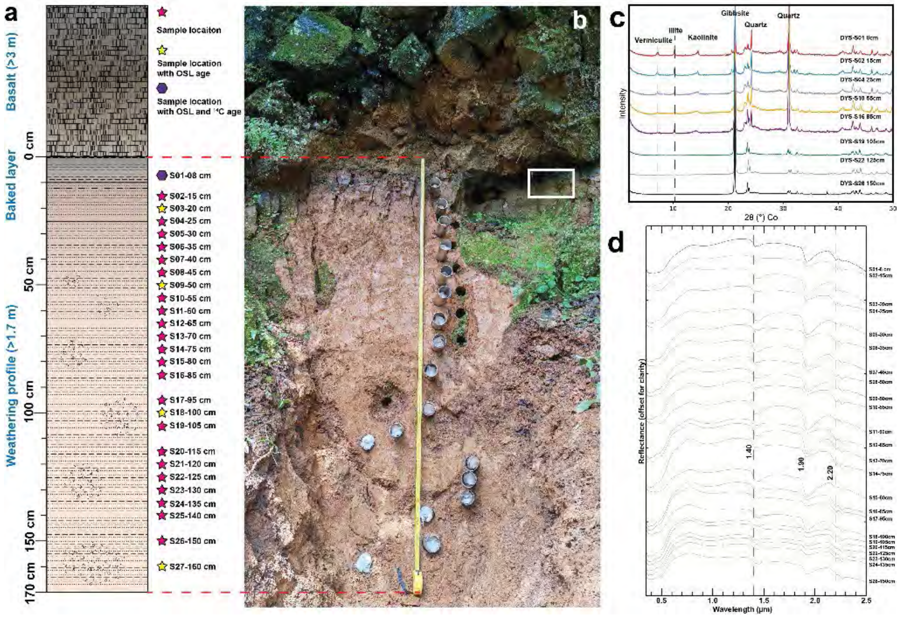

Figure 1. (a) A stratigraphy column of Tengchong weathering profiles and the field photo of the profiles (b). (c) Bulk powder XRD scans of Tengchong weathering profiles samples. (d) Visible and near infrared reflectance spectra (350-2500 nm) of Tengchong weathering profiles samples.

Session 21

Characterization of Phyllosilicates and Their Mineral Assemblages in Asteroids and Meteorites

Conveners: Marco Ferrari (Istituto di Astrofisica e Planetologia Spaziali - INAF, Italy), Toru Yada (Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, Japan), Damien Loizeau (Institut d'Astrophysique Spatiale(IAS), France), Slavka Andrejkovicová (University of Aveiro, Portugal), Janice Bishop (SETI institute & NASA Ames research center, USA)

CHARACTERIZATION OF NH_4^+-SMECTITES TO SUPPORT THEIR DETECTION ON CERES AND OTHER BODIES

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Remote sensing of the dwarf planet Ceres and other asteroids has observed spectral features due to NH_4^+ associated with phyllosilicates. We have collected reflectance spectra of a large suite of NH_4^+-treated smectites in order to characterize these spectral bands for comparison with spectra of Ceres, Ryugu, Bennu, and other planetary bodies. The spectral properties of these NH_4^+-smectites vary depending on the environmental conditions during measurement. Our experiments indicate significant reduction in the hydration features and enhancement of the NH_4^+ features for spectra of ammoniated smectite measured under dry air or vacuum conditions.

NH_4^+ bands are observed in spectra of our samples at 1.55, 2.00-2.02, 2.11-2.13, 3.05-3.06, 3.29-3.30, and 3.52-3.54 μm. The NH_4^+ bands near 2.12 and 3.06 μm are the strongest and would be easiest to detect in spectra acquired of planetary bodies. The band near 3.06 μm currently has had the best coverage in spectral data of asteroids and is similar to features observed at Ceres. Serpentines, carbonates, and hydrocarbons are also observed on Ceres, but the NH_4^+ bands appear to be connected to smectites there.

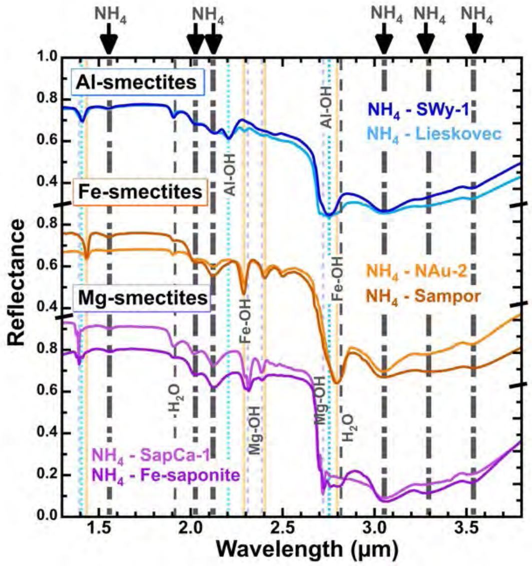

Figure 1. Reflectance spectra measured under dry air conditions from 1.3-3.8 μm of several NH_4^+-smectites from our study. Two examples are included for smectites with Al, Fe, or Mg in octahedral cation sites. Spectral bands due to NH_4^+, H_2O, Al-OH, Fe-OH, and Mg-OH are marked with different line types. The position of the NH_4^+ bands shift only slightly with the type of octahedral cation.

MULTI-TECHNIQUE STUDY OF THE COEVOLUTION OF PHYLLOSILICATE, CARBON, SULFIDE, AND APATITE IN RYUGU'S PARENT BODY

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We analyzed an asteroid Ryugu sample returned to Earth by JAXA's Hayabusa2 mission using nanoIR, SEM, and TEM microscopy. We identified multiple distinct carbon reservoirs within the phyllosilicate matrix and demonstrate infrared spectral affinities for some of the carbon to IOM. TEM studies of Ryugu samples have allowed us to better understand the interrelationship between the crystallographic orientiations of phyllosilicates and secondary minerals such as carbonate, sulfide, and apatite. Transport of elements provides a unifying theme for understanding these interrelationships.

Figure 1 summarizes the results from a multi-technique approach to understanding asteroid clay materials. We will discuss our results in more detail at the conference.

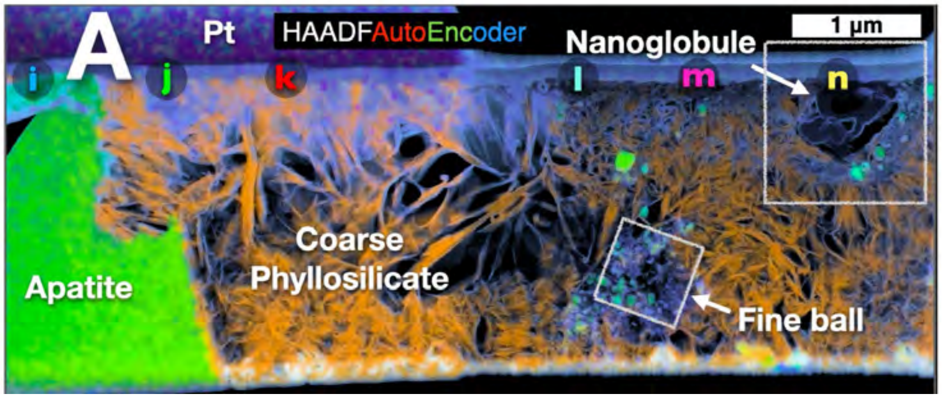

Figure 1. Autoencoder neural network phase map of a FIB section pulled out of Ryugu sample. Apatite and sulfides are green, phyllosilicates in orange, carbonaceous material is blue. A Nanoglobule and 'fine ball' are outlined. Positions of NanoIR spectra (i-n) taken are indicated with letters. Figure taken from Gainsforth& Dominguez et al., in press.

MULTI-ANALYTICAL INVESTIGATIONS OF TWO RYUGU PARTICLES

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The JAXA/Hayabusa2 mission collected samples from the surface of the C-type asteroid (162173) Ryugu [1]. The Ryugu surface spectra collected reveal a narrow absorption feature at 2.72 µm [2] resembling that observed on the surface of Ceres [3]. Laboratory analysis of returned grains revealed the presence of hydrated silicates, sulfides, oxides, carbonates, and organics, displaying a close compositional match with the chemically unfractionated, but aqueously altered, CI chondrites [4].

With this work, we aim to characterize two returned grains (C0091 and A0198) contributing to defining the physical and mineralogical characteristics of the asteroid Ryugu and understanding the formation and evolution of the C-type bodies.

The VIS-IR spectra obtained on the two particles show the almost ubiquitous presence of a deep V-band centered near 2.7 µm. In addition, absorptions near 3.4 µm and in the range 3.7-3.9 µm are detected in specific positions, returning an inhomogeneous surface composition. These features can be separately related to the presence of phyllosilicates, carbonates, and organics. Furthermore, on distinct points, the band at 3.06 µm indicates the presence of NH_4-bearing compounds. The µ-Raman spectra are characterized by the occurrence of the D and G-bands related to the presence of poorly ordered carbonaceous matter. Raman analysis identifies dolomite and calcite as the most common carbonates on both particles. EDX data confirmed the presence of hydrated silicates, sulfides, carbonates, phosphates, and oxides. The internal distribution of silicates, sulfides, and oxides in the interior of the two samples, as revealed by XRM data, is rather homogeneous. TEM/EDS and 3D Electron Diffraction investigations show that the matrix is mostly made of phyllosilicate flakes, with composition in-between serpentine and saponite, and amorphous carbonaceous matter. Sulfides, magnetite, apatite, and other minerals typical of low thermal alteration were also observed. Overall, the whole assemblage appears significantly porous.

Currently, our multi-analytical investigation highlights that the two grains are characterized by a generally similar composition and similar phase abundances. To date, interpretation of remotely sensed data coupled with spectroscopic investigation of analogs has not enabled a full understanding of the mechanisms of aqueous alteration and the mineral assemblage of C-type objects. For this reason, spectroscopic measurements, and nanoscale mineralogical investigations on Ryugu returned samples represent a unique chance to definitively understand these processes.

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SPECTRAL VARIABILITY IN CM CHONDRITE MATRICES

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CM (Mighei-type) carbonaceous chondrites are the most abundant hydrated phyllosilicate-bearing meteorites, and infrared (IR) spectroscopy studies have established them as some of the best spectroscopic matches to C-complex asteroids, including recent mission target Bennu. Lab-based IR studies focused on bulk spectra of individual meteorites have suggested links between bulk chemical/mineralogical indicators of aqueous alteration and spectral properties [1-3]. However, recent attention has been drawn to the observation that many CM chondrites are lithologically heterogeneous breccias [4]. Consequently, isolating and characterizing the spectral properties of individual clasts in CM breccias *in situ* is an important step to clarify the relationship between chemical/mineralogical and spectral changes associated with progressive aqueous alteration in CM chondrites (and related asteroids) to determine whether matrix or chondrules drive spectral properties and the specific mineral phase(s) responsible.

We have characterized spectral variations in interchondrule matrix (hereafter called 'matrix') for different CM lithologies from Nogoya (CM2.2-2.5 [4]) and Murchison (CM2.7 [4]). Backscatter electron (BSE) imaging and spatially resolved FTIR analyses at ~100um/spot were employed, and measurements for quantitative chemistry from EPMA maps are ongoing.

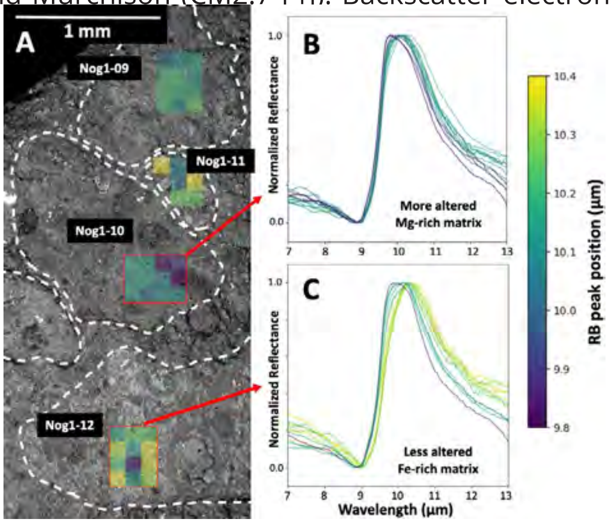

Figure 1. A) BSE image with overlain matrix RB maxima variability for FTIR spot measurements of clasts in Nogoya. Spectra shown for a B) more-altered and C) a less-altered CM lithology. RB maxima at longer wavelengths appear to spatially correlate with increased Fe-content in phyllosilicate matrix as evidenced by higher BSE contrast.

We observe spot-to-spot variation in the 3-μm metal-OH/H_2O absorption feature between 2.71 and 2.76 μm and the Si-O stretch (Reststrahlen band, RB) maximum between 9.8 and 10.5 μm. This generally correlates with the alteration state of the clast, which we have initially inferred by the BSE contrast of matrix regions [4]. While the position of the 3-μm feature in CM chondrite bulk spectra has been linked to the Fe/Mg content of matrix phyllosilicates [1], variation in the position of RB in bulk spectra has mainly been attributed to the relative abundance of anhydrous silicates (primarily in chondrules) versus matrix phyllosilicates, with RB maxima at higher and lower wavelengths respectively [2, 3]. However, our results reveal significant RB variation within matrix regions, indicating that phyllosilicate chemistry influences the position of the RB maximum (Fig. 1). As these values span the range of those previously reported for bulk CM meteorite spectra [e.g., 3], variations in phyllosilicate Fe-Mg site occupancy associated with aqueous alteration [5], may play a more important role in the bulk spectral properties of CM chondrites than is currently appreciated. We will describe the co-variation in 3-µm OH stretch, RB Si-O stretch, and EPMA measured chemical composition of different clast matrices with implications for the interpretation of asteroid spectra.

[1] Takir D., et al. (2013). *Meteorit. & Planet. Sci., 48*, 1618-1637. [2] McAdam M. M., et al. (2015). *Icarus*, *245*, 320-332. [3] Hanna, R. D., et al. (2020). *Icarus*, *346*, 113760. [4] Lentfort, S., et al. (2021). *Meteorit. & Planet. Sci.*, *56*, 127-147. [5] Rubin A. E. et al. (2007). *Geochim. et Cosmochim. Acta*, *71*, 2361-2382.

MICRO-FT-IR HYPERSPECTRAL SURFACE CHARACTERIZATION OF INDIVIDUAL RYUGU GRAINS: MATRIX COMPOSITION AND SPACE-WEATHERING EFFECTS.

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Sample-return space missions allow us to investigate materials from outer space with state-of-the-art laboratory techniques [1]. Constraining the material mineralogical and physical properties enables us to better understand their parent bodies' history and our Solar System [2, 3]. JAXA's Hayabusa2 mission [4] acquired spectroscopic data and samples from primitive body C-type asteroid Ryugu. Samples originate from two collect sites (A: surface, C: presumably sub-surface). Here, we look for spectral differences across the surface of individual grains to assess mineralogical differences and identify possible effects of space weathering (i.e., an ensemble of processes affecting the surface of airless bodies, which alters their surface spectral, elemental, and morphological properties [5]). Our samples comprised three mm-sized grains (two samples from site A and one from site C): A0226-1, A0226-2, and C0242 [6]. Grain A0226-2 separated from A0226-1. We characterized the samples' surface via micro-FT-IR hyperspectral imaging in the mid-IR (2-16 μm) to probe the spatial distribution of phyllosilicates, anhydrous phases, and organic matter.

The investigation is currently ongoing. A widespread hydrated silicate phase dominates the surface matrix, dotted with carbonates. We see no significant spectral variations at the scale of the individual grain for A0226-1 and C0242. However, fragment A0226-2 showed a localized region exhibiting spectroscopic features with a slight red-shift in peak position (+7 nm for the 2.7 μm hydration feature, +40 nm for the 10 μm silicate feature), accompanied by a decrease in band area and an increase in bandwidth to the average spectrum of A0226-2. These spectral changes are compatible with those induced by solar-wind ion implantation from space weathering [7, 8]. The accidental detachment of A0226-2 from A0226-1 may have exposed fresh surfaces from the grain's interior, allowing us to investigate weathering effects across the surface of an individual grain. Supplementary analysis will be led at a smaller scale using field-emission scanning electron microscopy to probe elemental and morphological differences related to space weathering on an individual grain.

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IMPORTANCE OF INFRARED SPECTROSCOPY ON SAMPLES RETURNED FROM EXTRATERRESTRIAL BODIES AS THEIR INITIAL DESCRIPTIONS

Yada, T.*[1], Abe, M.[1], Okada, T.[1], Pilorget, C.[2], Hatakeda K.[3], Nishimura, M.[1], Yogata, K.[1], Miyazaki, A.[1], Nakato, A.[1,4], Sakamoto, K.[1], Kumagai, K.[3], Loizeau, D.[2], Lourit, L.[2], Hamm, V.[2], Brunetto, R.[2], Riu, L.[1,2], Bibring, J.-P.[2], Tachibana, S.[1,5], and Usui, T.[1],

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Celestial bodies in the Solar System have been investigated for their infrared reflectance spectra, to estimate minerals and materials on the bodies. For example, hydroxyl (-OH) and interlayered water in phyllosilicates are responsible for 3 μm absorption features observed in C-complex asteroids. Absorption centers of lizardite, saponite to antigorite and cronstedtite are shifted from 2.71 toward 2.85 μm, which result in various kinds of broad absorption features around 3 μm in hydrous carbonaceous chondrites [1].

Samples returned from asteroids by space missions such as Hayabusa, Hayabusa2, and OSIRIS-REx are available for researchers in these years, which give us opportunities to study pristine asteroid samples without terrestrial contamination and alteration [2-5]. During the rendezvous of the spacecrafts at their target bodies, infrared reflectance spectroscopy has been carried out to identify what kinds of minerals and materials exist on their surfaces [6, 7]. In order to confirm the representativeness of the surfaces of their bodies, it is essential to analyze infrared reflectance spectra for bulk samples returned from the surface of the bodies. As for Hayabusa2, Ryugu samples are handled in the nitrogen-filled clean chambers, and two types of infrared spectrometers are equipped there: an FT-IR Jasco VIR-300 and a hyperspectral microscope MicrOmega, which is a similar type of instrument as the one on the MASCOT lander deployed from the Hayabusa2 spacecraft [8]. Using these instruments, infrared reflectance spectra of bulk Ryugu samples have been analyzed as initial descriptions to be figured out if these spectra are consistent with those of the global Ryugu surface obtained by NIRS3, an onboard infrared spectrometer of the Hayabusa2 [3, 4, 6]. This also indicates that Ryugu samples are mainly composed of phyllosilicates including hydroxyl (-OH), which is confirmed by XANES and TEM analyses on Ryugu samples [9-13].

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Session 22

Remote Identification of Phyllosilicates for Critical Metals Exploration and Resource Characterisation

Conveners: Carsten Laukamp, Commonwealth Scientific and Industrial Research Organisation (CSIRO), Perth, Australia, Ian Lau, Commonwealth Scientific and Industrial Research Organisation (CSIRO), Perth, Australia, Rui Wang (Institute of Earth Sciences, China University of Geosciences in Beijing (China), Janice Bishop (SETI institute & NASA Ames research center, USA)

PRELIMINARY RESULTS OF USING NEAR-INFRARED SPECTROSCOPY FOR SMECTITE QUANTIFICATION IN NATURAL MIXTURE

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Infrared spectroscopy (IR) is an inexpensive and fast method for identifying and quantifying mineral phases in different mixtures[1,2]. This research was carried out to identify the smectite's spectral signatures and percentage abundances in natural bentonite samples using Near-Infrared spectroscopy (NIR). Twenty natural bulk samples were collected from the Bartošova Lehôtka bentonite deposit in central Slovakia and pulverized to less than 250 micrometers in size. Reflectance spectra were measured using an ASD FieldSpec 4 Hi-Res spectroradiometer, which operates in the wavelength range between 350 nm (28571 cm^{-1}) and 2500 nm (4000 cm^{-1}). This study involved an analysis using two different sample spectra as endmember components, the former spectra were from pure smectite samples (>95% montmorillonite), while the latter represented the opposite endmembers and were from a sample containing over 85% non-clay minerals, such as feldspars (~50%), opal C/CT (~20%), quartz (~5%), mica (>5%), and others. The Semi-Supervised Linear Spectral Unmixing method (SSLSUx) was applied to determine the proportion of smectite associated with the non-clay phases in natural multicomponent mixtures[3,4].

As a result, the applied model was capable to generate accurate estimates for the abundance of smectite and non-clay from the mixture, mainly within ~15% variation of the abundances calculated by QXRD. The NIR linear spectral unmixing quantification method provided more accurate estimates than the CEC method and were even closer to the estimates achieved by QXRD. Moreover, the estimates for the mathematically generated and controlled models for mixtures with multiples of ten ratios (e.g., 10, 20, 30...90% smectite + non-clay mixture) were even more precise, within ~5%. To further improve the model's accuracy and assess the computed mixtures, the researchers plan to prepare natural mixtures of these hypothesized spectra and refit them to the calculated model using the supervised linear spectral unmixing method with identified endmembers and abundances.

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REGIONAL-SCALE MAPPING OF PHYLLOSILICATES USING THE NEW GENERATION OF VNIR-SWIR HYPERSPECTRAL SATELLITE SENSORS

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The latest generation of optical satellite sensors that collect reflectance spectra from across the visible-near infrared (VNIR, 380 to 1000 nm) and shortwave infrared (SWIR, 1000 to 2500 nm) wavelength region at hyperspectral resolution enable the regional-scale mapping of phyllosilicates at unprecedented detail. Typically, these new satellite hyperspectral sensors have a spectral sampling interval of about 10 nm in the SWIR, at a pixel size of 30 m, such as in the case of PRISMA (www.asi.it/en/earth-science/prisma/) and EnMap (https://www.enmap.org/), or 60 m for EMIT (https://earth.jpl.nasa.gov/emit/). The high spectral resolution across the SWIR allows the identification of combinations of the bending and stretching fundamentals of hydroxyl groups, which produce diagnostic spectral signatures of Al-phyllosilicates (e.g. kaolin, white mica, Al-smectite, pyrophyllite) as well as Fe-Mg-phyllosilicates (e.g. chlorite).

This paper provides examples of mapping the relative abundance, compositional variation and crystallinity of Al-phyllosilicates across geological provinces from the regional to kilometer-scale, describing its geological significance and application for critical metals exploration. For example, simple three-band ratios that target the relative depths and wavelength positions of major absorptions centered at around 2160 and 2200 nm are combined to infer the relative abundance and crystallinity of kaolinite, which supports the classification of in-situ versus transported regolith. The regolith classification helps with the identification of shallow regolith and potential sub-cropping areas, but also improves delineation of catchment areas. In greenstone belts of the central and eastern Pilbara craton (Western Australia), an elevated pyrophyllite abundance is highlighted by pixels with the strongest 2160 nm absorptions, providing insights into the extent of Archean hydrothermal alteration patterns that are potentially associated with mineral deposits.

The comparison of mineral maps derived from the satellite hyperspectral imagery with earlier developed mineral maps processed from multispectral satellite imagery (i.e. ASTER) shows that the higher spectral resolution of the new sensors also increases the level of confidence when assigning pixels to the respective mineral groups. Therefore, masking thresholds in the band ratio decision tree can be relaxed, improving the coverage of classified pixels. This is important for both the recognition of regional mineral patterns that are only retrievable from the SWIR, but also the identification of important critical metal host rocks, such as pegmatites, down to the tenement-scale.

USING AIRBORNE AND ORBITAL IMAGING SPECTROSCOPY TO DIFFERENTIATE LITHIUM BEARING HECTORITE FROM SPECTRALLY SIMILAR PHYLLOSILICATES AND CARBONATES

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Lithium has been designated as a critical mineral by the U.S. Geological Survey (USGS) due to its importance to the United States economy and over-all risk to supply. The Airborne Visible/InfraRed Imaging Spectrometer (AVIRISc) and the Earth Surface Mineral Dust Source Investigation (EMIT) imaging spectrometer, currently deployed on the International Space Station, are being used to identify and characterize potential new sources of lithium on Earth. Challenges exist, however, in mapping lithium bearing mica deposits using remotely sensed data, including similarity in spectral features among certain phyllosilicates and carbonates.

Spectral-based mineral maps generated using expert systems such as the USGS's Mineral Identification and Characterization Algorithm (MICA) and Tetracorder use spectral feature matching of diagnostic absorption features to identify the spectrally dominant mineralogy in each pixel of an imaging spectroscopy data set. Hectorite (a Li-bearing smectite), saponite (a non-Li bearing smectite), and sepiolite and vermiculite (non-Li bearing phyllosilicates) have a primary absorption in the shortwave infrared (SWIR) centered near 2.31 μm caused by a combination of the OH stretch and octahedral cation (primarily Mg^{2+})-OH bend fundamental absorptions and a secondary feature centered near 2.39 μm. Magnesium carbonates (e.g., magnesite) also have a primary SWIR absorption feature near the 2.31 μm position but lack a 2.39 μm feature. Around McDermitt caldera, NV, use of both the primary and secondary features in Tetracorder applied to EMIT data was not successful in detecting known hectorite occurrences. MICA analysis using only the 2.31 μm feature was able to map distributions of hectorite, however, with some confusion with these other spectrally similar minerals. For AVIRISc data covering a hectorite mine near Hector, CA, we found that the single feature approach, using only the primary absorption, was able to identify hectorite without significant false positives for saponite, sepiolite, vermiculite, and magnesite. In this contribution, we elaborate on these findings.

GEOSCIENCE FEATURE-GUIDED BAND MATH APPROACH FOR EMIT AND ENMAP HYPERSPECTRAL SATELLITE IMAGERY

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Traditionally, remote sensing for geological- and mineral-mapping in exploration has often been supported by satellite-based multispectral sensors, or deposit-scale drone or airborne surveys. Since 2019, global imagery acquired by the Italian Space Agency PRISMA hyperspectral satellite allows for low-cost regional-scale assessments that cover a range of geoscience applications. Since then, NASA's EMIT and DLR's EnMap hyperspectral satellite sensors are additionally contributing towards continental-scale coverage that can provide significant information on both the regolith and minerals outcropping on Earth's surface.

We adapt a feature-guided band math method initially designed for PRISMA products, to ENMAP and EMIT imagery in the prospective Gifford Creek area of the Gascoyne region of Western Australia. Here, the PRISMA, EnMap and EMIT hyperspectral satellite sensors all acquired imagery over the same region between September 2023 – March 2024. Using ENVI version 6.0, we identify diagnostic wavelength locations specific to each sensor and utilise band math to measure their intensities to map mineral indexes and compositions for regolith mapping and to further critical metals exploration.

This study demonstrates how a range of mineral- absorption features and regolith-diagnostic subsequent products can be created regardless of hyperspectral satellite sensor acquisition. We highlight the mosaicking potential of imagery acquired by different hyperspectral satellites to derive low-cost regional- and continental-scale mapping to aid mineral exploration at a scale that has been limited until now.

Session 23

General session

Conveners: Yuji Arai, University of Illinois at Urbana-Champaign; Joseph W. Stucki, University of Illinois at Urbana-Champaign

CHEMICAL COMPOSITION ANALYSIS OF WHITE AND CELADON CLAYS USING PORTABLE X-RAY FLUORESCENCE ANALYSIS: A COMPARATIVE STUDY OF CERAMICS EXCAVATED FROM HIRAIZUMI AND CHINA

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The Hiraizumi Cultural Heritage Site was inscribed on the World Heritage List in June 2011. In Hiraizumi, a medieval city from the late 10th to the 12th century, Chinese ceramics have been excavated in significant quantities. According to archaeological research and visual observation, the Chinese ceramics are estimated to be mainly white porcelain from southern China's Guangdong and Fujian provinces, blue and white porcelain from the Jingdezhen kiln, and celadon from the Longquan kiln. In this study, ceramic shards excavated from Hiraizumi and southern China were analyzed using a portable X-ray fluorescence analysis (XRF) to estimate their provenance comparing by their chemical composition analysis of base clays. Clarification of these results will elucidate the production, distribution, and consumption of ceramics from southern China. It will also reveal the influence of kiln systems and production techniques on the history of the ceramics, as well as the process of transmission and diffusion.

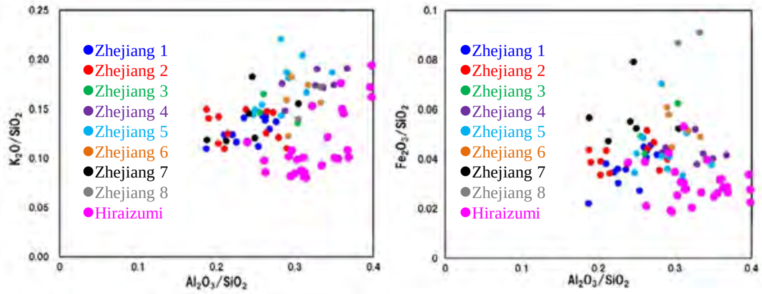

Fig. 1 Relationships between the main components analysis of clay excavated from Hiraizumi and Zhejiang province.

Portable XRF (DF-01, Riken Keiki) was used to measure the samples. X-ray used for the measurements was Cr*K*α (35 kV, 0.8 mA). X-rays were irradiated at a distance of 0.5 cm from the tip of the capillary to the sample. High-sensitivity measurements were performed by distributing high-purity helium gas from the capillary to the sample to allow analysis of low-sensitivity elements in an air atmosphere. Quantitative analysis was performed using the fundamental parameter method installed in the measurement software. The target elements were Al, Si, K, Ti, Fe, Ca, and Mn, and the results were estimated to an oxide concentration.

Figure 1 shows the relationships between the main components analysis of the clay excavated from Hiraizumi and Zhejiang province. SiO_2, the main element in the clay of the celadon, is 68-71%, which falls into the category of celadon excavated in Zhejiang province. The content of Al_2O_3 is 17-23%, K_2O is 5.5-8.2%, and Fe_2O_3 is 2.8-3.6%. There is a large overlap in these compositions between the two regions. On the other hand, the main elements of white porcelain excavated from Hiraizumi are 60-72%

SiO_2, 20-27% Al_2O_3, 5.5-12% K_2O, and 1.3-2.4% Fe_2O_3. There is a difference in the width of SiO_2 and Al_2O_3 between white porcelain and celadon, and there is also a noticeable difference in Fe_2O_3. Fe_2O_3 content in the Hiraizumi sample tends to be lower than that in the Zhejiang sample, suggesting that it is affected by the composition of the clay used to make the base clay. Fe_2O_3 content was affected by the addition of iron-rich Zijin clay.

EFFECTS OF PCO$_2$ ON HYDROXYAPATITE FORMATION AND ITS SOLUBILITY

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Hydroxyapatite is an important phosphorus (P) sink in calcareous soils. The activity of carbonate in soil pore water, however, is often underestimated because soil respiration and solution-calcite equilibria could elevate pCO$_2$ much greater than 415 ppmv. Thus far, the role of pCO$_2$ in the hydroxyapatite formation in calcareous soils has not been extensively investigated. Accordingly, the effects of pCO$_2$ (415, 8000, and 20,000 ppmv) on hydroxyapatite formation and stability were investigated at pH 8 using experimental geochemistry, Scanning Electron microscopy (SEM), and X-ray diffraction (XRD) analysis. X-ray diffraction (XRD) analyses showed hydroxyapatite under all pCO$_2$ values and Ca/P ratios (10, 50, 100), and the content of calcite increased with increasing pCO$_2$. The formation of calcium carbonate phosphate was also observed after 30d under pCO$_2$ up to 8000ppm. This is attributed to decreased calcium (Ca) activity and an increase in calcium carbonate formation. In a few reaction conditions, ikaite and calcium hydroxide were observed. Scanning Electron microscopy (SEM) showed rounded particles of hydroxyapatite in all samples regardless of pCO$_2$ and aging times. Hydroxyapatite synthesized at the Ca/P ratio of 10 under pCO$_2$ of 415 ppmv after 30 days was used for the dissolution experiments under pCO$_2$ = 415, 2,075 and 4,150 ppmv). The results showed that higher pCO$_2$ values facilitated the release of P from hydroxyapatite, suggesting the carbonate ligand-promoted dissolution mechanism. The variability of pCO$_2$(g) should be considered to better predict P solubility in calcareous soils.

RANDOM FORESTS FOR PHASE SELECTION IN X-RAY POWDER DIFFRACTION ANALYSIS OF MINERAL MIXTURES

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One of the main issues that contributes to poor results in quantitative phase analysis (QPA) of mineral mixtures using X-ray powder diffraction (XRPD) is that novice analysts often select incorrect phases to include when modeling an experimental diffraction pattern. One reason for this is that they do not know which phases are common v. rare, or which phases commonly occur together—knowledge that an expert analyst would be more likely to have (or at least know where to look up). This type of problem—for which accurate solutions cannot be obtained via a straightforward algorithm—is often tractable using machine learning (ML) approaches, as long as there is sufficient data to simulate missing expert knowledge.

To address this, we generated a database of 1.5 million simulated XRPD patterns and major element analyses of realistic mineral mixtures that included 86 minerals, for which experimental XRPD patterns were taken from the RockJock database. The simulated mixtures were generated by 1) randomly choosing a location from the Mineral Evolution Database (MED), 2) randomly choosing a number of phases to include between 2 and 15, 3) randomly selecting (at most) that many phases from among those that appeared at the selected location and were among our 86 target minerals, 4) randomly selecting a crystal structure for each phase from a set taken from the American Mineralogist Crystal Structure Database, 5) randomly selecting phase fractions that sum to one, 6) randomly selecting peak shape parameters from distributions obtained by fitting the experimental XRPD patterns, and 7) generating both simulated XRPD patterns and major element analyses from theory.

We then used balanced subsets of this data to train random forest ML models to detect the presence or absence of each mineral. These models were very successful, achieving >90% accuracy for all minerals when trained on both simulated XRPD and major element concentration data.

CATALYTIC MECHANISM OF COBALT-CONTAINING LAYERED DOUBLE HYDROXIDES FOR CARBON NANOTUBE SYNTHESIS

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Layered double hydroxide (LDH) is applied as a catalytic precursor for carbon nanotubes (CNTs) synthesis. In previous studies, large amounts of CNTs could be synthesized by using Co-containing LDH (Co-LDH) as a catalyst precursor, with Co as a catalytic active point. However, the synthesized CNTs produced multi-wall CNTs (MWCNT) including amorphous carbon. Smaller metal particle formed by the reduction treatment during CNT synthesis could enable the synthesis single-wall CNTs (SWCNT). In this study, the synthesis of Co-Mg-Al LDH by the hydrothermal (HT) method and homogeneous precipitation method using urea (UR) as precipitant with controlled Co content to smaller catalytic active point and the effects of LDH composition on the diameter and crystallinity of CNTs were investigated.

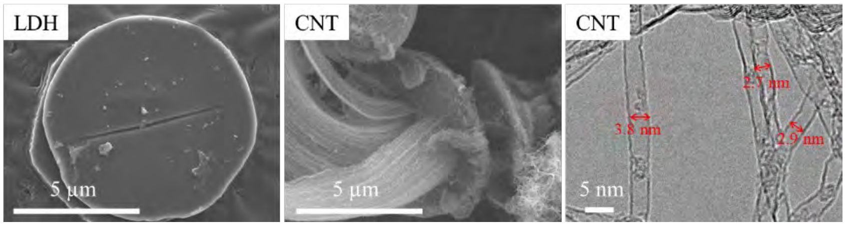

Fig. 1 SEM and TEM images of CNTs synthesized using Co-Mg-Al LDH-UR as a catalyst precursor.

Co-Al and Co-Mg-Al LDH were prepared by the HT and UR method. The CNT synthesis at 750°C by water-assisted chemical vapor deposition (CVD). The reduction treatment of Co-LDH was performed under hydrogen atmosphere.

The XRD pattern of Co-LDH revealed that it has a stacking structure derived from the LDH structure. The SEM-EDS mapping images reveal that the hexagonal platelet crystals are composed of Co in the central part and Mg in the outer part. This result is attributed to the formation of Co-Al LDH first at about pH 7.0, followed by the formation of Mg-Al LDH after the pH increased to pH 9.0. The synthesized Co-Mg-Al LDH was used as a catalyst precursor to synthesize CNTs (Fig. 1). The synthesized CNTs were SWCNT with a diameter of 4 nm or less. This is thought to be due to the decreased Co content, which reduced the catalytic active site and enabled the synthesis of CNTs with a smaller diameter. Furthermore, the analysis of Co-LDH after the reduction treatment during CNT synthesis. The XRD pattern derived from the LDH stacking structure disappeared, and the reflections derived from metallic Co appeared. The SEM and TEM images revealed that the plate-like crystals were maintained and only Co was present in particulate form. These results indicate that Co particles are formed from the basal layer of LDH by the reduction treatment and act as a catalyst for CNT synthesis.

The Co-LDH catalyst precursors were found to catalyze CNT synthesis, and this method has successfully produced SWCNT.

ATR-FTIR SPECTROSCOPY AS A COMPANION TECHNIQUE TO RANDOM-MOUNT XRPD FOR DETERMINING CLAY MINERAL IDENTITIES AND PROPERTIES

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Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR) is a vibrational spectroscopic technique that has widespread applications because of its ability to quickly return reproducible results, with little sample preparation and small sample sizes, to users with varying degrees of experience. While X-Ray Powder Diffraction (XRPD) is more typically used for inorganic mineral phase identification and quantification, we are developing protocols to use ATR-FTIR as a companion technique for identifying minerals that are difficult to distinguish from one another using random-mount XRPD. Some examples might include differentiating clay minerals based on cation occupancy of di/trioctahedral sites, and the behavior of hydroxyl groups.[1]

To date, we have developed sample preparation procedures to achieve highly reproducible spectra between runs and have begun attempting to quantify dilution and interparticle effects on spectra.

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STANDARDIZATION OF CLAY NANOPLATE PRODUCTS FOR BARRIER FILM APPLICATIONS

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Various approaches can be taken to improve barrier properties in the plastics films. There is a method of adding clay nanoplates to plastic to make nanocomposites. The high gas barrier phenomenon is described in the tortuous effect. Various clay products are sold such as, smectite, talc, kaolinite, mica, etc. Among them, products having a high aspect ratio and high affinity with the plastic is preferably used.

ISO/TS 21236-2: Nanotechnologies – Clay nanomaterials – Part 2: Specification of characteristics and measurements for clay nanoplates used for gas-barrier film applications specifies the characteristics to be measured of clay nanoplate and specifies industrially available measurement methods used to determine these characteristics. In addition, measurement protocols are described. It provides a sound basis for the research, development, and commercialization of clay nanoplate materials for application of barrier films for water vapor and dry gases.

Required characteristics of clay nanoplate samples for measurement or identification are mineral composition content, chemical composition content, cation exchange capacity, particle size, and loss on ignition. Among these characteristics, we were able to establish an analysis method that yields stable analytical values within a certain deviation, except for the mineral composition. On the other hand, there are concerns regarding mineral composition analysis using X-ray diffraction, such as the presence of amorphous materials and the accuracy of smectite quantification.

Recommended characteristics are methylene blue adsorption capacity, aspect ratio, film formability, and viscosity. Users of clay nanoplate products need to check the characteristic data described in the catalogue. Film formability is not only an important characteristic value for improving the clay content of the film, which is effective in improving gas barrier properties, but also relates to the orientation structure of nanoplates, which is a preferable structure for gas barrier films. Film formability is evaluated by visual observation of samples prepared by solvent casting. In general, smectite containing monovalent cations such as sodium and lithium as interlayer ions has good film formability.

An analysis report based on ISO/TS 21236-2:2021 will help you select clay nanoplate products suitable for gas barrier films. Round-robin tests are being conducted using representative product samples, brush up our evaluation methods, and reflect these in the systematic review process of ISO/TS 21236-2:2021, as well as build a product certification.

ASSOCIATION RULES FOR IMPROVED QUANTITATIVE PHASE ANALYSIS

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Quantitative phase analysis (QPA) of whole rocks and sediments using X-ray powder diffraction (XRPD) is a standard, workhorse technique for many types of geologists and soil scientists, and there are a number of methods for accomplishing this. Regardless of the method, however, the main source of analytical error in QPA is usually the likelihood of inexperienced analysts choosing inappropriate phases for modeling a sample XRPD pattern. The algorithms employed by standard XRPD analysis software to help the user choose phases to include typically involve simple peak-matching routines, which cannot mimic the sorts of background knowledge expert analysts use to make such decisions (e.g., the relative prevalence of different minerals, which minerals are likely to occur together, and the results of other analytical techniques).

This kind of scenario, where there is a gap between the data and computerized analysis that can be filled by expert knowledge, is often where machine-learning techniques can be profitably used to more fully automate the process. We will discuss the use of association analysis, which is a simple type of machine learning technique, to identify the phases present in mineral mixtures, based both on the features of XRPD patterns themselves, and on mineral prevalence and co-occurrence data found in the Mineral Evolution Database (MED). The idea behind association analysis, and specifically efficient generation of appropriate association rules was developed by Agrawal and Srikant. We propose utilizing association rules in a slightly different manner, using association rules as an added input to the decision-making process to pick the next most likely mineral as phases are added to the analysis serially. We emphasize that we use these association metrics *after* the first mineral is selected. In this talk we evaluate the effectiveness of using three well known rules, lift, support, and confidence, in addition to correlation metrics to perform forward phase analysis.

LAYERED DOUBLE HYDROXIDES (LDH) PREPARED BY COPRECIPITATION METHOD WITH MICRO FLOW RATES OF RAW SOLUTIONS

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In recent years, research on nanosheet production through exfoliation of the hydroxide layer has garnered attention as a method for developing new materials utilizing layered double hydroxide (LDH) as a host. However, in the carbonate-type LDH system, which exhibits the highest anion selectivity, it is considered challenging to detach the layered structure once formed. On the other hand, continuous direct synthesis of nitrate-type LDH nanosheets using a microreactor has been reported as a method for synthesizing LDH nanosheets without the exfoliation process. We thought that this method could be applied to the carbonate-type LDH system to synthesize carbonate-type nanosheets. In this study, we investigated the direct synthesis of Mg-Al-CO_3-type LDH using a simpler Y-shaped tube as the reaction field. Solution 1 (alkali solution) and Solution 2 (metal cation solution) were prepared and pumped at a predetermined flow rate, mixed, and reacted in the Y-tube (1.5 mm inner diameter). The resulting reaction solution was collected. Subsequently, the precipitate obtained by centrifuging the collected solution was washed with deionized water and dried to obtain a Mg-Al-CO_3-type LDH sample.

XRD pattern of all samples showed the rhombohedral pattern, indicative of the crystalline structure of LDH. In the patterns of the obtained samples, the intensity of the 00l peak, reflecting the stacking state of the hydroxide layers, was weaker compared to samples prepared using the conventional coprecipitation method. The specific surface areas of the samples prepared under different metal ion concentrations during preparation were 2-3 times larger than those obtained by the conventional coprecipitation method. This suggests that the difference in specific surface area depends on the amount of micropores in the sample. These results suggest that this method produces LDH fine particles with suppressed grain growth, although nanosheet formation is not achieved.

CHARACTERIZATION OF KAOLINITE SOURCE CLAYS; COMPARISON OF JCSS-1101 (KANPAKU KAOLIN) WITH KGA-1B (GEORGIA KAOLIN)

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Source Clays distributed by the Clay Minerals Society (CMS) are making significant contributions to research activities involving clay minerals worldwide. The Clay Science Society of Japan (CSSJ) has also been distributing Reference Clay Samples since 1990, which include typical clay minerals mined or produced in Japan (https://www.cssj2.org/english/reference_clay_e/). Among them is a kaolinite sample (JCSS-1101) mined at Kanpaku, Tochigi Prefecture, Japan. The kaolinite deposits originate from the hydrothermal alteration of late biotite-rhyolite during the Neogene period. Since the start of distribution, the lot has been renewed twice, with the newest lot (JCSS-1101c) replacing the previous lot (JCSS-1101b) from September 2020. This presentation reports on the characterization of JCSS-1101b and JCSS-1101c, and comparison with the CMS source clay (Georgia kaolinite) with low defects (KGa-1b), using XRD and various electron microscopic techniques with EDS analysis.

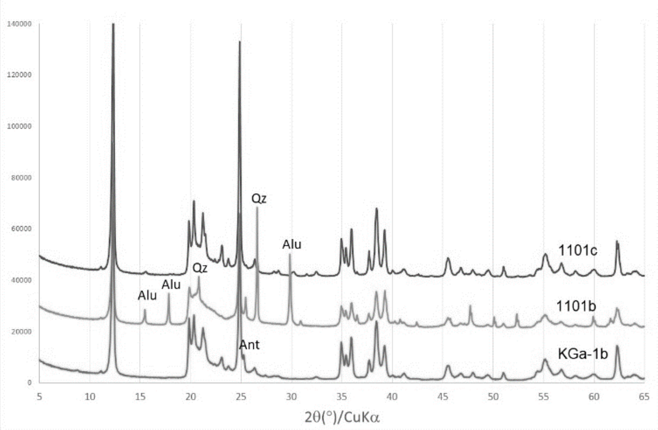

Figure 1. XRD patterns of the three kaolinite source clays. Alu: alunite. Ant: anatase. Qz: Quartz

The XRD pattern of 1101b showed the presence of alunite and quartz as impurity minerals, but these minerals were almost absent in 1101c (Fig. 1). Instead, very weak peaks other than those of kaolinite were detected in the pattern of 1101c, which were explained with svanbergite ($SrAl_3(PO_4)(SO_4)(OH)_6$), identified by STEM-EDS analysis. In the XRD pattern of KGa-1b, the {101} peak of anatase was clearly observed. The profile of the 02, 11 band of kaolinite in 1101c has changed from that in 1101b, with distinct peaks corresponding to ordered kaolinite stacking. Hinckley indices for 1101c and KGa-1b are 1.17 and 0.94, respectively.

STEM-EDS analyses of thin electron-transparent films prepared from pressed powder by using FIB confirmed a high density of alunite particles in 1101b, anatase particles in KGa-1b, and very fine particles containing Sr, Al, P, and S (svanbergite) in 1101c. EDS analysis indicated that kaolinite crystals in 1101b and 1101c were iron-free, whereas kaolinite in KGa-1b contained iron in the crystals. SEM imaging showed that the particle morphology of kaolinite in 1101c is mostly hexagonal thin plates with a wide range of sizes similar to KGa-1b, but large kaolinite plates in KGa-1b generally formed a vermicular stack. Fine isotropic particles were common in 1101b, which may be spherical halloysite.

STUDY OF TRANSMISSION ELECTRON MICROSCOPY OF ILLITE FROM YEONGDONG COUNTY, SOUTH KOREA: CANDIDATE FOR NEW ILLITE SOURCE CLAYS

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Presented by Tae-Hee Koo on behalf of Namgu Lee

Illite has a great potential across various industries such as cosmetics, construction materials, and livestock feed. Dongchang and Yongkoong Illite deposits, two illite deposits located in Yeongdong county in South Korea, associated with hydrothermal alteration of mica schist and granitic gneiss, respectively. To assess mineralogical and chemical properties of illite, size fractionation (bulk, >2 μm, 0.5-2 μm, <0.5 μm) has been performed by gravity sedimentation and centrifuge for both illite deposit samples. Particle size analysis, X-ray diffraction (XRD) analysis, and transmission electron microscopy (TEM) analysis were utilized to determine mineralogical and geochemical properties of illite.

Mineral identification for each size fraction were performed by XRD Rigaku Miniflex ▯. Illite and quartz with minor contents of kaolinite were measured for Dongchang Illite, while illite, quartz, albite, and microcline for Yongkoong Illite. To measure any smectitic layers in illite crystals, SYBILLA modeling was applied to glycolated XRD profiles. High-resolution transmission electron microscopy (HRTEM) bright field micrographs and selected area electron diffraction (SAED) patterns showed 10 Å lattice fringe and 20 Å periodicity, indicating that both samples exhibit the $2M_1$ polytype of illite. Energy dispersive spectroscopy (EDS) data showed that the elemental composition of Dongchang Illite exhibited a 0.75 Al/Si ratio and 0.81 interlayer charge, while Yongkoong Illite had a 0.72 Al/Si ratio and 0.95 interlayer charge.

MEASURING ELECTRIC FIELD AND ELECTROSTATIC FORCES OF CLAY MINERALS: THE PRINCIPLES, METHODS, AND APPLICATIONS

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A strong electric field of 108–109 V/m could be produced from the surface charges of clay minerals. Our recent quantum mechanism analysis indicated that the asymmetric hybridization of ionic/atomic orbitals will occur when ions/ atoms are in such a strong asymmetric electric field. It has been proved that new surface reactions occur between cations and the surface O atoms of clay minerals due to the asymmetric hybridization effects. It is the electric field and its initiated orbital asymmetric hybridization of surface atoms/cations that dominates the interactions between 'mineral-mineral', 'mineral-organic matter', and 'mineral-microorganism'. Therefore, quantitatively measuring the electric field and interaction forces of clay minerals aroused by the asymmetric hybridization effects are essential for understanding the physicochemical processes occurring on the surface of clay minerals.

This report elucidates the principles and methods of measuring clay mineral charges, electric field, electrostatic force/energy, etc.. Further, using this method to learn how the electric field and its initiated asymmetric hybridization effects of clay minerals enhances the Lewis acid-base reactions between the surface O and Cu2+/Ca2+/Mg2+/H2O and how it controls the occurrence of the soil porous process in water transport.

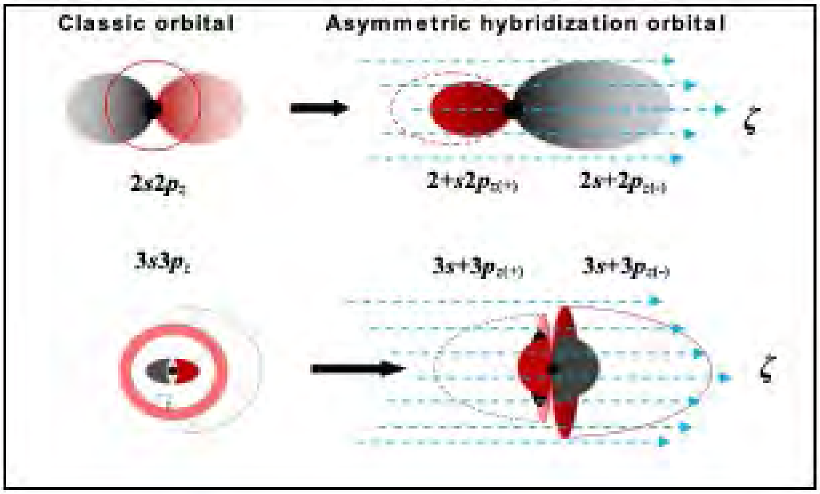

Fig. 1. The classic and the asymmetric hybridization orbitals of 2s2p and 3s3p outer shell orbitals

STANDARDIZATION OF CLAY NANOPLATE MATERIALS FOR QUALITY ASSESSMENT AND CERTIFICATION

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Clay nanoplate material, distinguished by their unique shape and properties, is an advanced nanomaterial with extensive potential applications across various industries. Ensuring the successful market acceptance of these materials requires a reliable assessment of their overall quality, with testing standards playing a pivotal role. Considering the promising application of these materials in gas barrier technology, a dedicated standard, ISO 21346-2:2021, specifies the characteristics to be measured and measurement methods to be adopted for comprehensively assessing the quality of clay nanoplate materials. This presentation provides an update on the standardization of clay nanoplate materials for quality evaluation and assurance, addressing testing laboratory designation for reliable measurement data and material certification for ensuring the quality.

In accordance with testing standards, manufacturers of clay nanoplate materials report their characteristic values to users. Throughout the processes, testing laboratories play a crucial role in determining reliable characteristic values for the materials, necessitating sufficient capability in relevant techniques. This led to the establishment of a testing laboratory designation system, enabling material manufacturers to identify proficient testing laboratories. The Nanomaterial Standardization and Certification Committee (hereafter referred to as the Committee), one of the AIST Consortia, has played the role of a designating body and provided guidelines for the designation. In the designation processes, the measurement capability declared by testing laboratories is examined by the Committee. The capability is reviewed from a technical viewpoint of the uncertainties in measurement results of characteristics. The Committee initiated the designation process in 2023, designating two testing laboratories as of 2024.

The Committee is currently developing a certification system for clay nanoplate materials. According to the system, material manufacturers will declare the quality of their commercial models of clay nanoplate materials, specifically showing the characteristic values with their tolerance in conformity with the ISO testing standards. The certification system requires that the characteristic values are measured by the designated testing laboratories. The Committee examines the declaration from technical viewpoints of the testing standards and the designation of testing laboratories, as well as an administrative point of the quality management system. The confidence of clay nanoplate materials in the market transactions is enhanced step-by-step through the stages of establishing testing standards, designating testing laboratories, and certifying commercial material models.

INTERACTIONS OF SMECTITES WITH BITUMEN: RELEVANCE TO NON-AQUEOUS SOLVENT BITUMEN EXTRACTION

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The non-aqueous extraction (NAE) is an alternative to the commercial water-based extraction process used to separate bitumen from the Alberta oil sands. Although the impact of various types of clay minerals on NAE process has been previously studied, the effect of different types of smectites has not been fully understood yet. In the present study, bentonites dominated by saponite, hectorite, nontronite, beidellite and montmorillonite were mixed with bitumen (recovered from high-grade Alberta oil sands) for several days and then washed with solvent (cyclohexane) to remove bitumen from the bentonites. The main goal was to better understand the impact of different smectites properties (specific surface area, pore structure characteristics, particle size, crystallite thickness, swelling ability, cation exchange capacity, layer charge and crystal-chemistry of smectites) on NAE process. The porosity, particle size and swelling ability were the key parameters of the studied samples affecting the solvent-based bitumen recovery under the studied conditions. Samples with larger initial total pore volume retained more organics after solvent bitumen extraction which indicated that the bitumen was retained primarily in pores distributed within the samples. The solvent bitumen recovery decreased with smaller particle size of the studied smectites. The particle size distributions (PSDs) of smectites did not changed in cyclohexane (no swelling) whereas PSDs were dramatically changed in water. With longer reaction time, the number of larger clay aggregates gradually decreased in favor of finer aggregates due to swelling of smectites in water. The efficiency of solvent-based bitumen extraction was substantially reduced for fine grained samples consisting of thin delaminated smectite particles formed because of swelling.

FLUVIO-LACUSTRINE FORMATION OF NEW CALEDONIA: POST-DEPOSIT PROCESSES AND DYNAMICS OF TRACE METALLIC ELEMENTS

PARMENTIER Jean-Baptiste[1], MATHIAN Maximilien*[1], PATTIER France[1], GAULLIER Virginie[2], MAURIZOT Pierre[3], TRIBOVILLARD Nicolas[2], ZANELLA Alain[4], MARCHAND Cyril[1] and GUNKEL-GRILLON Peggy[1]

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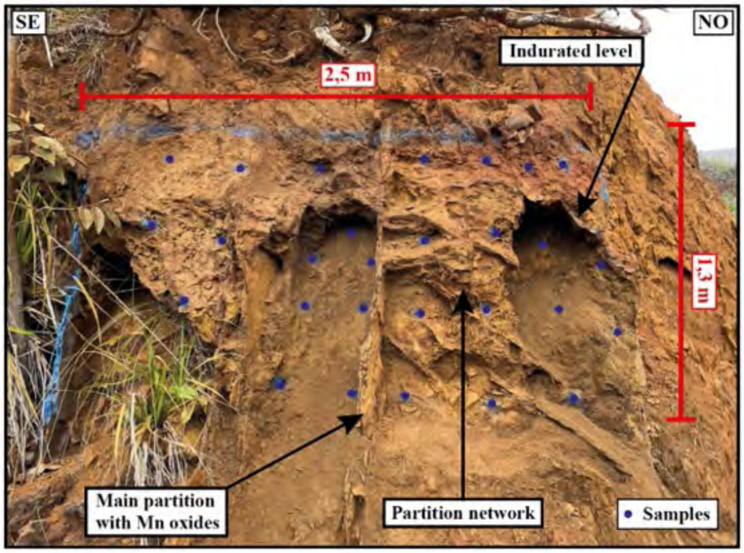
Located in the south-west Pacific, New Caledonia is an archipelago with a complex geodynamic history. Grande Terre, the main island, is covered by more than 25% of tropical regoliths developed on ultramafic rocks. These peridotites, naturally enriched in metallic elements (Fe, Mn, Al, Ni, Co, Cr), constitute most of the southern part of New Caledonia. Since approximately 27 Ma, these rocks have undergone weathering, under a humid and warm climate, and erosion. This combination has led to the formation of the fluvio-lacustrine system, by accumulation of sediments eroded from local summits in depressions and valleys. The sedimentary filling of this system is essentially of fluvial origin, with rare lacustrine occurrences. Its structure is complex and some sedimentary levels show abnormally high accumulations of Trace Metallic Elements (Ni, Co, Cr).

This poster will display the first results of a project aiming to understand the mobility of these metals in this system. These results are focus on outcrops hosting several networks of hardened iron oxides and Mn oxides partitions, intersecting clayey (figure below). The preliminary results, crossing X-Ray diffraction, X-Ray fluorescence and Scanning Electron Microscope with sedimentological analyses have revealed enrichments in Mn within the partitions. Such results point to the fact that fluid circulations that have affected the fluvio-lacustrine formation likely contributed to the remobilization of metallic elements prior to its structural organisation and caused the formation of several distinct generations of Fe and Mn oxides.



THE PHYLLOSILICATE STRUCTURE: THE OCTAHEDRAL SHEET DIMENSION

Petit, Sabine *[1], Decarreau, Alain[1], Grégoire, Brian[1], and Ferrage, Eric[1],

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A recent paper has been devoted to correlations between the chemistries of various minerals families (hydroxide and phyllosilicate) and their *b* (or equivalent) crystallographic unit-cell parameter values using data collected from the literature (Petit *et al*., 2023). These authors showed that using the mean ionic radius of octahedral cations, *R,* allows generalizing the various correlations that can be found in the literature between *b* and the octahedral chemistry, which are often restricted to limited types of sample series in terms of chemical composition or dioctahedral vs trioctahedral character. The present work now focuses on the results obtained for the hydroxide family (i.e. hydroxide, oxyhydroxide and layered double hydroxide), to study the dimensional properties of the octahedral sheet in more details.

Petit *et al*. (2023) observed a single *b vs R* regression irrespective of the di- or trioctahedral nature of minerals for the three types of hydroxide families studied. Correlation lines have similar slopes, despite the different crystallographic structures of the three types of minerals, implying that the O sheet dimension depends essentially on the shape and size of neighboring octahedra. The data are interpreted here based on an oxygen–cation–oxygen mean distance. For a system of flattened octahedra with a bond angle τ = O-M-O, where the oxygen ions are in the same plane, the equivalent *b* parameter is given by $b = 6(\mathrm{M–O})\sin(\tau/2)$, with the (M–O) distance being the sum of the effective ionic radii for cations (M) in six-fold coordination and oxygen ions (O) in four-fold coordination ($r(^{IV}O^{2-}) = 1.38$ Å; Brindley & Kao, 1984). Using the mean ionic radius of octahedral cations R, this relation can be easily rewritten as $b = 6(R + 1.38)\sin(\tau/2)$. Following this structurally-based interpretation, a relation $b = AR + C$ can be obtained for each family of hydroxides studied here using a simple model with $A = 6\sin(\tau/2)$ and $C = 1.38A$ (in Å). The A (and thus τ and C) were determined by fitting with the experimental regressions. The flattening angles obtained (97.3°, 96.3°, and 96.6° for $M^{n+(}OH)_n$, MO(OH), and LDHs, respectively) agree well with the data from structure refinement approaches.

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REMOVAL PERFORMANCE OF ARSENATE AND ARSENITE ANIONS OF LAYERED DOUBLE HYDROXIDE

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Arsenate and/or arsenite anions, which are one of the toxic anion species, must remove from water because of their adverse effects on the environment, ecosystem, and humans. Thus, the effluent standards (0.1 mg-As/L or less) and environmental standards (0.01 mg-As/L or less) are set in Japan. Thus, there is a need for a material that can efficiently remove arsenate and/or arsenite anion species dissolved in water. Layered double hydroxides (LDHs) are attracting attention as a material that can not only efficiently remove arsenate and/or arsenite anions species dissolved in water, but also recover them a recyclable resource through a regeneration process. In this study, the anion selectivity of LDH consisting of Ni and Al with chloride anions incorporated in the interlayer space (Cl-NiAl(*x*)LDH, *x* was Ni/Al molar ratio) toward arsenate and arsenite anion species was investigated.

In Fig. 1, the anion-exchange isotherm curves of Cl-NiAl(*x*)LDH from chloride to arsenate (a) and arsenite (b) anions species are shown. Arsenate-anion selectivity of Cl-NiAl(*x*)LDH decreased with an increase in *x* value, while the arsenite selectivity of Cl-NiAl(*x*)LDH showed the opposite trend, indicating that Cl-NiAl(4) LDH has a relatively high affinity for arsenite anion species. These results indicate that Cl-NiAl(4)LDH is an effective materials for arsenite anion species from water, which is generally considered difficult to remove by anion-exchange phenomenon.

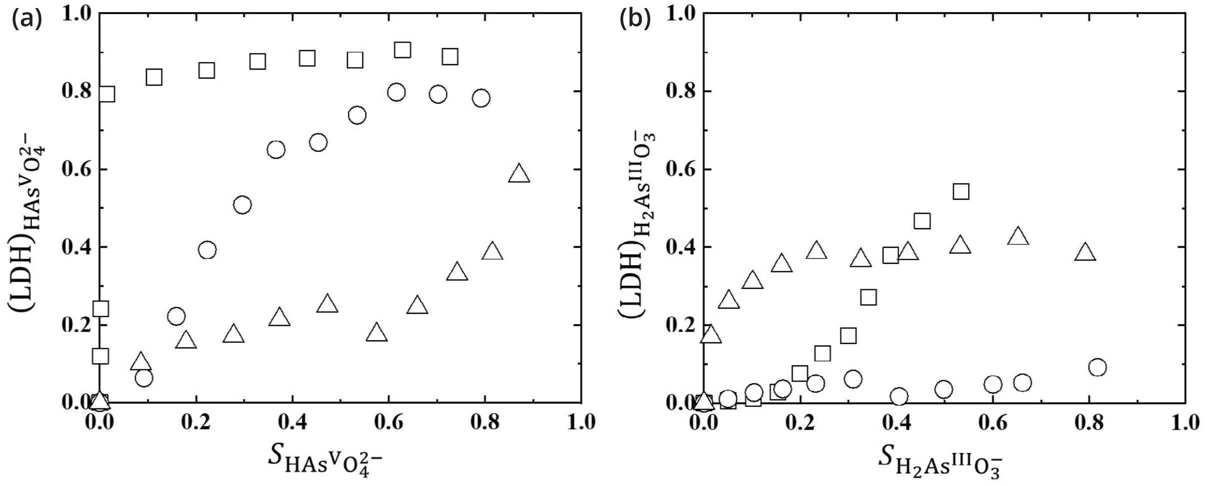

Fig. 1. Anion exchange isotherm curves of LDH consisting of Ni and Al (Ni/Al molar ratio: 2 (□), 3 (○), and 4 (△)) from chloride to (a) arsenate and (b) arsenite anion species.

THE ION-EXCHANGE MECHANISM OF HYDROBIOTITE AND BEHAVIOR OF THE INTERNAL WATER MOLECULES

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Vermiculite, sold as vermiculite from South Africa, has been analyzed by Miyawaki *et al*. and has been reported that the principal mineral was hydrobiotite and several mixed minerals such as vermiculite, apatite and titanite were mixed. Since the main component is hydrobiotite, the authors will henceforth refer to it as hydrobiotite (HB) rather than vermiculite (V). Both clay minerals, HB and V, are belonging to the smectite family, and their exchangeable cations are potassium and magnesium ions, respectively. Our previous reports have focused only on V, but the ion-exchange mechanism should be examined with its primary constituent mineral. The purpose of this study is to elucidate which mineral is preferentially working as the ion-exchanger when the vermiculite from South Africa is used as adsorbent for cesium ions. And the state of water molecules was also investigated to verify if water molecules were involved in the ion-exchange reaction.

Despite the fact that the main component of vermiculite is HB, magnesium ions are more abundant than potassium ions in the supernatant after ion exchange, indicating that ion exchange with V is a priority. It is well known that there are two sites of water coordination in vermiculite, one is the interlayer and the other is the magnesium in the framework. X-ray diffraction and thermal analysis showed that the latter also dehydrates as the amount of ion exchange increases.

SLOVAK BENTONITE DEPOSITS – A BRIEF OVERVIEW

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In 2022, the Slovak Republic for the first time reached the annual production of bentonite over 300 kt and it has ranked among the 10 largest producers in the world. There are two areas in Slovakia where bentonite deposits are concentrated, namely, the Central Slovak Volcanic Field (CSVF, 8 active deposits) and the Eastern Slovak Neogene Basin (ESNB, 2 active deposits). The highest-grade Slovak bentonites, containing 70-80 wt.% montmorillonite, are found in the CSVF, specifically in the Jastrabá Fm. It consists of rhyolitic volcanic products represented by extrusive domes, lava flows, tuffs and epiclastic volcanic rocks that form a continuous, 100–300 m thick complex of the Late Sarmatian to Early Pannonian age (12.2±0.3 - 11.4±0.4 Ma). The most of bentonite deposits of the Jastrabá Fm. were created by bentonitization of a marginal glassy/perlitic carapace of extrusive domes/flows and cryptodomes. Unaltered perlites appear in close surroundings of bentonite deposits as crumbly, porous glassy rocks with porphyritic texture containing 75-90 wt.% of volcanic glass. The higher number of phenocrysts in perlite limits the quality of bentonite, as the clays originate solely at the expense of volcanic glass of the Jastrabá Fm. Phreatomagmatic tuffs rich in pumice and perlite fragments are also affected by bentonitization in this area. Bentonitization of the glass was enabled by subsurface flow of fluids in the permeable rhyolitic rocks, driven by a decreasing hydraulic head in S-SE direction. These fluids were mostly of meteoric origin, acidified and heated by a steam resulting from boiling of hydrothermal fluids in the Kremnica epithermal Au-Ag deposit, located north of the bentonite deposits. The Michaľany-Lastovce bentonite (bentonitic clay) deposit is the largest and one of the earliest discovered bentonite deposits in ESNB. The deposit is hosted by Sarmatian volcanic-sedimentary rocks, including specifically argilitized rhyolite tuffs and tuffites, tuffitic clays and bentonites, up to 30 m thick. Diagenetically altered pyroclastic rocks from this deposit and surroundings have a relatively low content of montmorillonite (40-45 wt.%) and an increased content of opal-C or opal-CT (30-50 wt.%).

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