Classic Clays and Minerals

40th Annual Meeting of The Clay Minerals Society
and Spring Meeting of the Mineralogical Society of America

Workshops, Meetings, Field Trips, and Receptions

Saturday, June 7, 2003

7:30 AM Workshop Registration, Georgia Center for Continuing Education Lobby

8:00-4:30 Workshop: The application of vibrational spectroscopy to clay minerals and layered double hydroxides: Georgia Center for Continuing Education, Room R

8:30-5:00 MSA Council Meeting, Georgia Center for Continuing Education, Room VW

4:30-6:00 Workshop Reception, Georgia Center for Continuing Education, Lobby

5:00-10:00 CMS Executive Committee Meeting: Athena Board Room - Foundry Park Inn.

Sunday, June 8, 2003

8:00-5:00 Field Trip #1, Soils of the Piedmont: Departs/returns Classic Center

8:30-5:00 CMS Council Meeting, Georgia Center for Continuing Education, Room YZ

3:00-6:00 Registration – The Classic Center – Ballroom Pre-function Area

6:00-8:00 Opening Reception* - Foundry Park Inn, Athens Steam Factory Ballroom. Heavy hors d’oevres served (3 blocks north of the Classic Center)

* One beverage ticket will be provided for each registrant. Cash bar will also be available.
Monday Morning, June 9, 2003

7:15-10:30 Registration at the Classic Center

**Plenary Session Day 1**

Athena Ballroom E

8:00-8:30 Introductory Remarks
Paul Schroeder, General Chair, Department of Geology, University of Georgia, Athens, GA
Heidi Davidson, Mayor of Athens/Clarke County Government.
Wyatt Anderson, Dean of Franklin College of Arts and Sciences, University of Georgia, Athens, GA.

8:30-8:45 Jessica Elzea-Kogel, President of The Clay Minerals Society, Presidential Address.

8:30-8:45 Douglas Rumble III, President of Mineralogical Society of America, Presidential Address.

9:15-10:00 Peter Komadel, Recipient of the 2003 Jackson Award
CHEMICAL TREATMENTS OF SMECTITES

10:00-10:15 Coffee Break

10:00-3:30 Poster Setup

**Technical Sessions Day 1**

Remote-sensing IR Spectroscopy of Phyllosilicate Clays and other Hydrous Materials on Planetary Surfaces

Hall B

Convener: Bradley L. Jolliff, Washington University at St. Louis.

10:15-10:35 James L. Post* and Londa Borer, THE IDENTIFICATION AND COMPOSITION OF AMPHIBOLES WITH THE AID OF INFRA-RED SPECTROSCOPY

10:35-10:55 Bradley L. Jolliff*, Alian Wang, Ed A. Guinness, Karla E. Kuebler, and Larry A. Haskin, FROM MARTIAN METEORITES TO TERRESTRIAL ANALOGS AND FROM INFRARED TO RAMAN SPECTROSCOPY: IN SEARCH OF HYDROUS PHYLLOSILICATES ON MARS

OBSERVATIONS OF CINDER CONES ON THE SUMMIT OF MAUNA KEA VOLCANO: IMPLICATIONS FOR THE SURFACE MINERALOGY ON MARS
11:15-11:35 Ralph E. Milliken* and John F. Mustard, QUANTIFYING CHANGES IN WATER CONTENT OF MONTMORILLONITE USING REFLECTANCE SPECTROSCOPY
11:35-11:55 Paul L. Gassman* and Thomas A. Blake, MID-INFRARED REFLECTANCE SPECTROSCOPY OF CONDENSED COMPOUNDS ON CLAYS, SOILS, AND QUARTZ SANDS

Engineered Particulate Systems: I
Hall C

Conveners: Brij M. Moudgil, University of Florida and Bob Pruett, IMERYS.

10:15-10:35 J. Nalaskowski and J.D. Miller*, STRUCTURAL CONSIDERATIONS IN THE SURFACE CHARGE OF KAOLINITE AS DETERMINED BY AFM FORCE MEASUREMENTS
10:35-10:55 Wen-An Chiou*, Akira Ishikawa and Kurio Fukushima, IN SITU TEM STUDY OF SMALL CLAY PARTICLES IN LIQUID ENVIRONMENT (CANCELLED)
11:15-11:35 Scott Brown*, Ivan Vakarelski and Brij M. Moudgil, POLISHING WITH SELF-ASSEMBLED SURFACTANT MEDITAED DISPERSION OF NANOPARTICULATE SYSTEMS
11:35-11:55 Marie C. Kissinger* and Kevin W. Powers, PRODUCTION AND CHARACTERIZATION OF HIGH ASPECT RATIO METAL PLATELETS BY MEDIA MILLING
Microbial Formation and Degradation of Minerals: A System Approach: I
Hall D

Conveners: Chuanlun Zhang and Andrew Neal, Savannah River Ecology Laboratory, University of Georgia

10:35-10:55  Jinwook Kim*, Hailiang Dong, Steven W. Newell, and Dennis D. Eberl, THE EVIDENCES FOR MICROBE-MEDIATED SMECTITE-TO-ILLITE TRANSFORMATION
11:35-11:55  Hailiang Dong* and Jinwook Kim, BIOMINERALIZATION ASSOCIATED WITH MICROBIAL REDUCTION OF MAGNETITE: TRANSMISSION ELECTRON MICROSCOPY AND ELECTRON ENERGY LOSS SPECTROSCOPY STUDY

Monday Afternoon, June 9, 2003

12:00-1:00  CMS Past Presidents Lunch: Foundry Park Inn, Magnolia A

Distal Impact Products and Stratigraphy
Hall B

Conveners: Michael Roden and R. Scott Harris, University of Georgia and Edward F. Albin, The Fernbank Museum.

1:15-1:55  Billy P. Glass*, KEYNOTE ADDRESS: UPPER EOCENE DISTAL EJECTA LAYERS
2:15-2:25  Coffee Break

2:45-3:05  R. Scott Harris*, Mack S. Duncan, Michael F. Roden, and Paul A. Schroeder, Evidence of Impact-Generated Deposition on the Late Eocene Shores of Georgia

3:05-3:25  Ed Albin* and Harlan Trammell, Recovery of a Large (86.4 g) Splash-Form Tektite from Dodge County, Georgia (USA)

3:25-3:45  Michael Roden* and Steven M. Holland, Principle Component Analysis of Bulk Compositions of Eocene Tektites from Eastern North America

**Engineered Particulate Systems: II**
**Hall C**

Conveners: Brij M. Moudgil, University of Florida and Bob Pruett, IMERYS.

1:15-1:35  M. S. Hassan, E.A. Abdel Aal, and H. El-Shall, Engineering Structure and Texture of Kaolinite Through Thermal and Chemical Modifications


1:55-2:15  Haydn H. Murray*, Engineered Clay Products for Industrial Use

2:15-2:25  Coffee Break


2:45-3:05  A. A. Zaman*, A. Nguyen, S. Pregler, A. Bhaskar, and C. L. Beatty, Polymer-Silicate Nanocomposites: An Overview


3:25-3:45  Hyojin Lee* and William M. Carty, The Use of Inorganic Plasticizers for Technical Ceramics Extrusion

**Microbial Formation and Degradation of Minerals: A System Approach: II**
**Hall D**

Conveners: Chuanlun Zhang and Andrew Neal, Savannah River Ecology Laboratory, University of Georgia

1:15-1:35  Jennifer T. McGuire*, Andrew S. Madden, Michael A. Velbel, Danita S. Brandt and David T. Long, Fossilization of Microorganisms on an Annual Timescale in an Anaerobic Aquifer: Geochemical
CONTROLS AND IMPLICATIONS FOR PRESERVATION OF EVIDENCE OF EXTRATERRESTRIAL LIFE
1:35-1:55 Gregory A. Konesky*, GEOMICROBIOLOGICAL ELECTRON FLOW AS A TERRESTRIAL POWER SOURCE AND POTENTIAL INDICATOR OF EXTRATERRESTRIAL LIFE
1:55-2:15 D. Craig Cooper*, Andrew H. Neal, Ravichandran K. Kukkadapu, Aaron J. Coby, and Flynn W. Picardal, EFFECT OF SEDIMENT MINERALOGY ON MICROBIOLOGICALLY INDUCED (DMRB) CHANGES IN DIVALENT METAL SPECIATION
2:15-2:25 *Coffee Break

Industrial Clays
Hall D

Convener: Chris Romanek, University of Georgia, SREL, Aiken, SC.

2:25-2:45 Ungsoo Kim* and William M. Carty, APARENT ALTERATION OF CLAY STRUCTURE BY EXTRACTION TECHNIQUE
2:45-3:05 Wanda A. Allo and Haydn H. Murray, MINERALOGY, GEOCHEMISTRY AND POTENTIAL APPLICATIONS OF A WHITE BENTONITE IN SAN JUAN PROVINCE, ARGENTINA
3:05-3:25 Ira E. Odom*, PROPERTIES AND DIAGENESIS OF SOME NA BENTONITES NEAR BIG BAND NATIONAL PARK, TEXAS
3:25-3:45 Gilles O. Allard*, METAMORPHISM OF CLAYS IN HYDROTHERMAL ALTERATION SYSTEMS PRODUCE MINERALOGICAL ANOMALIES USEFUL IN MINERAL EXPLORATION

**Poster Session Day 1**

Note: Authors should be present during from 3:35 – 5:30 PM. Posters will also be left up for display until Wednesday noon.

**Fire Hall** (snacks and beverages served)

**Distal Impact Products and Stratigraphy**

P0 - David T. King, Jr.* and Lucille Petruny, CHICXULUB DISTAL IMPACT EJECTA IN ALABAMA: BASAL, MICROTEKTITE-RICH LAYER BELOW TSUNAMI SANDS AT SHELL CREEK STRATIGRAPHIC SECTION
Earth Materials: Soils, Shales, and Sandstones

**P1** - Soyoung Sung* and Soo Jin Kim, ROLE OF HYDROXY–AL INTERLAYERED VERMICULITE AS STORAGE OF MOBILE AL3+ IN THE FOREST SOILS DEVELOPED ON THE GRANITE BEDROCK IN KOREA

**P2** - Youjun Deng*, James B. Harsh, Markus Flury, Jeffrey Boyle, James Young, and Joseph Ford, MINERAL PHASE TRANSFORMATION IN CONDITIONS MIMIC SEDIMENT SOLUTIONS UNDERLYING LEAKED HANFORD WASTE TANKS

**P3** - Gyoo Ho Lee*, Yungoo Song, Hi-Soo Moon, Jang-Han Yoo, Ji-Won Moon, LONG-TERM LEACHING OF JEJU ANDISOLS WITH HCL SOLUTION: BUFFER CAPACITY AND ALUMINUM SOLUBILITY CHANGE


Industrial Minerals

**P5** - Robert J. Pruett*, TITANIA MINERALS AND IMPLICATIONS FOR THE ORIGIN OF GEORGIA SEDIMENTARY KAOLIN

**P6** - M. A. Taher*, THE EFFECT OF SILICA FUME ON THE BEHAVIOR OF BURNT CLAY-LIME PASTES

**P7** - H. D. Ruan* and D. G. Schulze, DEHYDROXYLATION OF BAUXITE CHARACTERIZED BY FOURIER TRANSFORM INFRARED SPECTROSCOPY AND X-RAY DIFFRACTION

**P8** - Schulz* and William M. Carty, ADSORPTION OF SODIUM POLY(ACRYLIC ACID) ON ALUMINA AND CLAY SURFACES: THE EFFECT OF HUMIC AND FULVIC ACID

Medicinal Applications of Minerals

**P9** - Ulli Limpitlaw*, THE PALLIATIVE AND CURATIVE USES OF FOSSILS AND MINERALS
Microbial Formation and Degradation of Minerals: A System Approach

P10 - Jennifer Kyle* and Paul A. Schroeder, BIO/LITHOFACIES OF OCTOPUS SPRING SINTER IN YELLOWSTONE NATIONAL PARK, WYOMING


Mineral Structures

P12 - Takeo Ebina*, Rwaichi J.A. Minja, Abhijit Chatterjee, and Fujio Mizukami, ANALYSIS OF HYDRATION BEHAVIOR OF SMECTITES BY HUMIDITY-CONTROLLED THERMOGRAVIMETRY


P14 - Chul-Kyoo Lee*, Yungoo Song, Chul-Min Chon, Shin Ae Kim, STRUCTURAL CHANGES IN HYDROXYL ION OF TRIOCTAHEDRAL MICA WITH INCREASING TEMPERATURE ; IN-SITU NEUTRON POWDER DIFFRACTION

P15 - M. Klementova*, M. Carpenter, and M. Rieder, SYSTEM 3SNO2-MNTAO6: SYNTHETIC VS. NATURAL SAMPLES

Role of Minerals in Natural and Mediated Environmental Restoration

P16 - John Yang*, Yiliang Li, Chuanlun Zhang, and Baolin Deng, IN SITU FORMATION OF PYROMORPHITE FROM VARIOUS LEAD MINERALS

P17 - Seung Yeop Lee* and Soo Jin Kim, SORPTION CHARACTERISTICS OF POLYCYCLIC AROMATIC HYDROCARBONS AND CADMIUM ON ORGANOCLAYS

P18 - Ji-Won Moon*, Hi-Soo Moon, Yungoo Song, Jin Kyoo Kang, Yul Roh, Gyoo Ho Lee, MINERALOGICAL INVESTIGATION OF CORROSION CONTROLLING FACTORS AND STABILITY OF SURFACE COATING MATERIALS IN THE IRON-BASED ELECTRO-ENHANCED PERMEABLE REACTIVE BARRIER

P19 - Debra H. Phillips*, David B. Watson, Yul Roh, URANIUM RETENTION IN SHALE SAPROLITE ON THE NABIR FRC SITE-RELATIONSHIPS WITH PHOSPHORUS, SULPHUR, AND FE, MN AND AL OXIDES
**Archeological Mineralogy**

**P20** - Debra H. Phillips*, Yul Roh, and Marta Adams, PROVENANCE OF AN ARCHAEOLOGICAL CLAY DEPOSIT FROM AEGINA, GREECE

**P21** - Christine M. Shriner*, James G. Brophy, Haydn H. Murray and George E. Christidis, MINERALOGY OF SEDIMENTS AND FOSSIL REMAINS AT A NEOGENE AGE FOSSIL SITE IN NORTHEAST TENNESSEE

**Monday Evening, June 9, 2003**

7:00-9:00 Clays and Clay Minerals Editor’s Dinner, Foundry Park Inn, Athena Board room.
Tuesday Morning, June 10, 2003

**Plenary Session Day 2**

Athena Ballroom E

8:15-8:20 Announcements: Paul Schroeder, General Chair, Department of Geology, University of Georgia, Athens, GA

8:20-9:15 Alain Manceau, 2003 Brindley Lecture. HETEROGENEITY, MULTIPLICITY, VARIABILITY: THE ENVIRONMENTAL CLAY SCIENTIST'S TRILOGY

Introduction by Victor Drits

Medicinal Applications of Minerals: I

**Hall B**

Convener: Lynda B. Williams, Arizona State University

9:40-10:00 Lynda B. Williams*, Melanie Holland and Dennis D. Eberl, KILLER CLAYS! A MEDICINAL APPLICATION OF MINERALS

10:00-10:15 Coffee Break

10:15-10:55 A. G. Cairns-Smith*, BETWEEN CLAY MINERALS AND ORGANIC MOLECULES

10:55-11:15 Ray E. Ferrell* and Wanda S. LeBlanc, CHIMAYO, SPIRITUAL HEALING, AND MEDICINAL CLAY

11:15-11:35 Paul Kostyniak*, Patricia M. Costanzo, Joseph Syracuse, Rossman F. Giese, Jr., ANTIMICROBIAL ACTIVITY OF MODIFIED CLAY MINERALS

Minerals Structures: I
Hall C

Convener: Sridar Komarneni, Penn State University and Alyx S. Frantzen, Austin State University

9:40-10:00 Erick J. Acosta, Youjun Deng, Norman G. White, Joe B. Dixon, Kevin McInnes, Scott A. Senseman, Alyx S. Frantzen*, and Eric E. Simanek, DENDRITIC SURFACTANTS SHOW EVIDENCE FOR FRUSTRATED INTERCALATION: A NEW ORGANOCLAY MORPHOLOGY
10:00-10:15 Coffee Break
10:15-10:35 P. Walker* and A.S. Frantzen, EFFECTS OF CATION EXCHANGE CAPACITY AND INTERLAMELLAR CATION IDENTITY OF SMECTITE CLAYS ON THE VISIBLE SPECTRA OF PORPHYRINS
10:35-10:55 Stephen Guggenheim* and A. F. Koster van Groos, CLAYS AND METHANE HYDRATE
11:15-11:35 J. Cole and A. S. Frantzen*, DETERMINATION OF THE ENTHALPY OF HYDRATION OF CLAY MINERALS UTILIZING SOLUTION CALORIMETRY

Earth Materials: Soils, Shales, and Sandstones: I
Hall D

Convener: Heather Dion, Savannah River Ecology Laboratory, University of Georgia

9:20-9:40 Georg H. Grathoff*, John Baham, Curt D. Peterson and Catrina M. Johnson, AUTHIGENIC AL, FE, SI MINERALS OF VARYING CRYSTALLINITY IN DUNAL SOILS NEAR NEWPORT, OREGON, USA
9:40-10:00 D.A. Spears*, BENTONITES AND TONSTEINS
10:00-10:15 Coffee Break
10:15-10:35 Donald M. Thieme*, DETRITAL AND PEDOGENIC MINERAL PHASES IN A BURIED SOIL FORMED IN SUSQUEHANNA RIVER ALLUVIUM OF MID-HOLOCENE AGE
10:35-10:55 A. El-Shater* and A. El-Haddad, PALEOENVIRONMENTAL SIGNIFICANCE OF CLAY MINERAL ASSOCIATIONS ACROSS THE CRETAUCEOUS-TERTIARY IN UPPER EGYPT
10:55-11:15 M.A. Chappell*, D.A. Laird, and M.L. Thompson, EFFECTS OF SAMPLE HANDLING (AIR-DRYING) ON SORPTION OF ATRAZINE BY SOILS AND CLAYS


12:00-1:15 CMS Sustaining Member’s Lunch: Foundry Park Inn, Athena room

Tuesday Afternoon, June 10, 2003

Medicinal Applications of Minerals: II
Hall  B

Convener: Lynda B. Williams, Arizona State University

1:30-1:50 Celso de S. F. Gomes*, POSITIVE EFFECTS OF MINERALS IN THE HUMAN HEALTH
1:50-2:10 Jill R. Scott*, Timothy R. McJunkin, and Paul L. Tremblay, PROBING MICROBE/MINERAL AFFINITY IN HETEROGENEOUS GEOMATRICES USING LASER-BASED OPTICAL AND CHEMICAL IMAGER (LOCI
2:10-2:30 Brandon Canfield*, Lynda Williams, and John R. Holloway, ABIOTIC ORGANIC SYNTHESIS IN CLAYS AT HYDROTHERMAL VENT CONDITIONS

Minerals Structures: II
Hall  C

Convener: Sridar Komarneni, Penn State University and Alyx S. Frantzen, Austin State University

1:30-1:50 Andrey Kalinichev, R. James Kirkpatrick*, and Jianwei Wang, MOLECULAR MODELING OF THE INTERLAYER H-BOND NETWORKS IN LAYERED DOUBLE HYDROXIDES: STRUCTURE AND DYNAMICS
1:50-2:10 Jeffrey E. Post*and David L. Bish, SYNCHROTRON POWDER X-RAY DIFFRACTION STUDY OF SEPIOLITE
Earth Materials: Soils, Shales, and Sandstones: II
Hall D

Convener: Heather Dion, Savannah River Ecology Laboratory, University of Georgia

1:30-1:50 Javier M. Gonzalez* and David A. Laird, SMECTITE CATALYZED DEHYDRATION OF GLUCOSE
1:50-2:10 Kathryn L. Nagy*, Jacob S. Waples, George R. Aiken, and Joseph N. Ryan, THE ROLE OF NATURAL ORGANIC MATTER IN CINNABAR (HGS) DISSOLUTION
2:10-2:30 Pauline Michel*, Norbert Clauer, Raymond Michels, Alain Trouiller and Marcel Elie, EXPERIMENTAL APPROACH ON CLAY-ORGANIC MATTER INTERACTIONS BASED ON CONFINED AQUEOUS PYROLYSIS
2:30-2:45 Coffee
2:45-3:05 Jutta R.V. Pils* and David A. Laird, MECHANISMS GOVERNING FLOCCULATION AND DISPERSION OF SMECTITIC COLLOIDS
3:05-3:25 Paul A. Schroeder* and Ö. Isik Ece, CLAY MORPHOLOGY, MINERALOGY, AND CRYSTAL CHEMISTRY OF HYDROTHERMALLY ALTERED VOLCANIC ROCKS IN THE TURPLU AREA, BALISEKIR, TURKEY
3:25-3:45 Ö. Isik Ece* and Paul A. Schroeder, ACID-SULFATE ALTERATION AND GENESIS OF ALUNITE-HALLOYSITE DEPOSIT AT TURPLU MINE, BALIKESIR, TURKEY
3:45-4:05 Olajohumo Johnson Ademola*, TBA
Teaching mineralogy, petrology and clay science
Hall B

Conveners: Stephen Guggenheim, University of Illinois - Chicago, David Mogk, Montana State University, D. Perkins, University of North Dakota, and Audrey Rule, S.U.N.Y. at Oswego

2:45-3:05  Dexter Perkins*, IT’S ALL ABOUT ENGAGEMENT AND ACTIVE LEARNING
3:05-3:25  David W. Mogk*, INTEGRATING RESEARCH AND EDUCATION IN MINERALOGY
3:25-3:45  Audrey C. Rule*, USING HUMOROUS CARTOONS TO REINFORCE LEARNING IN MINERALOGY
3:45-4:05  Peter J. Heaney* and Lisa Greer, USING ELECTRONIC RESPONSE TECHNOLOGY TO TEACH MINERALOGY IN LARGE CLASS SETTINGS
4:05-4:25  Michael A. Velbel*, INTERLAYER CATION DIFFUSION IN VERMICULITE: A LABORATORY EXERCISE IN GEOCHEMICAL KINETICS
4:25-4:45  Joe B. Dixon* and G. Norman White, IMPROVING CLASSIC CONCEPTS OF CLAY MINERALS TO AID UNDERSTANDING AND APPLICATIONS
4:45-5:05  Audrey C. Rule*, USING POETRY IN TEACHING ABOUT MINERALS

Tuesday Evening, June 10, 2003

6:30-7:30  Reception* – Georgia Center for Continuing Education – Pecan Tree Courtyard and Lower Lobby.  Note: A special UGA shuttle bus will depart from the Classic Center, Foundry Park Inn, and Holiday Inn every 15 minutes starting at 6:00 PM. The last departure will be 7:30 PM.

7:30-11:00  Banquet – Georgia Center for Continuing Education – Banquet area.  Note: A Shuttle bus will depart from the Georgia Center 15 minutes starting at 10:00 PM. Drop offs will be at the Foundry Park Inn, and Holiday Inn. The last departure will be 11:45 PM.

9:00-11:00  Music and dancing, featuring the “Common People Band”

* One beverage ticket will be provided for each registrant.  Cash Bar (no checks/charges) will also be available.
Wednesday Morning, June 11, 2003

Plenary Session Day 3

8:00-8:50 Vernon J. Hurst, Pioneer in Clay Science Lecture
CLAY MINERALS: DEFINITIONS, CLASSIFICATION, AND OUTLINE OF ORIGINS
Introduction by Bill Barker

Role of Minerals in Natural and Mediated Environmental Restoration: I
Hall B

Conveners: Dean Hesterberg, North Carolina State University, Andreas Scheinhost Institute of Terrestrial Ecology, Zurich, Switzerland, and Richard J. Reeder, SUNY at Stony Brook.

9:00-9:20 Opening remarks by session organizers.
9:20-9:40 Armand Masion*, Jérôme Rose, Astride Vilgé-Ritter, Emmanuel Doelsch, Paul M. Bertsch, Jean-Yves Bottero, NUCLEATION AND GROWTH OF Fe(III) AND Al(III) COLLOIDS IN THE PRESENCE OF COMPLEXING ORGANIC AND INORGANIC LIGANDS
9:40-10:00 E. De Grave*, M. Schärer, R.E. Vandenberghe, E. Frossard and S. Sinaj, MÖSSBAUER PHASE ANALYSIS OF AN AMENDED SOIL
10:00-10:15 Coffee Break
10:15-10:35 Nidhi Khare* and Dean L. Hesterberg, COMPETITIVE SORPTION OF PHOSPHATE BETWEEN Fe- AND Al-OXIDES IN MIXED-MINERAL SYSTEMS
10:35-10:55 Kathleen A. Carrado*, Susan M. Macha, David M. Tiede, IMMOBILIZATION OF CYTOCHROME C BY MESOSTRUCTURED SYNTHETIC CLAYS
10:55-11:15 Evelyn Krawczyk-Bärsch*, Thuro Arnold, Felix Brandt, Dirk Bosbach & Gert Bernhard, NATURAL ATTENUATION OF URANYL(VI) DURING THE DISSOLUTION OF DIFFERENT CHLORITES IN MIXED-FLOW EXPERIMENTS
11:15-11:35 Jordi Cama*, Carles Ayora, and Xavier Querol, and Natàlia Moreno, ILLITE ADSORPTION OF TOXIC CATIONS FROM CONTAMINATED AZNALCOLLAR SOIL (SPAIN)
11:35-11:55 Robert C. Thomas* and Christopher S. Romanek, TRACE METAL RETENTION IN VERTICAL FLOW CONSTRUCTED WETLANDS TREATING LOW PH, FERRIC IRON-DOMINATED ACID ROCK DRAINAGE
Emerging Interdisciplinary Research Directions in Clay Science: A Symposium Honoring the Career of Vernon J. Hurst

Hall C

Conveners: Bill Barker, University of Wisconsin-Madison and Nathan D. Melear, University of Georgia-Athens

9:00-9:20 Michael A. Velbel* and Jason R. Price, REGULARLY INTERSTRATIFIED VERMICULITIC PRODUCTS OF BIOTITE WEATHERING -INFLUENCE OF PARENT-MICA POLYTYPE

9:20-9:40 Jason R. Price* and Michael A. Velbel, CLAY MINERAL GENESIS RATES FROM THE COWEETA HYDROLOGIC LABORATORY, NORTH CAROLINA, USA, AND THE RESPONSE TIMES OF CLAY MINERALS TO CHANGES IN CLIMATE

9:40-10:00 Amy Anschutz, David J. Burleson, Yohan Guyodo, Subir Banerjee, and R. Lee Penn*, ENHANCED CHEMICAL REACTIVITY OF GOETHITE (ALPHA-FEOOH) NANOPARTICLES

10:00-10:15 Coffee Break

10:15-10:35 Jeffrey R. S. Brownson*, Timothy J. Lee, Marc A. Anderson, USE OF NANOPARTICULATE METAL OXIDES IN THIN FILM DEVELOPMENT FOR PHOTOCATALYTIC WAVEGUIDES


10:55-11:15 Anibal Quintana* and Antonio S. Lara, SELECTIVE ADSORPTION OF N-NITROSAMINES BY CLAYS AND ORGANO-CLAYS

11:15-11:35 Evgenya S. Shelobolina*, Robert T. Anderson, Yury N. Vodyanitskii, Derek R. Lovley, CLAY MINERALS AS A SOURCE OF ELECTRON ACCEPTOR FOR MICROBIAL Fe(III) RESPIRATION IN A PETROLEUM-CONTAMINATED AQUIFER

Mineral liquid crystals (note: This session continues into afternoon)

Hall C

Convener: Bill Barker, University of Wisconsin-Madison and Nathan D. Melear, University of Georgia-Athens

11:35-11:55 Jean-Christophe P. Gabriel*, LIQUID CRYSTALS PROPERTIES OF CLAYS AS WELL AS PHOSPHOANTIMONIC LAYERED ACIDS
Application of Clay Minerals to Radionuclide Removal from Aqueous Solutions: I

Hall D

Convener: Martine C. Duff, Westinghouse Savannah River Company

10:15-10:55 Abraham Clearfield*, THE USE OF CLAYS AND MICAS IN NUCLEAR WASTE REMEDIATION
10:55-11:15 Youjun Deng*, James B. Harsh, Markus Flury, Jeffrey Boyle, James Young, and Joseph Ford, INCORPORATION AND ADSORPTION OF CS IN ZEOLITIC MINERALS FORMED IN CONDITIONS SIMILAR TO THE UNDERLYING HANFORD WASTE TAN
11:35-11:55 Andreas Bauer*, Thomas Rabung, Francis Claret, Marcel Elie, Thorsten Schäfer and Thomas Fanghäne, INFLUENCE OF TEMPERATURE ON SORPTION OF EUROPIUM ONTO SMECTITE

Wednesday Afternoon, June 11, 2003

12:00-12:30 Clay Minerals Society Annual Business Meeting - Hall C

Role of Minerals in Natural and Mediated Environmental Restoration: II

Hall B

Conveners: Dean Hesterberg, North Carolina State University, Andreas Scheinhost Institute of Terrestrial Ecology, Zurich, Switzerland, and Richard J. Reeder, SUNY at Stony Brook.

1:30-1:50 Siddhesh Shevade*, Robert Ford, Phil Kaiser and John Wilson, UTILITY OF SYNTHETIC ZEOLITES IN REMOVAL OF INORGANIC AND ORGANIC WATER POLLUTANTS
1:50-2:10 Valentine Nzengung* and Seth Rameley, EVALUATION AND ENHANCEMENT OF NATURAL ATTENUATION OF CHLORINATED ORGANICS IN AQUIFER SOLIDS
2:10-2:30 Valentine A. Nzengung*, K.C. Das, James Kastner, John Dowd, CHALLENGES OF STIMULATING IN-SITU BIODEGRADATION OF PERCHLORATE IN CLAY-RICH SOILS
2:30-2:45 Coffee Break
2:45-3:05 Azza Wagdy and Alanah Fitch*, PLANAR WAVEGUIDES FOR CLAY SPECTROELECTROCHEMISTRY
3:05-3:25 Necip Güven* and Michael C. Cheshire, HYDROTHERMAL REACTION PRODUCTS OF CHRYSOTILE ASBESTOS

Mineral liquid crystals
Hall C

Convener: Jean Christophe P. Gabriel, Nanomix Inc.

1:30-2:00 Patrick Davidson*, LIQUID CRYSSTALLINE PROPERTIES OF MINERAL SUSPENSIONS
2:00-2:30 P. Levitz*, LIQUID-SOLID TRANSITIONS OF LAPONITE SUSPENSIONS: STRUCTURE, STABILITY AND JAMMING
2:30-2:45 Coffee Break
2:45-3:00 Laurent J. Michot, Isabelle Bihannic*, Katharina Porsch, Dominique Poly, Solange Maddi, Julien Mougel, Christophe Baravian, PHASE DIAGRAMS OF SODIUM WYOMING MONTMORILLONITE. INFLUENCE OF PARTICLE ANISOTROPY
3:00:3:15 Teruyuki Nakato*, and Nobuyoshi Miyamoto, LIQUID CRYSSTALLINE NATURE OF NIOBIUM OXIDE NANOSHEET SOLS PREPARED BY EXFOLIATION OF LAYERED NIOBATE K4NB6O17
3:15-3:40 Emmanuel P. Giannelis*, STRUCTURE AND DYNAMICS OF POLYMER NANOCOMPOSITES
4:05-4:25 David J. Chaiko*, THE LIQUID CRYSTAL BEHAVIOR OF ORGANOCLAYS

Application of Clay Minerals to Radionuclide Removal from Aqueous Solutions: II
Hall D

Convener: Martine C. Duff, Westinghouse Savannah River Company

1:30-1:50 Francis Claret*, Thorsten Schäfer, Andreas Bauer, Gunnar Buckau and Lise Griffault, IMPACT OF CLAYS/ORGANICS INTERACTION IN NUCLEAR WASTE DISPOSAL
1:50-2:10 Jeffrey G. Catalano*, and Gordon E. Brown, Jr., URANYL SORPTION ONTO MONTMORILLONITE: EFFECTS OF STRUCTURAL Fe(III), CARBONATE, AND INORGANIC ANIONS
2:10-2:30 Martine C. Duff*, Douglas B. Hunter, David T. Hobbs, Mark J. Barnes, Samuel D. Fink, Nancy L. Dietz and Jeffrey Fortner USE OF SYNTHETIC MONOSODIUM TITANATE AND Mn OXIDE FOR RADIONUCLIDE REMOVAL FROM HIGH-LEVEL WASTE SIMULANT
2:30-2:45 Coffee Break
2:45-3:05 David J. Chaiko*, NEW ORGANOCLAYS FOR THE REMOVAL OF TC FROM WATER

5:00-7:00 Special CMS/MSA Hartsfield Shuttle departs from Classic Center with pick-ups at the Foundry Park Inn (5:05 PM – W. Dougherty Street) and Holiday Inn (5:10 PM).

5:00-7:00 CMS Executive long range planning meeting. Foundry Park Inn, Hoyt House Private Room.

5:00-6:30 UGA reception for Vernon J. Hurst. Fire Hall, Classic Center.
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DENDRITIC SURFACTANTS SHOW EVIDENCE FOR FRUSTRATED INTERCALATION: A NEW ORGANOCLAY MORPHOLOGY

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Evidence for a new organoclay morphology described as frustrated intercalation is observed using a series of dendritic (branched) polymeric surfactants wherein the linear portion of the molecule bearing a cationic anchor penetrates into the interlayer of the clay leaving the branching portion exposed to solvent. For the smallest branched surfactant, complete intercalation of the organic component (5%-50% w:w) yields a variety of organoclay phases. Organic content is corroborated by UV spectroscopy and thermal gravimetric analysis (TGA). X-Ray powder diffraction (XPD) reveals increasing lattice spacings with increasing organic content. IR spectroscopy and TGA support an increasingly hydrophobic interlayer. For the larger branched surfactants displaying frustrated intercalation, the organic content does not exceed 20% (w:w) as determined by TGA. XPD reveals little difference in lattice spacing as surfactant is added. IR and TGA show that interlayer water is preserved. A linear isomer of a larger, branched dendritic surfactant, however, does intercalate into the clay (5-33%) yielding morphologies that depend on the amount of surfactant added supporting the hypothesis that shape – and not size – is important.
Evolving Trends in Specifications of Kaolin Used in the Paper Industry

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Over the last 25 years, there have been great changes in the characteristics of paper produced around the world. In this talk, the drivers for change are defined and the technical responses identified, some equipment-related but many depending on the minerals used as fillers or coating pigments.

We consider from a fundamental point of view the impact of ‘engineering’ mineral particles for size and shape on the important end-use properties such as gloss, brightness, and print quality. We then focus on three paper types: uncoated groundwood (SC), LWC/MWC offset (coated #5, #4, #3) and coated woodfree (CFS, #2, #1), detailing the changes in characteristics that have occurred over the 25-year period and understanding how this was achieved through new types of kaolin products.

Finally, we note that kaolin is now engineered to give optimum mineralogy, particle size, particle size distribution and particle shape, and that the optimum kaolin depends on the particular application (specific equipment, formulation additives etc). Nonetheless, the trends over the 25-year period can be summarised as brighter, finer, platter and steeper particle size distribution.
RECOVERY OF A LARGE (86.4 g) SPLASH-FORM TEKTITE FROM DODGE COUNTY, GEORGIA (USA)

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We report on the discovery of a large 86.4 g georgiaite from northern Dodge County, Georgia. It was found in a ploughed field, on the surface of the Miocene Altamaha Formation, in the spring of 2003. One of the authors (Trammell) purchased the specimen from the original finder. The tektite is an oval disk that exhibits a beautifully etched-sculpted surface. Its dimensions are 7.1 x 4.7 x 1.6 cm, and it has the characteristic translucent drab-olive color common to Georgia tektites. To date, this tektite is the largest “splash-form” georgiaite on record – surpassing a 70.5 g specimen found in the 1970’s. It is suggested that the georgiaites of the Altamaha Formation where deposited as a channel lag. The Altamaha Formation consists of fluvial channel cut-and-fill structures. These deposits include pebble to gravel-sized sediment or channel lag. If present in the deeper portions of a channel, tektites would accumulate with pebbles and gravel to form thin discontinuous lenticular patches. The 35.2 Ma age of the tektites requires that they were eroded from an upper Eocene parent stratum, transported downslope, and deposited with these younger sediments.
METAMORPHISM OF CLAYS IN HYDROTHERMAL ALTERATION SYSTEMS PRODUCE MINERALOGICAL ANOMALIES USEFUL IN MINERAL EXPLORATION

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Clay-rich assemblages are protoliths for aluminosilicate concentrations due to metamorphism. Research on a kyanite-rich deposit at Graves Mountain, Georgia, led to a search for an analog in geologically young geothermal and hydrothermal systems. The Otake geothermal system in Japan provides a classic model. The alteration pipe has been subdivided into five zones characterized by the following minerals: 1) silica (cristobalite and quartz); 2) alunite; 3) halloysite-kaolinite-dickite-pyrophyllite; 4) montmorillonite-sericite-chlorite; 5) heulandite-laumontite-wairakite-albite-adularia. The Na$_2$O and CaO in the glasses and feldspars of the original felsic volcanic rocks are leached by the hydrothermal system leaving an alteration system enriched in SiO$_2$, Al$_2$O$_3$, FeO, MgO, K$_2$O, TiO$_2$, MnO. If the hydrothermal system is a sulfide-rich ore-producing system, an addition of Mn, S, F, Be, PO$_4$, SO$_4$, Sn, Cu, Pb, Zn, Au is the norm.

Clays are excellent adsorbant for those cations and anions. The metamorphism of such an assemblage results in a suite of minerals rich in Al (pyrophyllite, andalusite, kyanite, sillimanite), rich in Al + Fe (chloritoid, staurolite, almandine), rich in Al + Mg (chlorite, anthophyllite, cummingtonite, cordierite, sapphire, phlogopite), and exotic minerals like nigerite, hogbomite, gahnite, tourmaline, dumortierite, kornerupine, topaz, rhodonite, bustamite, apatite, lazulite, rutile, barite, and many other rare minerals, which were formerly regarded as mineral curiosities but interpreted here as “mineralogical anomalies”. The exploration geologist, in his quest for the elusive ore deposit, can use the mineralogical anomalies with the same confidence as the more familiar geochemical and geophysical anomalies.
INTERACTIONS OF MINERALS WITH REAGENTS: USE OF SURFACE ANALYTICAL TECHNIQUES TO STUDY THE ADSORPTION OF POLYMERS ONTO MINERAL MIXTURES

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Reagents are critical to many industrial mineral operations. Reagent choices are often based on performance evaluations made using small-scale mimics of the unit operation of interest. This approach is undoubtedly a very effective way of screening existing reagents. However, in order to optimize reagent performance there is value in combining this approach with more fundamental measurements. In this paper we will present some work in which we have utilized X-ray photoelectron spectroscopy (XPS) to study the adsorption of polyacrylamide onto kaolin, quartz and feldspar. We will present some initial results from a study using conventional XPS techniques to study the adsorption of polyacrylamide onto separate samples of (i) kaolin particles, (ii) quartz particles and (iii) feldspar particles. These data establish the utility of the XPS technique for study of polymer adsorption onto this particular suite of minerals. We will then present data from a study that utilized small area XPS to characterize the competitive adsorption of polyacrylamide onto a mixed mineral system comprising kaolin and silica particles. Finally, we will present some initial results from atomic force microscopy and molecular simulation studies of reagent adsorption onto kaolin.
A white bentonite deposit of Pleistocene age located in San Juan Province, Argentina, was mapped and sampled in order to determine its extent, mineralogy, and physical and chemical properties. The bentonite occurs in the Lower Member of the Las Trancas Formation which is a hydrothermally altered rhyolitic to rhyodacitic pumice and breccia.

The major minerals present are smectite and opal along with minor amounts of quartz, clinoptilolite, feldspar and biotite. The majority of the quartz, clinoptilolite, and biotite occurs in the >325 mesh fraction. The smectite is mainly a sodium montmorillonite along with some calcium and magnesium in the exchange positions. The less than 5 micron fraction consist of almost pure smectite and opal CT. Scanning electron micrographs show a typical “corn flakes” texture, which is characteristic of sodium montmorillonite.

The physical and chemical properties including particle size, surface area, water and oil absorption, swelling index, cation exchange capacity, viscosity, and brightness indicate that this wet processed white bentonite could be used in many industrial applications. These include paper coating and filler, paint, pharmaceuticals, cosmetics, etc. Also the fine particle size fraction of less than 2 microns could be used to make an excellent quality organoclay.
ENHANCED CHEMICAL REACTIVITY OF GOETHITE (alpha-FeOOH) NANOPARTICLES

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Nanoparticle growth and phase transformations are critically important to the geochemical cycling of both natural and anthropogenic chemical species. Goethite (alpha-FeOOH) is a common and important mineral in the biogeochemical cycle of iron and other metals at the Earth's surface. Furthermore, this mineral commonly occurs as nanoparticles in the 3-10 nm size range (e.g., Penn et al., Geology, 2000). Goethite nanoparticles can be synthesized with a range of particle sizes, size distributions, and microstructures. Recent work demonstrates that the rate of redox using hydroquinone to reduce the goethite nanoparticles is strongly particle size dependent. For example, reactions using ~3.5 nm and ~30x350 nm goethite particles show that the rate of redox is 10-15 times faster (normalized to total surface area of the particles) in experiments using the smaller goethite nanoparticles. Results from high-resolution transmission electron microscopy, X-ray diffraction, low-temperature magnetometry, Mössbauer spectroscopy, and X-ray photoelectron spectroscopy of the synthetic goethite nanocrystals before and after reduction will be presented.
The temperature upon which thermodynamic data used for performance assessment purposes is based on is usually 25°C. However, in the near field environment of a spent fuel or vitrified high level waste repository the temperature will remain elevated for a long time period. Thermal calculations\textsuperscript{1} have shown that the temperature in the bentonite may attain 70-90°C under saturated conditions for 1000 years after repository closure. According to these calculations temperature then slightly decreases to 40-50°C after about 10,000 years, which is the expected life span for the canisters. For the Swedish KBS-3 concept temperatures for the bentonite backfill are calculated to reach up to 80°C at the inner boundary\textsuperscript{2}. After 1000 years temperatures are assumed to decrease to 40-55°C. From the above references it is apparent that there may be significant temperature differences for long time periods between thermodynamic standard conditions (i.e., T= 25°C) and the ones expected in the repositories. Therefore in this study the effect of temperature (20-80°C) on sorption of Eu(III) onto smectite was studied by wet chemistry, time resolved laser fluorescence spectroscopy (TRLFS), scanning transmission X-ray microscopy (STXM) and pyrolysis GC-MS.

The SWy-2 montmorillonite used in this study was purchased from the Source Clay Minerals Repository of the Clay Mineral Society. The < 1 µm size fraction was separated by sedimentation. The material was converted to the homoionic K form by thoroughly washing 10 times with 0.1 M KClO\textsubscript{4}. The experiments were carried out at 20°, 60° and 80°C as a function of pH in 0.1 M KClO\textsubscript{4}. High density polyethylene Zinsser bottles and quartz cuvettes with a solid/solution ratio of 2.5 g L\textsuperscript{-1} for the sorption experiments and 0.25 g L\textsuperscript{-1} for the TRLFS experiments were used. All experiments were performed under argon atmosphere.

The sorption edges for both types of reaction vessels and for any temperature are similar. At low pH the exchangeable sites of smectites, with predominant non-specific adsorption, are mainly occupied by K. Above pH 6 the K\textsubscript{D} for Eu(III) increases strongly. XRD measurements showed that the structure of the clay minerals did not change during the course of the experiment. The sorption mechanism of Eu(III) on smectite was studied by TRLFS. The fluorescence emission lifetimes contain information about the coordination sphere of Eu(III). Single component spectra with mono exponential decay behavior are found for all temperatures for both reaction vessels at pH < 4 corresponding to the Eu(III) aquo ion. At higher pH values and higher temperatures a different evolution for the different types of reaction vessels was observed. At 25°C (pH > 6) fluorescence emission lifetime of 190-200 µs were found for the two types of reaction vessels, corresponding to 5 waters in the first coordination sphere. At 60 and 80°C (pH > 5) the fluorescence emission lifetime increased significantly in the Zinsser bottles to 800-950 µs indicating a complete loss of water in the first coordination sphere. In the quartz cuvettes under the same conditions a lifetime of 190 µs was measured. DOC, STXM and GC-MS measurements showed a release of organic material from the Zinsser bottles at higher temperatures. Possible mechanisms and relevance to nuclear waste disposal will be discussed.

\textsuperscript{1} Johnson J. W., et al.. (2001) NTB Report 01-04, Wettingen, Switzerland.

IMPACT OF Fe/Zn RATIOS ON Zn(II) SPECIES FORMED IN NEUTRALIZATION SLUDGES

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The Canadian mine industry produces annually large volume of neutralization sludges that are disposed in ponds or co-deposited with tailings. In a previous project, Zinck et al. (1996) extensively characterized neutralization sludges from eleven Canadian mining sites. The results indicated that all sludges contained an important hydrated amorphous phase that was apparently effective in scavenging several heavy metals. However, the long-term stability of these metal species remains unknown. Among the different metals present, Zn was of concern because of its relatively high concentration in many sludges. Knowledge of detailed Zn speciation would help assess the long-term stability of Zn in the aged sludges. The objective of this study was to determine using a combination of studies on model systems and actual mine sludges the impact of Fe/Zn molar ratios on Zn(II) species formed.

An initial laboratory experiment was performed to characterize the Zn(II) species formed during co-precipitation with ferrihydrite at three Fe/Zn molar ratios, and using three different alkaline reactants (KOH, Ca(OH)₂ or Ca(OH)₂ enriched with carbonates). Results of x-ray absorption spectroscopy (XAS) analyses showed that co-precipitated samples of Zn with ferrihydrite yielded predominantly isomorphic substitution of Zn within the ferrihydrite at Fe/Zn = 100 and adsorbed Zn as inner-sphere surface complex at Fe/Zn = 10. In the presence of carbonates, Zn in excess of that co-precipitated or adsorbed on ferrihydrite was precipitated as Zn carbonate hydroxide.

Overall, the results from these modeled systems were consistent with our initial XAS analyses of Zn speciation in neutralization sludge. The XAS characterization of three types of mining sludges varying in Zn concentration (0.5 to 2200 mmol kg⁻¹) suggested that a mixed, poorly-crystalline Zn-carbonate/Zn-hydroxide mineral was dominant in two sludges with relatively low Fe/Zn molar ratios. In the sludge with the greatest Fe/Zn molar ratio, Zn adsorbed on non-crystalline iron oxide minerals was also significant.

The Zn speciation data provide insight that can help project how changes in chemical conditions may affect changes in sludge chemistry, thereby influencing Zn mobility and waste management strategies. For example, if Zn mainly occurs as carbonate or hydroxide species, then moderate acidification of the sludge would potentially release Zn. Therefore, co-disposal of sludges with acid-generating tailings is not advisable. On the other hand, if Zn species bound to Fe-oxide minerals are dominant, then Zn could be remobilized under reducing conditions, unless Zn-sulfide formed. These issues should be considered when using water cover as a disposal option for the sludge.

Reference:
POLISHING WITH SELF-ASSEMBLED SURFACTANT MEDITAED DISPERSION OF NANOPARTICULATE SYSTEMS

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Dispersion of nano particles is very crucial in many industrial systems of today. Surfactants have been used for dispersion in many of these processes for a long time. The processing conditions and the hydrophobicity of the particles dictate the scheme of reagents to be used in each of these systems. Dispersion by surfactants has been attributed to the formation of surfactant structures at the interface. The concentration and chain length of these molecules are known to affect the different kind of structures formed at the interface.

Rapid advances in the microelectronics industry demand a very thin layer of material removal with atomically flat and clean surface finish during manufacturing of microelectronic devices. Chemical Mechanical Polishing (CMP) is the technique that is applied to planarize the wafer surfaces by using slurries made of ultrafine (nanosized) particles and chemicals. In CMP an abrasive particle is pressed against the wafer surface at forces that are at least an order of magnitude greater than commonly experienced in colloidal suspensions. Description of the lateral and normal force during this interaction is critical to the determination of polishing mechanisms. The origin of these forces was explored through techniques such as adsorption, contact angle, zeta potential, and polarized Attenuated Total Reflection Fourier-Transform Infra-Red Spectroscopy (ATR-FTIR). The roles of the solution pH and salt concentration as well as the force barrier introduced by the self-assembled surfactant structures on material removal were studied. The results of the normal force and friction analyses were correlated with the polishing measurements. The findings of this investigation assisted in determining the necessary conditions that can lead to enhance CMP performance and develop criteria for selecting ideal dispersant systems to stabilize nanoparticulate systems in severe environments.
USE OF NANOPARTICULATE METAL OXIDES IN THIN FILM DEVELOPMENT FOR PHOTOCATALYTIC WAVEGUIDES

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Aqueous sol-gel techniques allow us to create metal oxide thin-films with tailored physical-chemical attributes. Nanoparticulate sols are coated onto substrates, forming ceramic thin films that have unique surface characteristics such as high specific surface areas, nanoporosity, tailorable surface charge, and a range of semi-conductive or electron-insulative properties. Since these nanoporous oxide materials possess high surface areas, which often exceed 300 m²/g, these materials can serve as effective absorbents in both the gas and liquid phase. Our current work involves developing UV transparent waveguides for photocatalytic oxidation systems. These systems are designed for the treatment of wastewaters contaminated with both organics and arsenic. Polymethylmethacrylate (PMMA) could serve as an effective substrate material, transparent in the wavelength range necessary for photoactivation of anatase (TiO₂). However, the nonpolar nature of PMMA inhibits uniform thin film coatings and the material has a relatively low melting point relative to most metal oxide sintering temperatures. Pre-coating the substrate with an acidified silica undercoat provides both a uniform pre-coat and an electron-insulating barrier between the substrate and photocatalyst. The undercoat is then followed by deposition of a photoreactive anatase surface film. Theses particles are effectively sintered by low-temperature heating and UV treatment. PMMA can be effectively coated with our metal oxides via spray coating and dip coating techniques yielding a durable ceramic coating. We have developed methods for characterizing the thin films via reflective light microscopy, contact angle measurements, ellipsometry, and profilometry.
Newton thought that in the beginning God had made matter by forming atoms with detailed properties that “most conduced to the end for which He had formed them”. Current anthropic cosmology agrees with the apparent contrivance. Atoms are indeed complicated objects, as they have to be for strong durable covalent bonds to be made and unmade between them. The atoms of chemistry can be seen as units of a wonderful construction kit from which all the materials around us are formed. There are two well-recognised systems of joinery within the atomic construction kit. Living materials make use of the fact that some atoms, critically carbon, can be joined up with each other precisely to make molecules of enormous complexity. Most durable minerals depend rather on bonds between oxygen on the one hand and silicon and/or small metal atoms on the other. But it is too simplistic to assign these molecule-making and crystal-making systems to the living world and the mineral world respectively. There are strong bonded crystalline materials — “minerals” — to be found within organisms, while the formation of minerals, especially clay minerals, may be as much a polymerisation as a crystallisation. In any case the mineral and organic worlds are interwoven, as the thriving subject of geomicrobiology makes increasingly clear.

Strong bonded minerals are generally seen to play only a passive role in medicine. This may change. Line Brunet de Courssou has successfully used the humble clay poultice (illite or montmorillonite) to treat a horrifying flesh eating disease in Africa caused by Mycobacterium ulcerans (a relative of the causative agents of tuberculosis and of leprosy). Possible mechanisms of the action of these clays will be touched on.

Are there such things as mineral antibiotics — clays for example? What general properties might they have? How would we make them? Clay minerals are much more difficult to synthesise precisely with every atom where you want it than are organic molecules: because they form through a kind of self-assembly there is less scope for design. That is the bad news. The good news, although far on the horizon, is that there is a particular frequent feature of layer crystals — a variable stacking sequence — that tends to propagate through crystal growth, and this might provide a means of producing particular, complex stacking sequences in quantity. In this connection I will touch on a speculation about the origin of life on Earth.

**Selected bibliography**


ILLITE ADSORPTION OF TOXIC CATIONS FROM CONTAMINATED AZNALCÓLLAR SOIL (SPAIN)

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Metal cations release from contaminated Aznalcóllar soil (South-Spain) is studied as a function of solution pH. Amounts of 15 and 25 Tm per ha of synthetic NaP1 zeolite were added to the upper part of the contaminated soil (Moreno et al., 2001). As 5% (wt.) of raw NaP1 zeolite is made of NaOH (Cama et al., 2002) the lixiviation of the zeolite/soil mixture makes the pore-water pH increase from 3.5 to 7.5 as sodium hydroxide dissolves. As the pH increases the high metal concentrations in the leaching solutions sharply decrease. The cation exchange capacity of the zeolite accounts for the aqueous metal remove. However, one of the clay minerals that made up this soil, illite, has the capability to adsorb metal cations. Also, pH increase may be responsible of Al and Fe depletion due to formation of aluminum and iron hydroxide phases, which in turn, may adsorb aqueous metals circulating through the soil. In the present communication we study the adsorption capacity of illite to retain the toxic cations in solution by conducting batch experiments with Aznalcóllar soil suspensions. The presence of 20% of illite in the contaminated soil adsorbs the divalent cations. Complexation of metal surface species (=SOM⁺) and deprotonation of amphoteric sites of illite (=SOH) are the surface reactions considered to be responsible for the metal uptake.

References:


ABIOTIC ORGANIC SYNTHESIS IN CLAYS AT HYDROTHERMAL VENT CONDITIONS

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If life on earth first emerged from the depths in hydrothermal vent systems, a necessary prebiotic era of chemical evolution and accumulation of organic matter must have preceded. Catalytic properties of clay minerals are industrially relevant and have been examined under a wide variety of conditions. However, these properties are not well characterized for hydrothermal vent environments, where clays naturally occur and may have been key in a prebiotic era.

Reactions of saponite, montmorillonite, and illite with methanol have been examined under simulated seafloor and subseafloor volcanic conditions (300°C, 1 kbar). In this environment the dioctahedral montmorillonite quickly reacts to illite, while the trioctahedral saponite is unreactive. Reaction progress has been monitored through hydrothermal experimentation in welded gold capsules for up to 5 weeks, with specific attention on the first week of reaction, during which the most rapid reaction of montmorillonite to illite occurs.

Methanol, the precursor organic molecule in the experiments, has been shown to react to a variety of complex classes of molecules including \( n \)-alkanes, \( n \)-alkyl-benzenes, \( n \)-alkyl-naphthalenes, \( n \)-alkyl-phenols, \( n \)-alkyl-naphthols, and long-chain methyl esters. While producing some similar organic product molecules, reactions starting with pure illite yielded significantly lower product concentrations than those with the smectites. Although similar investigations have assigned the catalytic properties of clays strictly to the surfaces, our observations indicate that the expandable interlayers of the smectite clay minerals provide additional sites for catalytic reaction producing different products.
IMMOBILIZATION OF CYTOCHROME C BY MESOSTRUCTURED SYNTHETIC CLAYS

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The enzymatic transformation of soil, sediment, or groundwater contaminants, whether organic or inorganic, may be mediated by immobilization of the enzyme onto a support such as a clay. The utility of various hectorite clay matrices for the preparation of catalytically active enzyme composites by simple sorption processes was examined. The hectorites compared include commercially available Laponite RD, mesostructured synthetic hectorites (both with and without a template present), and a surface-modified mesostructured hectorite using silanes. The composites were evaluated by the amount of cytochrome c that was incorporated within the matrix and the fraction of active enzyme measured in the composite. The quantity of sorbed cytochrome c was determined by optical absorption spectroscopy of the supernatant solution and by thermal gravimetric analysis (TGA) of the prepared composites. Typical enzyme densities were on the order of 20-40 wt%. The enzyme density determined by TGA was often more conservative than the indirect determination by optical absorption. There was no correlation between wt% loading and either the surface area or the pore volume of the matrix. Rather, other characteristics such as surface compatibility appear to play the major role in this regard. Immobilized enzyme activity was examined qualitatively by EPR and quantitatively by chemical reduction. These experiments revealed the effects of organo-tailoring of the inorganic matrices in terms of steric hindrance of enzyme in active conformation and denaturation within a clay pore microenvironment.

Acknowledgement: This research was performed under the auspices of the U.S. Department of Energy under contract #W-31-109-ENG-38.
URANYL SORPTION ONTO MONTMORILLONITE: EFFECTS OF STRUCTURAL FE(III), CARBONATE, AND INORGANIC ANIONS

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Smectites are common soil constituents at US Department of Energy sites like Hanford, WA. They are a potentially important sorbent of uranium(VI) and other radionuclides released during leakage of high-level waste. Surface complexation modeling (e.g., McKinley et al., 1995) and EXAFS studies (e.g., Hennig et al., 2002) of uranyl sorption to montmorillonite have indicated that under near-neutral conditions, U(VI) adsorbs primarily to aluminol edge sites. However, most studies to date have used Fe-poor montmorillonites (SAz-1 and STx-1); the possibility of adsorption onto potentially more reactive iron edge sites has not been considered.1,2 Additionally, most spectroscopic studies have been done in CO2-free systems, and only with NaNO3 as the background electrolyte. The design of these studies precluded the formation of ternary surface complexes containing carbonate and common inorganic anions.

In this study, we have used EXAFS and ATR-FTIR spectroscopies to investigate the adsorption of U(VI) onto montmorillonite, with a focus on complexation at edge sites. In the first part of our study, we have examined U(VI) adsorption onto the Source Clay smectites SAz-1 (low-Fe), SWy-2 (medium-Fe), and SWa-1 (high-Fe), as well as on hematite, which serves as a useful model compound for an Fe-rich octahedral layer in Fe-rich smectites. EXAFS spectroscopy suggests that U(VI) has a higher affinity for Fe edges sites than for Al edge sites.

In the second part of our study, we have examined the effects of dissolved carbonate on uranyl surface complexation on SWy-2. EXAFS spectroscopy demonstrates that dissolved CO2 has little effect on uranyl surface complexation at low pH, where cation exchange is dominant. However, at higher pH, edge-site uranyl surface complexes appear to be type-A ternary complexes with carbonate. Unfortunately, carbonate and nitrate cannot be distinguished by EXAFS; ATR-FTIR spectroscopy results will be presented to clarify whether carbonate, nitrate, or both are contained in the uranyl surface complexes.

Finally, we have examined the effect of common inorganic anions on uranyl surface complexation on SWy-2. EXAFS spectroscopy was used to evaluate the possible formation of uranyl ternary surface complexes containing the traditional “indifferent” background electrolytes nitrate, chloride, and perchlorate, as well as sulfate and phosphate. Detailed analysis of EXAFS spectra from these systems suggests that ternary complexes are formed in all cases. ATR-FTIR spectroscopy results of the oxoanion-containing systems will be presented as well.
NEW ORGANOCLAYS FOR THE REMOVAL OF TC FROM WATER

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Amine-treated montmorillonite clays have been used as a low-cost medium for the
removal of oil and grease from water. The clay surface is treated with a long-chain amine to
render the surface hydrophobic. They typically can absorb about 50% of their weight and are
less expensive than activated carbon. Treatment below the exchange capacity of the clay allows
co-extraction of cationic metal species. A new class of self-activated organoclays has been
developed at Argonne with absorption capacities 2-4 times greater than conventional
organoclays. The organoclays are prepared by treatment with long chain amines at loadings
slightly below the exchange capacity of the clay and are self-activated by co-adsorption of
hydrophilic polymers. Their ability to extract humates, pertechnetate, and perchlorate from
ground water will be discussed.

Work supported by the U.S. Department of Energy, Office of Nuclear Energy, Science and
THE LIQUID CRYSTAL BEHAVIOR OF ORGANOCLAYS*

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The proper design of surfactant coatings used to make nanoclays remains a critical technical/economic challenge to the commercial production of light-weight, engineered plastics for high-volume applications. Surfactant treatment alone has not been very successful in promoting clay exfoliation in hydrophobic polymers like the polyolefins. A popular approach has involved the use of functionalized oligomers to aid exfoliation. However, it is becoming clear that exfoliation alone does not guarantee a nanocomposite with significant improvement in mechanical or barrier properties. In many ways, onium-treated clays bear a strong resemblance to the lamellar liquid crystal (LLC) phases of oil/water/surfactant systems. The thermodynamic factors which affect the behavior of LLC phases also influence the swelling and dispersion of organoclays. A basis for the design of self-dispersing organoclays providing improved barrier and mechanical properties in polyolefins will be presented.

EFFECTS OF SAMPLE HANDLING (AIR-DRYING) ON SORPTION OF ATRAZINE BY SOILS AND CLAYS

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The influence of sample handling (air-drying) on atrazine sorption by a reference smectite and three smectite-dominated soils was investigated. Surface horizon samples of three soils (Sparta, a sandy, mixed, mesic Entic Hapludoll; Sperry, a fine, smectitic, mesic Typic Argialboll; and Zook, a fine, smectitic, mesic Cumulic Vertic Endoaquoll) with clay fractions dominated by smectite were collected and stored in sealed containers at 4°C without drying. Portions of these soil samples were air-dried. A batch equilibration technique was used to determine atrazine sorption affinity. Both the moist and air-dry samples were suspended in 10 mM CaCl$_2$ for 24 hrs. Afterwards, atrazine was added and the suspensions were allowed to equilibrate for another 24 hrs. Freundlich sorption constants, K’$_F$ (adjusted for the water-solubility of atrazine), were less for the air-dry Sparta and Zook samples than for the moist Sparta and Zook samples. The air-drying treatment had no effect on K$_F$ values for the Sperry samples.

The effects of air-drying on K- and Ca-saturated Panther Creek (PC) smectite were also studied. Separate samples of Na-saturated PC (<2 µm) were K- or Ca-saturated by dialysis, first against 0.2 eq L$^{-1}$ KCl and CaCl$_2$ solutions and then against 10 meq L$^{-1}$ KCl and CaCl$_2$ solutions, respectively. The cation saturation process took 3 weeks. Sample handling effects were tested either by keeping the homoionic PC in the 10 meq L$^{-1}$ suspension (moist) or by air-drying and then resuspending the homoionic PC samples in 10 meq L$^{-1}$ KCl or CaCl$_2$ solutions (dry) for seven days. Air-drying the clays increased the atrazine distribution coefficient, K$_D$, by approximately one order of magnitude for both K- and Ca-PC. Before atrazine addition, x-ray diffraction analysis of the clay suspensions showed that the air-dry treatment decreased both basal-plane d-spacings and the size of coherently diffracting domains for the PC clay. Our results suggest that hysteresis induced by air-drying regulates the physical organization (hydrated phase) of smectites, which in turn influences atrazine sorption affinity. A similar sample-handling effect also appeared to alter the affinity of the soil samples for atrazine. However, the physical state of soil organic matter could also be affected by air-drying. Thus, there may be multiple causes for the effect of air-drying on atrazine sorption by soil materials.
Perhaps the most outstanding property of finely divided substances is the tremendous surface-to-mass/weight ratio which they possess. With the ever-increasing research and development in nanomaterials, the precise determination of particle size is crucial in material research. Small particles such as clay minerals, because of its large surface area to volume ration and their high chemical activity on the particle surface, when added to composites affects (and often enhances) the physical, chemical and mechanical properties of materials immensely. There lies a need to develop a method of characterizing these particles individually. Although there is a wealth of literature in scientific and technical journals on methods for determining the size of particles, the study of size analysis of small particles using TEM is few and far between. This is due to the difficulty in observing tiny particles with large surface area to volume ratios and their high chemical activity on the particle surface. Dispersants of various sorts could be used to stabilize the system, but specimens also tend to form aggregates when they dry either in the air or vacuum. The key to size analysis lies within keeping the particles well dispersed in nature (wet or specific liquid environment). This paper presents the in situ study of particle size using special environmental cell (EC) TEM and cryo-TEM techniques.

Two types of materials, both non-clay minerals as well as typical clay minerals are presented in this paper. (1) Surface-modified fume silica were dispersed in H$_3$C(OC$_2$H$_4$)$_4$OCH$_3$ (tetraglyme). (2) Smectite clay minerals from different locality were purified and dispersed in de-ionized water with a very small amount of (NaPO$_3$)$_6$ as the dispersion agent. This suspension acts as a base solution for different methods for the comparison purpose. In addition to the conventional sedimentation-air drying method, a special environmental cell (EC) technique and cryo quick freeze method were carried out for in situ observation of small particles in liquid environment.

Smectitic clay particles normally show thick aggregates and often without any distinguishable morphology in a conventional TEM. The very low dispersion ratio is resultant of preferred orientation of platy clay particles and surface chemistry of clays. By using EC technique, however, well-dispersed clay and non-clay particles in the liquid medium can be clearly observed. The flaky morphology of montmorillonite observed in the EC indicates the platelet nature of clay particles “floating” in the water inside EC. On the other hand, the cryo quick freeze method that robbed settlement time of particles also depicts the well-mixed clay orientation. Both in situ techniques not only enables us to have a 3-D imaging of the clay particles but also provides the thickness information and thus the aspect ratio of clay particles that would be very difficult to measure otherwise. Furthermore, while cryo-TEM offers dispersed clay distribution with mixed/random orientation of clay particles, EC-TEM provides dynamic in situ observation of individually dispersed (clay) particles in the liquid environment.
IMPACT OF CLAYS/ORGANICS INTERACTION IN NUCLEAR WASTE DISPOSAL

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Deep geological disposal in clay rich formations of low organic matter (OM) content (~1% carbon in weight) is favored in several countries, e.g. Switzerland (Opalinus clay) and France (Bure argillite). Physical and chemical perturbations of the disposal near field will occur due to the shaft excavation (OM oxidation), the nature of the waste (elevation in temperature for high level waste) and introduction of geotechnical barrier and waste package material. Disposal of intermediate level waste will introduce large amounts of cement as waste package material. Cement dissolution will lead to high alkaline conditions in the near field. Under high alkaline conditions, high concentrations of dissolved organic carbon (DOC) are released, and an increase of oxygen containing functional groups within the DOC is observed [1]. In order to get assignments on these released DOC, spectroscopic techniques such as ultraviolet-visible (UV/Vis), Fourier-transform infrared (FTIR) and fluorescence spectroscopy have been used. First results indicate that this alkaline plume could be an important source for highly mobile metal complexing humic and fulvic acids influencing the radionuclide mobility in a nuclear waste repository [2].

Moreover, in high pH solutions the clay mineralogy (Bure argillite) was not affected over the observation period of two years, contrary to analogues studies in pure smectite systems [1,3]. C (K-edge) and K (L2, L3 edge) NEXAFS investigations using scanning transmission X-ray spectromicroscopy (STXM) show passivation of clay reactive sites by sorbed organic matter, even after two years in alkaline solution. This leads to kinetic hindrance in clay mineral dissolution [1,4].

A detailed understanding of the clay-OM association is prerequisite for reliable predictive modeling. The difference in burial history of the above mentioned host rock formations should influence the initial clay-OM association and consequently the chemical transformational of OM release. For this purpose, initial rock samples, are additionally studied on the by C (K-edge), K (L2, L3 edge) STXM in order to get a selective chemical and mineralogical mapping.

THE USE OF CLAYS AND MICAS IN NUCLEAR WASTE REMEDIATION

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We have prepared alumina silica and zirconia pillared montmorillonite as possible exchangers for removal of $^{137}$Cs and $^{90}$Sr from highly alkaline waste solutions. The pillaring process inserts inorganic polymers between the layers which props open the layers. This process, after calcinations at 500°C, converts the two-dimensional clay mineral to a three-dimensional porous ion exchanger. Surface areas from 160-290 m$^2$/g were obtained. These pillared clays were highly effective in removal of Cs$^+$ from groundwater simulants but less effective in strong base. The most effective interfering ion is K$^+$ but alkaline earths did not interfere. The zirconia pillared clay was the most effective sorbent for Cs$^+$ removal. The silica pillared clay gave the best results for Sr$^{2+}$ uptake in a particular Hanford site stimulant (pH>14).

A sodium mica, prepared from K-phlogopite, was highly selective for Cs$^+$. As the Cs$^+$ uptake increased to about half the exchange capacity, the mica layers were pulled together to trap the Cs$^+$ and prevent further exchange. The potential for such micas and pillared clays in actual remediation situations will be discussed.

DETERMINATION OF THE ENTHALPY OF HYDRATION OF CLAY MINERALS UTILIZING SOLUTION CALORIMETRY

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The process of hydration refers to the interaction of water molecules with solute molecules. When each individual particle is removed from the solute mass and becomes completely separated and surrounded by water, the solute is hydrated. This process is accompanied by a release/absorption of energy, referred to as the enthalpy of hydration (\( \Delta H_{\text{hyd}} \)). The process of hydration can be thought of as three separate processes each of which has a specific enthalpy. The first contribution to the enthalpy of hydration is the separation of the solute particles (\( \Delta H_1 \)). The solvent molecules must also be separated (\( \Delta H_2 \)). The final phase of this process is the interaction between the separated solute and solvent molecules (\( \Delta H_3 \)). Each of the first two processes are endothermic (\( \Delta H_{1,2}>0 \)) and the last is exothermic (\( \Delta H_3<0 \)). If the overall process of hydration is exothermic, the final interaction between solute and solvent particles is the predominant process.

Enthalpies can be determined using a variety of techniques. These are generally referred to as calorimetry. All calorimetric processes relate a temperature change to the energy associated with a specific process. Solution calorimetry examines processes that occur in the liquid phase.

This research is specifically interested in the application of solution calorimetry to the determination of the enthalpy of hydration of montmorillonite clays. Five standard clays from the Source Clays Repository are being analyzed; SHCa-1, SWy-2, STx-1, SAz-1, SCa-3. In addition to the sodium form, each is being exchanged with potassium, magnesium, aluminum, and calcium. Each of these cations has a different hydration sphere and each will have a different hydration energy. The clays are all pretreated and saturated with the desired cation. After dialysis, each clay sample is dehydrated at 130°C. This temperature is sufficient to drive off all adsorbed water but is moderate enough to prevent the removal of structural water.
Dissimilatory metal reducing bacteria (DMRB) can either directly mediate or indirectly induce geochemical processes that alter the speciation and lability of metallic contaminants within natural environments. Most investigations into the effect of DMRB on metal speciation utilise synthetic iron oxyhydroxide minerals as the Fe(III) source, thereby allowing well-controlled experiments. However, this technique does not emulate the actual mineralogical composition of natural systems – and does not account for the effect of clay minerals that may control metal geochemistry within environmental systems. Our experiments with a model divalent metal that is subject to both surface complexation and ion exchange reactions (Zn$^{2+}$) indicate that DMRB-induced changes in metal speciation are quite different for clay minerals than for iron oxyhydroxide minerals.

These data demonstrate that microbial Fe(III) reduction alters the proportion of Zn-aq in slurries containing goethite and hydrous ferric oxide (HFO), but has little effect in parallel slurries containing selected iron-bearing natural sediments. These data also indicate that microbial goethite and HFO reduction increases the proportion of HCl-insoluble Zn while microbial reduction of Fe(III) in natural sediments has virtually no effect on HCl-insoluble Zn. XAS data indicate that the Zn$^{2+}$ bonding environment in an Fe-bearing clay sediment changes significantly as microbial iron reduction proceeds, while corresponding shifts are not seen in experiments where goethite provides the Fe(III) source. These observations can be explained by a conceptual model, whereby Zn is released from surface complexes (via Fe-reduction) and then reacts with ion exchange sites on clay mineral surfaces in natural sediments. This process can prevent net solubilization of Zn, and prevent Zn from participating in the surface reactions that occur in the corollary experiments with pure iron oxyhydroxide minerals. These results indicate that metal mobility predictions based on microbial experiments with synthetic Fe-oxide minerals may have limited applicability to “real world” systems.
The need for quantitative determination of mineralogy is widespread throughout nearly all subdisciplines of the geological sciences. We developed a method of determining the abundance of kaolinite and alunite in drill core using visible and near-infrared reflectance spectroscopy (VIS-NIR) calibrated through the analysis of natural samples and artificial mixtures using a modified version of the powder X-ray diffraction method of Srodon et al. (2001) and the RockJock computer program (Eberl, 2003). We collected VIS-NIR spectra of diamond drill core and cuttings at consistent intervals in 207 drill holes at the Cerro Colorado and Spence porphyry copper deposits in northern Chile. Representative core samples were collected in the field and then characterized in the laboratory by cutting small 2 x 2 cm chips, collecting VIS-NIR spectra along all flat surfaces of the sample, and then collecting spectra of the same samples after they had been powdered in a mortar and pestle. The quantitative mineralogy was subsequently determined using powder X-ray diffraction, and these results were used to construct a computational model to predict alunite and kaolinite abundance in unknown samples.

Several approaches to construct a quantitative model give acceptable results. The simplest and fastest computational model uses either the depth or integrated area of diagnostic NIR absorbance peaks to predict abundance of constituent minerals. However, overlapping bands contribute to variable levels of inaccuracy in this approach. Superior results can be achieved through a chemometric model that uses partial least squares regressions between reflectance spectra and the X-ray diffraction results. We show that our model accurately predicts alunite and kaolinite abundance in natural samples.

Once a robust correlation model is constructed, the quantitative data can be integrated into a 3-D geologic model that facilitates interpretation of the distribution, abundance, and formation of these minerals. We consider that this approach is a rapid, accurate, and reproducible method to quantify mineralogy, and it can be used to improve the quality of mapping-based research in a variety of geological environments.

References:


LIQUID CRYSTALLINE PROPERTIES OF MINERAL SUSPENSIONS

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Although the vast majority of liquid crystals are organic compounds, there are a few minerals (akaganeite, boehmite, gibbsite, goethite, imogolite, montmorillonite clays ...) that also form liquid crystalline phases [1]. These phases are comprised of rod-like, disc-like or ribbon-like mineral moieties dispersed in a solvent, usually water. The most frequent liquid-crystalline phase is the nematic one in which the anisotropic moieties are all aligned in a common direction but their positions are more or less randomly distributed. The nematic phase is therefore both fluid and anisotropic (birefringent). This orientational ordering phenomenon has important consequences: For instance, the mechanical properties of the material are deeply affected since the nematic phase is strongly shear-thinning. Moreover, liquid-crystalline phases can orient their preferred axis when submitted to a magnetic or an electric field. This effect is at the basis of the use of liquid crystals in display technology. A few mineral liquid crystals are indeed sensitive to a magnetic (or electric) field which provides us with a unique opportunity to rotate at will the suspended anisotropic moieties by a purely external non-invasive action. In fact, aqueous suspensions of goethite nanorods form a nematic phase that has the most spectacular magnetic properties ever reported for a liquid crystal [2].

MÖSSBAUER PHASE ANALYSIS OF AN AMENDED SOIL


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Fe oxides and oxyhydroxides are believed to control P sorption, P availability and to a certain extent P losses in many agricultural soils. In general, the chemical forms of the Fe present in a soil are governed, among others, by the soil redox conditions and by microbial activity. The effects of these parameters on the Fe mineralogy and P availability are being examined in detail for the grass-land soils of two in-field study sites located in the vicinity of Zurich as part of the program “Remediation of grass land soils over-fertilized with phosphorous”. Since 57Fe Mössbauer spectroscopy is a unique tool to identify and quantify Fe phases present in a natural environment, this technique forms a useful compliment to the more conventional experiments within the framework of mentioned project.

A soil from the field was amended with two different amounts (4 and 50 g Fe/kg soil) of Ca(OH)2 and Fe(II) (as an FeSO4.7H2O solution). After the addition of these chemicals, samples of the non-amended and amended soil were subjected to incubation in the laboratory for eight weeks. For each treatment a sample was incubated under aerobic conditions, anaerobic conditions, and switching aerobic to anaerobic conditions and back every two weeks. Also, for each of these incubation processes sterilized (using γ-radiation) and non-sterilized samples were obtained. This brings the total number of samples to eighteen. For each of these samples, Mössbauer spectra (MS) were collected at room temperature (RT) and 80 K, and selected samples were also measured at ~15 K. The presence of hematite, goethite, an unidentified, mixed Fe2+/Fe3+ phase (probably a clay mineral), and a poorly crystalline Fe oxide was recognized. The latter phase is attributable to ferrihydrite. A major effect is noticed for the highest amendment rate, which clearly produces a drastic increase in the amounts of goethite/ferrihydrite relative to the amounts of hematite and the mixed Fe2+/Fe3+ phase. Apparently, the added Fe2+ cations are converted to these hydrous Fe oxides that were already present in the parent soil. Sterilization has no measurable influence on the partition of Fe among the various phases. An exclusively anaerobic incubation obviously hinders the conversion of the added Fe(II) salt to hydrous Fe oxides, but simultaneously seems to promote the crystallinity of these oxides that do form.
INCORPORATION AND ADSORPTION OF CS IN ZEOLITIC MINERALS FORMED IN CONDITIONS SIMILAR TO THE UNDERLYING HANFORD WASTE TANKS

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Several zeolite or zeolitic feldspathoids have been found in Hanford sediments reacted with solutions simulating the high-level radioactive wastes stored in the underground tanks at the DOE Hanford site. The new mineral phases, especially the colloid fraction, may facilitate the transport of radioactive nuclides, such as cesium-137 from the tank solutions, in the vadose zone. Cancrinite, sodalite, Linde Type A (LTA) zeolite and allophane have been found in our previous experiments when no cesium was present in the initial solutions. The objective of this study is to investigate: (1) the effect of the presence of cesium on the mineral types formed; (2) the distribution of adsorbed and incorporated cesium in zeolite and zeolitic feldspathoids; and (3) the chemical environments of adsorbed and incorporated cesium.

The feldspathoids and zeolite formed in the presence of Cs⁺ were analyzed with X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and room temperature solid state NMR. The presence of Cs⁺ in the simulated solutions did not affect the types of minerals formed in 1 M NaOH solutions until the Cs⁺ concentration was greater 0.1 M. A concentration is not likely to occur in the sediment underlying the Hanford tanks. Elemental mapping indicated that incorporated Cs⁺ is homogeneously distributed in cancrinite and sodalite. High concentrations of Cs⁺ promoted the formation of highly crystalline cancrinite in hexagonal bar shape. The presence of Cs⁺ in solutions precluded the influence anions have shown in the non-cesium system. The presence of chloride anion is favorable for the formation of pure sodalite in a non-cesium solution, yet no sodalite has been found in the precipitates formed at high Cs⁺ concentration (0.5 M).

Adsorption experiments indicated that Cs⁺ can access the internal parts of LTA, cancrinite and sodalite, but the diffusion appeared more difficult than that of Na⁺ and K⁺. Cesium exchange in cancrinite and sodalite caused structural disordering of the minerals as reflected by the XRD patterns. Incorporated and sorbed Cs⁺ showed 40 ppm chemical shifts on the ¹³³Cs NMR patterns of LTA, indicating different chemical environments. Similar shifts were observed on cancrinite and sodalite lepispheres. We speculate that the adsorbed cesium is located in the larger α cages of LTA zeolite, while the incorporated cesium is present in the smaller β cages. Cesium cannot migrate from one cage type to the other due to the size of the cesium ions. For the same reason, incorporated Cs⁺ cannot be easily replaced by other ions (e.g. Ca²⁺ or K⁺). Incorporating or adsorbing Cs⁺ did not distinctly shift the peak position or split the peak of ²³Na NMR. This can be the result of the high motion of Na⁺ ions and water molecules inside the cages or channels, which averages out the chemical environment of the ions. Low temperature ¹³³Cs and ²³Na NMR will be preformed to pursue the detailed assignments and analysis on the chemical environments of the cations inside the minerals.
MINERAL PHASE TRANSFORMATION IN CONDITIONS MIMIC SEDIMENT SOLUTIONS UNDERLYING LEAKED HANFORD WASTE TANKS

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High-level radioactive waste solutions stored in the underground tanks at the DOE Hanford site have leaked into the vadose zone. Feldspathoids and zeolites have been found when simulated tank solutions reacted with the sediments. The objective of this research is to systematically study the mineralogy changes of the precipitates formed in a series of simulating Hanford tank waste solutions reacted with dissolved silicate from sediments.

Pure sodium silicate was used to represent the dissolved silicate from the sediments. Sodium aluminate was added to the silicate solution in the presence of different salts including sodium nitrate, sodium nitrite, sodium carbonate, sodium phosphate, sodium sulfate and sodium chloride. Most experiments were carried out at 80 °C. The precipitates were periodically monitored by X-ray diffraction, scanning and transmission electron microscopy, and Fourier transform infrared (FTIR) spectroscopy.

Allophane, Linde Type A zeolite, cancrinite and sodalite formed depending on the experimental conditions. It appears that amorphous allophane first formed at lower OH concentrations (<8 M) and then converted to Linde Type A (LTA) zeolite. The anions added played an important role in the transformation of crystalline phases. When nitrate or sulfate appeared in the 1 M NaOH system, LTA zeolite fully converted to lepispheric cancrinite/sodalite within four weeks. Pure cancrinite formed in the presence of Na2SO4 after 32 weeks of reaction. Smaller particles were observed in precipitates formed in 4 M and 8 M NaOH. Nitrite or chloride salts slowed the transformation of LTA zeolite to other minerals. Pure sodalite formed after 32 weeks reaction in the presence of NaCl. Carbonate showed less hindrance on the formation of cancrinite/sodalite. Phosphate did not show a distinct effect on the mineral phase formed. When multiple salts (mixtures of two to six of the salts mentioned above) appeared in the system, a cancrinite/sodalite mixture formed rapidly if NaNO3 was present.

The formation of cancrinite and sodalite is favored at high temperature. No cancrinite or sodalite formed after 24 weeks reaction at room temperature. High concentrations of NaN3 slowed the formation of cancrinite/sodalite. When the solution was saturated with NaNO3, allophane dominated the precipitate and cancrinite/sodalite were less developed in terms of the lepispheric morphology. At high OH concentration (16 M), highly crystalline cancrinite formed in nitrate and sulfate solutions while high crystalline sodalite formed when carbonate, phosphate, chloride or no additional salts were present. Both cancrinite and sodalite formed in the presence of nitrite, and hexagonal needle-shaped cancrinite formed at longer reaction time (e.g.32 weeks).

Energy dispersive spectra (EDS) and infrared analyses indicate the electrolytes were not incorporated in LTA zeolite. On the contrary, a distinct Cl peak appeared in sodalite formed in the presence of NaCl, and a distinct sulfur peak appeared in cancrinite formed with Na2SO4. No phosphorous peak, however, was observed in the sodalite formed with phosphate salt. FTIR spectra have indicated that NO3−, NO2− and CO32− can enter cancrinite as ion pairs with Na+. It is likely that allophone, Linde type A zeolite, cancrinite and sodalite will be the major minerals in the new precipitates formed in the sediments underlying Hanford waste tanks.
IMPROVING CLASSIC CONCEPTS OF CLAY MINERALS TO AID UNDERSTANDING AND APPLICATIONS

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During the preparation of a new soil mineralogy book it became evident that reliance on older classic clay concepts was pervasive (2). Thus it is proposed to examine recent data that better represent clays found in the field. In teaching we present images that may persist in the minds of students and where they are too simplistic they may prove to be misleading when applied. The examples to be given come from soils, sediments, weathered rocks, and one synthetic phase. Halloysite is overshadowed by kaolinite in many presentations of this mineral. The range of halloysite properties e.g. aspect ratio is extremely wide (5). Both chemical and physical properties are likely to be influenced by this wide diversity. Unfortunately, x-ray diffraction gives relatively weak patterns of halloysite that can lead to its being overlooked in mixed clay systems and other methods are needed, e.g. transmission electron microscopy, to identify and characterize it. Iron oxides once thought to be amorphous are now frequently recognized as single crystal aggregates of sub-micron size (1). Use of techniques such as selective dissolution on a prepared x-ray mount has permitted the characterization of short range ordered Fe oxides in rice paddy soils (7). Manganese oxides give weak x-ray diffraction peaks and have diverse properties that influence their effectiveness as oxidizing agents (3, 4). The identification of Fe and Mn oxide minerals is greatly aided by pre-concentration with high gradient magnetic separation and use of selective dissolution techniques. Sulfides are toxic to marine organisms and are often thought of in terms of pyrite, marcasite, mackinawite, and amorphous material. Recent research in formulated clay systems modeling the marine environment revealed a new colloidal Fe sulfide that may form in natural systems (6). Refinement of techniques and the use of a variety of methods continues to give better concepts of clay minerals in soils and sediments that students need to become effective scientists and practitioners.

This study was undertaken to investigate the mechanisms of mineral transformations associated with magnetite reduction by *Shewanella putrefaciens* strain CN32. Magnetite was generated via microbial reduction of hydrous ferric oxide. Biogenic magnetite in solutions buffered with bicarbonate was inoculated with strain CN32 and provided with lactate as the electron acceptor. Fe(II) production was determined by Ferrozine assay, and the resulting solids were characterized by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). At the end of the incubation experiment, the Fe(II) concentration was 1.5 to 1.7-fold greater in the bioreduced sample than in the uninoculated control. Initial reduction proceeded via intimate association between bacterial cells and nanometer sized magnetite crystals, where cells were coated by magnetite crystals. Magnetite crystals at the close contact with cells show non-typical selected area electron diffraction pattern, where the strongest lines for magnetite (d = 2.53, 1.48, 2.97, and 1.62 Å) are either missing or very weak. Magnetite crystals that are not in contact with cells show typical SAED pattern. As bioreduction proceeded, siderite formed in the space that was previously occupied by bacterial cells, and cells appeared to have lysed. Newly formed siderite SAED pattern shows typical siderite reflections (d = 2.80, 3.60, 1.96 Å) as well as a strong line at d = 2.57 Å corresponding to the strongest line of magnetite. These characteristics suggest that microbially mediated magnetite to siderite transformation within our experimental time frame (14 days) was not complete, and siderite and magnetite co-existed at the nanoscale. Quantitative analytical electron microscopy (AEM) analyses show nearly stoichiometric Fe/O ratio for magnetite, but non-stoichiometric Fe/O ratio for siderite, illustrating transitional nature of newly formed siderite. Siderite characteristically contains a minor amount of Ca. The transitional nature of magnetite and siderite is further confirmed by EELS. Magnetite at the cell-magnetite interface shows 50-60% of Fe(III), as opposed to 66%. Conversely, siderite shows ~90% of Fe(II) in its structure, as opposed to 100% Fe(II). In conclusion, microbial reduction of Fe(III) in magnetite resulted in the magnetite to siderite transformation. Considering the drastic difference in the structure of these two minerals, we infer that such a biomineralization may have involved dissolution of magnetite and precipitation of siderite. Multiple lines of evidence suggest that intermediate products, such as magnetite with some characteristics of siderite, or siderite with some characteristics of magnetite resulted. Such a complex biomineralization process may be common in nature where environmental conditions are much more variable.
USE OF SYNTHETIC MONOSODIUM TITANATE AND MN OXIDES FOR RADIONUCLIDE REMOVAL FROM HIGH-LEVEL WASTE SIMULANT

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Disposition of High-level Waste (HLW) material produced from spent nuclear fuel reprocessing is a prime mission for the U.S. Dept. of Energy. We have examined two treatment methods that involve minerals for the removal of radionuclides from highly alkaline and high ionic strength HLW simulant solutions. Specifically, these two materials were tested for their ability to remove strontium (Sr), uranium (U), plutonium (Pu) and neptunium (Np). The first of these treatment methods involved the use of monosodium titanate, which is primarily an amorphous material that has a micro-crystalline fringe. The second material that we have examined was made in situ by a reaction between permanganate ion and a reductant (formate or hydrogen peroxide) in the HLW simulant solution. This reaction results in the precipitation of a birnessite-like manganese (III,IV) oxide material, which has a small particle size (a few tens of nm) and two morphologies: hexagonal- and fractal-shaped. We will discuss the spectroscopic characterization of these materials, their applicability to HLW treatment and the mechanisms of radionuclide removal.
ANALYSIS OF HYDRATION BEHAVIOR OF SMECTITES BY HUMIDITY-
CONTROLLED THERMOGRAVIMETRY

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Humidity controlled thermogravimetry (TG) was applied to determine a weight of distinct hydrated waters present in smectites. Samples were kept under 80% relative humidity (RH) N2 gas followed by a TG measurement at dynamically controlled heating rate. Iwasaki and Watanabe1 reported by using humidity controlled XRD that both Na- and Ca- smectite have a basal spacing of 1.52 nm under 80% RH. As a result, stepwise weight loss was determined attributed to various types of hydrated waters such as, interlayer waters, waters located at edges of smectite platelets, and waters around cations or negatively charged sites.

First, TG analysis of an organic monomer-bentonite composite (Hojun Kogyo Co., BEN-GEL SH) was carried out. Hydroxyl groups at the edges of bentonite layers are silylated by alkyltrialkcoxyisolane in the composite. A large weight loss around 300K, a broad weight loss up to 330K are observed. The weight losses are attributed to interlayer waters.

Second, TG analysis of synthetic Na-saponite (Kunimine Kogyo Co., Smecton) was carried out. A dehydration peak is observed at 295K, and it is attributed to interlayer waters as seen in the case of silylated smectite. A dehydration peak at 309K which is not observed in the case of silylated smectite is attributed to waters hydrated to hydroxyl groups at the edges of the smectite platelets.

Third, Ca-saponite was analyzed in the same way. A DTG peak is observed at 301K attributed to interlayer dehydration. A dehydration peak is observed at 313K attributed to dehydration of hydroxyl groups located at the edges of the smectite layer. In addition, three dehydration peaks at 321K, 331K, and 343K are observed. Each step in the dehydration process is equivalent to the layer charge. This result and the fact that there were no correspondent peaks in the case of Na-smectite allow us to propose that these peaks are attributed to the hydrated waters at the Ca2+ and the negative charged sites.

ACID-SULFATE ALTERATION AND GENESIS OF ALUNITE-HALLOYSITE DEPOSIT AT TURPLU MINE, BALIKESIR, TURKEY

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The western end segments of 1200 km-long left lateral strike-slip “North Anatolian Fault” extends as NE-SW trending en-echelon faults in the Biga Peninsula. Halloysite and alunite deposits at Turplu mine are located about 20 km north of the southern part of these en-echelon faults and therefore, acid-sulphate alteration related to clay deposits were formed along the major fault zone between Late Oligocene calc-alkaline tuffs and exotic Permien limestone blocks in the western boundary of regional uplifted Triassic Karakaya Complex and mineralization controlled by the intersection of minor faults.

The occurrence of alunite-halloysite deposit requires multi-stage hydrothermal alteration events of andesitic tuffs and ashes. The thickness of alunite-halloysite deposit is about 12 m on the underlying karstic limestone blocks, which are good drainage system for the leaching of parent rocks by SO₄-rich geothermal waters. Small halloysite-rich zone found in the upper part of alunite deposit, but these two minerals generally observed in exploration galleries as mixed together in 2-20 cm thick bands, which were subject to intense soft sediment deformation and also, co-existence indicates simultaneous occurrence of these two minerals in favoring geochemical environments.

Mineralized zone gradually finished in overlying highly altered andesitic rocks that are rich in smectite due to multi-stage sulfate-rich solutions were used up before reaching to andesitic rocks. In addition, permeability in andesitic tuffs and lavas were not the same and flowing of geothermal waters became stagnant in fine pores where the differential mobility of elements significantly reduced, which increased salinity and alkalinity, favoring the formation of smectite. Geochemical data revealed that some alunite (white, relatively hard and compact) samples contains up to 9 wt.% P₂O₅, which suggests the effects of relatively high temperature acid-sulfate alteration produced in deep magmatic hydrothermal environment.

Five stages genetic model is proposed for the origin of magmatic hydrothermal alunite-halloysite deposit. During stage-1, calc-alkaline tuffs and ashes as a parent rock deposited on overlying karstic limestone blocks. Stage-2, major cations (Al, Fe, Ti, Ca, Mn, Na and K, but not Si) dissolved from initial parent rocks under acidic pH conditions, migrated through intense leaching and differential mobility of certain elements at different Eh/pH conditions. Stage-3 involved more than 65 % mass reduction of initial parent rocks to form gibbsitic soil due to progressive downward Si-leaching and upgrading of gibbsite through Si-leaching at pH < 2. In stage-4, the widespread formation of alunite was formed from intermediate parent rock of gibbsite into the zone of oxidation by hypogene HSO₄⁻ input; 3Al(OH)₃ + K⁺ + H⁺ + 2HSO₄⁻ = KAl₃(SO₄)₂(OH)₆ + 3H₂O and halloysite also formed by the presence of excess Si. Stage-5 involved mainly pyrite mineralization along the fault zone and the bottom zone to limestone during the early diagenesis.
ORIGIN OF SMECTITE AND RELICT METEORITES AT THE K-T BOUNDARY AT STEVNS KLINT, DENMARK

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The K-T boundary marl at Stevns Klint, Denmark (i.e. the Fish Clay) has anomalous concentrations of Ir and related platinum group metals, shocked quartz, and glass attesting to meteorite impact during the K-T boundary transition. An unusual Mg-rich smectite is the predominant mineral in the clay fraction of this marl. Trace amounts of detrital illite are present in the clay fraction. Labradorite with angular edges is interpreted to be pyroclastic. Transmission electron microscopic analyses show the smectite is formed by the alteration of impact-derived glass within the Fish Clay during early sediment diagenesis. The major elemental composition of smectite in the Fish Clay is similar both to the major element composition of glass in the Fish Clay and to the major elemental composition of the black glass at the K-T boundary in Haiti. The Fish Clay smectite has relatively large octahedral Mg and Al contents. In addition, small goethite pods are found within domains of smectite. The Fe/Ni ratios of the goethite pods are comparable to those of Fe/Ni chondrites and the goethite pods also have relatively large Zn contents. Although we did not find PGE within these pods, we interpret the goethite pods to represent relics of the impacting meteorite(s).

The K-T boundary marl at Stevns Klint contains detrital phases (illite, quartz), impact-derived phases, and pyroclastic labradorite. A mosaic of geologic events must be considered in determining the causal factors of the mass extinctions seen at the K-T boundary. Our study illustrates the usefulness of TEM to characterize the mineralogy and phases present in distal ejecta formed from meteorite impacts.
Detrital muscovite in the Cretaceous and Tertiary kaolin deposits of central Georgia has been dated using K-Ar and $^{40}$Ar/$^{39}$Ar methods. All muscovite is significantly depleted in K, which has been removed during intense weathering in the sedimentary weathering environment. K contents of muscovite separates as percent K$_2$O range from 0.94 to 8.20. The finer grained muscovites are typically more depleted in K$_2$O than the coarser muscovites. Likewise, the Tertiary sediments are typically more depleted in K$_2$O than those of Cretaceous depositional age. It is therefore likely that depletion of K in the post-depositional weathering environment is more significant than during weathering of the initial source.

Electron microprobe analysis reveals that the Tertiary muscovites tend to have lower K$_2$O contents at their weathered margins. The altered zones are approximately 10-15 microns wide in grains with diameters ranging from 150 to 300 microns. Some larger grains (300-600 microns diameter) show random patterns of K-depletion, possibly related to the presence of fractures or other imperfections. Apparent dates of muscovite separates range from 166 ± 4 Ma to 374 ± 8 Ma. Both the muscovite ages and K$_2$O contents increase with increasing stratigraphic age.

$^{40}$Ar/$^{39}$Ar spot analysis of a single, large detrital grain from the base of the Tertiary deposits reveals an age profile through the grain from the margin to the center. The oldest age, near the center of the grain is 292 ± 13 Ma; the youngest, nearest the edge of the grain is 223 ± 10 Ma. Although the grain generally exhibits older ages nearer the center; younger nearer the edges, K$_2$O analysis via electron microprobe reveals no discernable relationship between $^{40}$Ar/$^{39}$Ar age and K$_2$O content.

Since the source of these micas must have been largely the metamorphic terrane of the Southern Appalachian orogen, and since the currently exposed part of that terrane contains muscovite that ranges upward in K-Ar age from about 250 Ma, it appears that weathering has for many of these samples caused relatively more argon loss than potassium loss.
PALEOENVIRONMENTAL SIGNIFICANCE OF CLAY MINERAL ASSOCIATIONS ACROSS THE CRETACEOUS- TERTIARY IN UPPER EGYPT

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The clay mineral stratigraphy across the Cretaceous-Tertiary boundary has been considered by investigating columnar sections from Eastern Desert (Wadi Qena), Red Sea region (Gabal Dwui), Western Desert (Kharga region) and by taking in account previous data on various exposed areas around the world. Clay mineral assemblages display significant variations from the Maastrichtian to the Paleocene, and the in the boundary layer itself. The mineralogical variations recorded are diversified. In some localities the amount of smectite increases, in others kaolinite or both smectite and kaolinite increase, and sometimes other minerals such as chlorite, illite, random mixed-layer, and even palygorskite are concerned. There is, therefore, no uniform clay mineralogical trend in the different sections investigated.
The medicinal uses of clay are intertwined with folk medicine, religious ceremony and belief in the healing power of spirits. The miracles of Chimayo provide a vivid illustration of this. “Sacred earth (clay)”, from the Mission Church is reported to have healing powers and miraculous cures are documented in local newspapers. The ancient Tewa people of this area about 35 miles north of Santa Fe, New Mexico, recognized several springs draining the volcanic deposits for their ability to cure simple maladies by the consumption of a slurry made with the spring sediments. The springs have dried and the current tradition emphasizes the spiritual nature of the healing. “Blessing” by the parish priest, rather than clay properties, is responsible for the modern cures.

The material distributed to the faithful at Chimayo is a clayey, silty sand containing 5-15 weight percent clay. Its less-than-two micrometer fraction is dominated by a randomly interstratified illite/smectite with more than 70% smectite layers. A poorly ordered kaolinite is a minor constituent. The mineralogy is similar to the clay distributed during feast days at Esquipulas, Guatemala, but there is no uniformity among medicinal clays in use worldwide.

The notion that all clays are alike hinders research on the medical consequences of clay consumption. One researcher may report high levels of blood K among clay users and another attributes low blood K to clay eating. Neither investigator considers that their study might deal with a different clay and attributes the contradictory results to unknown factors. Samples from several locations around the world have a diverse clay mineral composition, suggesting that local custom is the dominant factor in the selection of medicinal clays and their variable effects. Spidergrams of major and trace element variability in Chimayo and other healing clays are just as variable as the clay mineral composition. Differences in element ratios extracted with 0.5N HCl may vary by two-three orders of magnitude. All results point to the importance of variable clay content as a major factor in healing clays.
NANOSHEETS BASED MINERAL LIQUID CRYSTALS (CLAYS AND MORE): STRUCTURE AND APPLICATIONS

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In this presentation, we will report findings on the structure of suspensions of clays (bentonite, Laponite) as well as phosphatoantimonate single layers. These finding shows that above a critical concentrations, such materials tend to form liquid crystalline phases (mesogens) in which the sheets tend to orient themselves parallel to each other (nematic phase). This is shown by studying by optical measurements as well as small angle X-Ray scattering. In the case of H₃Sb₃P₂O₁₄ an additional position order is found where the distance between the nanosheets can be controlled up to 250 nm leading to the first lamellar mesophase made of covalent sheets. Usage of the mesogenic properties of these mineral liquid crystals in various applications, such as nanocomposites or NMR, will also be reported.


BIRNESSITES OBTAINED FROM THERMAL DECOMPOSITION OF KMnO₄.
CRYSTAL STRUCTURE OF A LARGE FAMILY.

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Birnessite is a manganese oxide containing predominantly Mn⁴⁺ cations in layers of edge-sharing octahedra. Layer charge deficit arises from the presence of Mn³⁺ and/or vacant octahedra within layers and is compensated for by the presence of interlayer cations which are typically hydrolyzable in natural varieties. Despite the relatively low abundance of manganese, birnessite is ubiquitous in nature and is essential to the geochemistry of soil and oceanic nodules because of its remarkable cation exchange capacity, sorption, and redox properties. In particular, because of its high affinity for pollutants (heavy metals, organics, …) this mineral plays a pivotal role in their fate in contaminated environments.

Recently, synthetic birnessites have attracted additional attention because of their electrochemical properties. Birnessite species rank among the promising cathode materials for secondary lithium batteries if their lamellar framework is stable during insertion/de-insertion cycling. Such birnessite varieties have been obtained from the thermal decomposition of KMnO₄. Crystal structures of birnessite samples synthesized at 700-1000°C were determined using a variety of X-ray diffraction techniques. The structure refinement of fine-grained birnessite was performed for the first time on a single crystal (800°C sample), whereas the Rietveld technique allowed to refine the structure of the 1000°C sample. Birnessite samples synthesized at different temperatures have different layer sequences, different unit cell and super-cell parameters, specific distribution of heterovalent Mn, and specific distribution of interlayer K and vacant layer octahedra thus demonstrating the key influence of temperature on birnessite structure.

Furthermore, the trial-and-error approach used to fit XRD patterns of defective samples allowed to reveal the nature and content of stacking faults which are common in birnessites. In addition to the widespread interstratification of layers having identical thickness but different interlayer displacements a new type of structural disorder was observed. Specifically, the alternation of layers with the same thickness and interlayer displacement but whose dimensions are incommensurable in the ab plane is reported. In the birnessite structure, incommensurable layers are randomly interstratified, in contrast to the "hybrid structures" reported in the literature (asbolanes, valleriite, tochilinite, …) in which they alternate regularly, allowing their description with a set of unit cells having different sizes and shapes.
MID-INFRARED REFLECTANCE SPECTROSCOPY OF CONDENSED COMPOUNDS ON CLAYS, SOILS, AND QUARTZ SANDS

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We have collected and examined mid-infrared reflectance spectra from reference clays, quartz sands, two soils and simulated soils in the laboratory. We are determining the feasibility of developing a reflectance spectrometer for detecting low volatility compounds on the surface of these materials. Comparisons of uncoated, and coated, reference clays, quartz sands and simulated soils to natural soils leads to an improved understanding of the mechanisms governing the surface adsorption of these compounds.

The compounds of interest are those associated with hazardous materials, environmental contaminants, and residues from chemical weapons use. In the laboratory, both specular and diffuse reflectance infrared spectra are recorded from 4600 to 500 cm⁻¹ using a globar source, KBr beamsplitter, and MCT detector. Specular reflectances are recorded with incident and reflectance mirrors at the same angle relative to the surface normal. Diffuse reflectance spectra are collected with a Harrick Praying Mantis accessory. Unpolarized spectra of the uncoated and coated materials and their ratios are presented and changes in the volume scattering, Christiansen, and Restrahlen features are noted. Spectra from a number of analyte and sand, soil or clay combinations will be presented. We seek to establish the sensitivity limits for detecting the target compounds on a variety of materials with environmental relevance in the laboratory and enabling extension of laboratory measurements to remote detection capabilities.
Work in polymer nanocomposites has exploded over the last few years. The prospect of a new materials technology, which can function as low-cost alternative to high-performance composites for applications ranging from automotive to food packaging to microelectronics has become irresistible to researchers around the world. In this talk I will review our current efforts in nanocomposites for applications ranging from fuel cells to drug delivery. Additionally, I will focus on correlating their properties to nanostructure and interfacial dynamics.
UPPER EOCENE DISTAL IMPACT EJECTA LAYERS

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Impact ejecta layers have been found in upper Eocene marine deposits. There are probably only two layers, but the number has been a matter of controversy. The younger layer contains glass spherules (microtektites) that are believed to belong to the North American tektite strewn field defined by glass bodies (called tektites) that have been found in Texas and Georgia. Microtektites belonging to this strewn field have been found on Barbados and in sediment cores taken in the Gulf of Mexico, Caribbean Sea, and NW Atlantic off New Jersey. Unmelted impact ejecta consisting of shock-metamorphosed rock and mineral grains, including quartz and feldspar with multiple sets of planar deformation features, coesite, stishovite, and zircon containing a high-pressure zircon polymorph have been found in the layer. The high-pressure zircon polymorph was first recognized in this ejecta layer and has been named reidite in honor of Alan F. Reid who first produced this high-pressure phase in the laboratory. Radiometric dating of the tektites indicates that this layer was formed ~35 m.y. ago. Based on the age and geographic variations in thickness of the North American microtektite layer, it has been proposed that the 85-km-diameter Chesapeake Bay crater (buried at the mouth of the Chesapeake Bay) may be the source crater for this ejecta layer. A slightly older layer consists of glassy spherules that have partly crystallized to clinopyroxene and are thus called clinopyroxene-bearing spherules (or cpx spherules). The cpx spherules also often contain Cr- and/or Ni-rich spinels. This layer appears to be global in geographic extent and may have been derived from the 100-km-diameter Popigai impact crater in northern Siberia. In some places the cpx spherules have been altered to pyrite or clay. The layer is associated with a positive Ir anomaly. Unmelted impact ejecta is rare in this layer and shocked quartz has been identified at only one site and coesite at another site.
Unfortunately, research in recent years has been mainly addressed to the negative effects of minerals in the human health, and the results of much of this research are being presented in scientific journals and meetings, as was the case of the very recent International Mineralogical Association (IMA) meeting held on September 2002, in Edinburgh.

However, it is well established that some particular minerals are of paramount importance for good human health, either being part of the composition of drinkable spring waters and eatable vegetables and fruits, or being incorporated in many pharmacs after being submitted to some degree of industrial processing.

Presently, there is a growing interest on treatments using natural means, alternative to those of the conventional medicine. It is the so-called naturoltherapy, that involves distinct processes and methods, such as: phytotherapy, hydrotherapy, mudtherapy, thermotherapy, etc.

Whenever naturoltherapy involves minerals or other mineral resources we can name it geomedicine, a scientific area that comprises the fundamentals and practices of the application of geomaterials as conditioners of human health. In fact, particular types of clay/mud, sand, rock salt and spring water, intervene both as chemical and physical conditioners in human health.

Naturopathologists believe that good health depends upon three main factors: structural, biochemical and emotional. Minerals and the other mineral resources referred to would be included in the second group of factors, since biochemical interactions between them and the human body will take place.

The present paper provides information about the properties and application methods of mineral resources, such as particular types of clay/mud and sand.

In order to be effective in geomedicine clay/mud needs to exhibit specific qualities, such as: fine granularity, high specific surface area, high specific heat, high adsorbing and absorbing capacity, low cooling rate, high cation exchange capacity, easy handling, as well as pleasant sensation when applied directly onto the skin. Clays are pelitic or lutitic geomaterials, and particular types of clay/mud are used worldwide, either in Thalassotherapy Centres or "in situ" in geologic sites located, as a rule, in littoral regions where marls or marly limestones do occur, for therapeutic treatments called mudtherapy or peloidtherapy (or pelotherapy, in short), generally under the form of both mud baths and hot cataplasms or patches called peloids.

The relevant physical and chemical properties of the clay/mud used in Portuguese thermal spas as well as of the biogenic carbonate sands (mainly bioclasts of red calcareous algae) which occur both on the beach and frontal dune of Porto Santo island, Madeira archipelago, are disclosed in the present paper. The sands referred to have been used for many years with reckoned success, however just on an empirical basis, under the form of sand baths, to improve the living quality of patients suffering from arthro-articular, muscular and orthopaedic diseases. This particular type of sand that also exists in certain other islands, either of the biogeographic region called Macaronesia (that comprises Azores, Madeira, Canarias and Cape Verde archipelagos) or of the Caribbean Sea and Coral Sea, is characterized by particular chemical and thermal properties that justify, if applied under controlled conditions, its use in geomedicine.
SMECTITE CATALYZED DEHYDRATION OF GLUCOSE

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Soil organic matter (SOM) plays many important agricultural and environmental functions. Thus, a better understanding of the formation of humic materials in soils is necessary to develop soil management practices that enhance SOM formation. The objective of this study was to determine whether smectites abiotically catalyze transformation of glucose under conditions relevant to SOM formation. Four cation-saturated smectites were incubated under abiotic conditions with glucose solutions for 21 days at 37 °C. After the incubations, glucose recoveries in the solutions ranged from 18.3 to 98.3%. However, soluble organic C recoveries ranged from 95 to 109.3%, relative to the amount of C added as glucose. The transformation products of glucose were identified as 5-(hydroxymethyl)-2-furfural and 4-oxopentanoic acid (levulinic acid). The results provide evidence that smectites catalyze glucose dehydration under abiotic conditions to form furfural compounds and levulinic acid. These transformation products are known to be highly reactive and are likely to be polymerized or co-polymerized with other organic compounds. Accordingly, the catalytic transformation of glucose by smectites is suggested as one of the pathways for the incorporation of new C into the soil organic matter during the formation of humic materials in soils.
AUTHIGENIC AL, FE, SI MINERALS OF VARYING CRYSTALLINITY IN DUNAL SOILS NEAR NEWPORT, OREGON, USA

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We identified a suite of clay minerals of varying crystallinity in dune sheet soils, suggesting redistribution of Fe, Al, and Si within the last 20 to 70 ky. These soils are located near Newport, Oregon, USA, receive 1720mm of precipitation annually, and were emplaced during the late Pleistocene, 20ky to 70ky ago. Authigenic minerals identified using XRD include: crystalline gibbsite and vermiculite as well as poorly crystalline allophane, imogolite, and ferrihydrite. By SEM we identified Fe-Si-Al phases in varying proportions coating and cementing the sand grains in the B and C horizons. Vermiculite is commonly found in the <2µm size fraction of the B horizon. In the C horizon we find allophane and imogolite replacing roots and woody material, as well as nodules of crystalline gibbsite precipitating in the pore spaces of coarser sands and cavities. Overall the poorly crystalline Fe-Si-Al cement imparts significant strength to the sands. The precise mineral nature of this cement is not clear and will be investigated further (i.e. TEM and dissolution experiments); we suspect they may be some combination of ferrihydrite, allophane, imogolite, vermiculite, and X-ray amorphous material. In addition, we find active ferrihydrite precipitation together with Fe oxidizing bacteria on the surface of ephemeral pools at the sea cliff beach interface, suggesting active Fe leaching from the dune deposits. These pools stain the beach sands red during the summer and fall. The water that drains these sand dunes is weakly acidic with a pH close to 6, slightly reducing, and a TDS of up to 600ppm. The amorphous Fe is removed from these pools with high tide events and may serve as an important source of Fe to near shore fisheries.
Methane hydrate is comprised of H2O and methane. Methane hydrate is a waxy, white solid in appearance, stable at temperatures of 0 - 4 °C at pressures of about 25 - 40 bars, and occurs in sediment found on continental margins, on the ocean floor and in permafrost. The large methane content makes it a potential economic resource. In addition, methane is a greenhouse gas, and thus, methane hydrates may play an important role in global climate change. As a potentially unstable cement in sediment, methane hydrate can produce overpressures and fluidize sedimentary layers at or near the base of the continental-margin sediment column, thereby producing landslides and debris flows. The methane hydrate structure is that of a clathrate, where H2O molecules form cages where guest molecules, such as CH4, reside.

Na-rich montmorillonite is characterized as having large amounts of H2O present when surrounding electrolyte concentrations are dilute. As interlayer distances increase with increasing H2O content and electrostatic effects between the interlayer cation and the 2:1 layer become less important, the interlayer H2O becomes more like bulk water. Thus, in the presence of methane and at the appropriate conditions of temperature and pressure, it seems possible that a methane hydrate complex could be intercalated in a Na- and H2O-rich montmorillonite interlayer.

Intercalated Na-rich montmorillonite – methane hydrate has been synthesized for the first time. The upper limit of stability for the intercalate in pressure and temperature is parallel to that of methane hydrate but at temperatures that are about 0.5 to 1 °C lower than for methane hydrate. The low-temperature stability of the intercalate is at -11.5 °C at ~40 bars, where methane and some H2O are expelled from the region between the silicate layers (interlayer). In contrast, methane hydrates do not dissociate at these low temperatures.

Clay–methane intercalates are a new class of materials, and they may form an additional, previously unrecognized reservoir of methane. If clay–methane intercalates are found naturally, they may represent a potential energy resource. Furthermore, they may affect global climate change, and lastly, they represent a potential geologic hazard. The limitation in the stability of smectite – methane hydrate intercalate at low temperatures suggests that, if present in large quantities, it may release sufficient methane at decreasing temperatures to ameliorate a planetary cooling event.
HYDROTHERMAL REACTION PRODUCTS OF CHRYSOTILE ASBESTOS

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Chrysotile asbestos is legally declared a carcinogenic health hazard, which was seriously challenged as “Asbestos Removal Fiasco” by P.H. Abelson (Science, 247, page 1017, 1990) and others. In this study, the products of a sequential acid/base treatment of chrysotile using formic acid and NaOH are presented. These reaction products have very different morphological features, aspect ratio, and crystal structures. The reaction products may therefore be harmless and may have potential use in industry and agriculture. Chrysotile from Thetford Mines in Quebec, Canada was treated first with formic acid at concentrations 0.5 to 3.0N and subsequently with NaOH for 48 hours at 200°C in Teflon-lined Parr bombs (12 ml). The reaction products were examined with X-ray diffraction and Analytical Electron Microscopy. A kerolite-type 2:1 layer silicate with a basal spacing of 0.985 nm and thin foil morphology was found to grow from chrysotile fibers during the acid treatment. The acidizing reaction at 200°C seems to involve an incongruent dissolution with the removal of Mg²⁺:

\[
\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8 + 12\text{H}^+ \rightarrow \text{Mg}_4\text{Si}_4\text{O}_{10}(\text{OH})_2\cdot\text{nH}_2\text{O} + 3\text{Mg}^2+.
\]

This intermediate phase was separated from acid solution and then treated with a NaOH solution at pH=12-13. The hydrothermal treatment in alkaline conditions produces a magnesian smectite in the form of large thin flakes. The alkaline digestion at 200°C can be represented by the following reactions:

\[
\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2\cdot\text{nH}_2\text{O} + \text{xNa}^+ \rightarrow \text{Na}_x(\text{Mg}_{3-x})\text{Si}_4\text{O}_{10}(\text{OH})_2
\]

or considering the presence of iron impurity in the chrysotile sample:

\[
\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2\cdot\text{nH}_2\text{O} + \text{xNa}^+ + \text{xFe}^{3+} \rightarrow \text{Na}_x\text{Mg}_3(\text{Si}_4-x\text{Fe}^{3+})\text{O}_{10}(\text{OH})_2.
\]
EVIDENCE OF IMPACT-GENERATED DEPOSITION ON THE LATE EOCENE SHORES OF GEORGIA

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Although 35 Ma tektites are found in younger Coastal Plain alluvium throughout southern Georgia, a discrete impact layer had never been identified in Eocene sediments. Harris et al. (2002) and Schroeder et al. (2002) recently identified possible shocked quartz grains in a coarse-grained sand layer at the base of the Upper Eocene Twiggs Clay in east-central Georgia. Albin and Wampler (1996) previously had concluded based on glauconite ages and biostratigraphy that any ejecta layer associated with the 35 Ma Chesapeake Bay impact should be preserved at this horizon.

Approximately 1 in 250 of the quartz grains in the fine-grained fraction exhibit possible planar deformation features (PDF’s). Less than 1 in 1000 quartz grains from the medium-grained fraction contain similar features. Orientations of the planar features relative to the optic axis were determined using a spindle stage and universal stage. Planar features in grains displaying at least two intersecting sets show a preference for the \{10-13\} and \{10-11\} forms. Planes corresponding to \{11-22\} and \{51-61\} also were observed. These orientations suggest shock pressures ranging from about 18 GPa to <25 GPa (Langenhorst and Clymer, 1996). Consistent with shock metamorphism (Montanari and Koeberl, 2000), these grains all appear to exhibit reduced refractive indices \(n\). One well-rounded grain displays a prominent set of planar features corresponding to \{10-12\} and \n<1.52. This suggests that the grain experienced pressures >25 GPa. The absence of PDF’s, such as \{10-13\}, which form at lower pressures may indicate that the grain was part of a very porous sedimentary target (Grieve et al., 1996) (a hypothesis supported by the grain’s high-degree of rounding).

Ten km down-dip from the occurrence of shocked quartz, the same stratigraphic interval is occupied by a 0.5 to <2 m-thick diamicrite. Previously interpreted as a volcanioclastic deposit (Huddleston and Hetrick, 1986), Harris (2003) argued that the origin of the diamicrite should be re-evaluated. The diamicrite consists of kaolinite and smectite clasts supported by a gray kaolin matrix. Very-poor sorting and locally-developed reverse grading suggest debris flow emplacement (Prothero, 1996). Texturally the deposit is similar to surge deposits associated with documented impact deposits (Pope et al. 1999; Warme et al., 2002). Clast-size-frequency distributions suggest that either the source of the smectite clasts or the sedimentary processes acting on them were distinctly different than for the other materials. These clasts may represent altered particles ballistically transported into a debris flow, possibly triggered by secondary impacts or seismic events associated with the Chesapeake Bay impact. An impact origin for this deposit is supported by the discovery of goethite spherules similar to altered microkrystites associated with the K-T boundary (Ruiz et al., 1997), armored smectite clasts similar to impact lapilli (Warme et al., 2002), and possible shocked quartz.
A kaolinite sample, from Egypt, was calcined for 2.0-6.0 hours at various temperatures ranging between 500° C and 886° C. The metakaolinite produced during dehydroxylation of kaolinite was leached with sulfuric acid for 1.0 hour. A study of the structural and textural changes of kaolinite revealed that the specific surface area as well as pore volume and micro pore surface area increased progressively by increasing temperatures up to 886° C for 2.0 hours. On the other hand, all these parameters decreased as the calcination time was increased to 6.0 hours. The mechanisms responsible for the observed changes in these properties are discussed.
USING ELECTRONIC RESPONSE TECHNOLOGY TO TEACH MINERALOGY IN LARGE CLASS SETTINGS

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The relationship between atomic structure and the behavior of solids is foundational in introductory Earth science courses. Virtually all university-level textbooks in physical geology begin with a chapter on Earth materials, and the texts use concepts of crystal chemistry and phase stability to develop their presentations of larger scale Earth processes. Because of the quantification and the visualization that is required of mineralogical concepts, however, students often have difficulty grasping this material on first exposure. Likewise, it is challenging for instructors to gauge the level of student involvement and comprehension of these ideas, particularly in large classroom settings.

Since Spring 2002, we have experimented with electronic student response systems to monitor student understanding of mineralogy and petrology in Geosc 020: Planet Earth, a general education course with ~150 students per class. The Classroom Performance System (CPS), manufactured by eInstruction, is a wireless, infrared response system that collects and sorts student responses to questions posed in class by an instructor in multiple-choice format. After extensive discussion in peer groups, students key in their answers with their individually registered remote control units, and the results are then displayed in a histogram using a standard LCD projector. This technology allows the instructor to gauge student comprehension of a given topic instantaneously and to alter lecture content accordingly. In addition, students can measure their level of understanding of course material and concepts relative to their peers.

Our assessment of the CPS system and associated teaching and learning techniques have consisted of a 21-question student survey, daily course attendance data, and informal feedback from over 25 Penn State faculty and administrators who have visited the classroom over 3 semesters. The vast majority of students surveyed (65-77%) felt CPS technology helped them gauge their level of understanding of course material. An even higher percentage of students (71-85%) agreed that CPS use reinforced important concepts presented in lecture. The percentage of student respondents who would recommend CPS use in Geosc 020 as well as other courses at Penn State ranged from 63% to (in our last survey) 88%. Between 65% and 80% of students felt that CPS technology helped them learn. Based on this success, we are developing a database that includes questions of a mineralogical and petrological nature that will be made available to all interested instructors.
Layered double hydroxides (LDHs) are a complex group of phases with wide-ranging technological applications and increasingly recognized geochemical significance. They are unusual among oxide and hydroxide phases in having large, permanent anion exchange capacities, and enhancing their range of applications and understanding their geochemical significance require better understanding of the structure and dynamics of the interlayer and surface anions and water molecules. IR spectroscopy has been widely used to investigate their structures, but published data have been recorded mostly at ambient conditions without accurate control of relative humidity (RH). Our previous work (Hou et al., Am. Min., 88, 167, 2003) using water-vapor sorption, NMR, and RH controlled XRD has shown clearly that LDHs have widely variable RH-dependent hydration, expansion, structural and dynamical behaviors that significantly depend on such factors as the anion size, charge, and configuration, and on the hydroxide-layer composition. We have grouped LDH phases with small inorganic anions into three types based on basal spacing expansion and water accessibility to the interlayer.

We present here environmental FT-IR spectroscopic data obtained under systematically controlled relative humidity conditions for well-characterized samples of Mg₃Al and LiAl₂ LDH phases containing interlayer SO₄²⁻, SeO₄²⁻, PO₄³⁻, HPO₄²⁻, MoO₄²⁻, ClO₄⁻, SeO₃²⁻, CO₃²⁻, Cl⁻, OH⁻, and NO₃⁻. These results are in very good agreement with our previous data. For significantly expandable phases (Δd: 1.5 – 3.0 Å), with mostly tetrahedral oxyanions, the IR spectra show not only the expected decreased intensity and frequency shifts for the OH stretching and HOH bending bands with decreasing RH, but also splitting of anion ν₃ band at low relative humidity due to decreased site symmetry. This site symmetry decrease is due to loss of interlayer water. It is in good agreement with our NMR observations that at very low RH ³⁵ClO₄⁻ and ⁷⁷SeO₄²⁻ show relatively large uniaxial chemical shift anisotropy, whereas at high RH the uniaxial CSA pattern is either fully averaged (³⁵ClO₄⁻) or significantly reduced (⁷⁷SeO₄²⁻). In contrast, LDHs that are essentially non-expandable (Δd: 0 – 0.2 Å) and show little interlayer water exchange, the IR spectra vary little with RH. For phases with intermediate expansion behavior, there is significant RH-dependent change in the IR spectra, again in agreement with the NMR data. In addition, the changes in the IR spectra due to hydration and dehydration are fully reversible for all phases, suggesting that RH-driven cross-linking (grafting) reactions do not occur.
POTENTIAL CLIMATIC IMPACT OF THE MIDDLE ORDOVICIAN MILLBRIG-KINNEKULLE VOLCANIC ERUPTION

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The Middle Ordovician Millbrig K-bentonite in North America and the Kinnekulle K-Bentonite of northern Europe represent the same volcanic eruption and constitute one of the largest explosive ash falls known in the geologic record. The total dense rock volume of magma ejected is estimated to have been 1251 km$^3$ with an mass discharge rate near the theoretical maximum of $10^9$ kg/s. The eruptive column reached a height of 55 km and was sustained for about 15 days creating a plume of fine ash and aerosol compounds that spanned the Iapetus Ocean between Baltica and Laurentia.

Melt inclusions preserved in unaltered quartz, apatite and zircon phenocrysts provide useful information on the composition of the parent magma at the time of crystallization. Microprobe analyses of apatite melt inclusions give average compositions equivalent to rhyolite with a calculated water content of 4-5 wt %. Total sulfur expressed as SO$_2$ averages 0.038 wt %, which is about twice the petrographic value reported for the 1991 eruption of Mt. Pinatubo. We estimate the volume of sulfur injected into the stratosphere during the Millbrig-Kinnekulle eruption was 59 Mt of elemental S equivalent to 118 Mt of SO$_2$. The conversion to sulfate aerosol would have yielded approximately 177 Mt of H$_2$SO$_4$ droplets. This is 1 to 3 orders of magnitude larger than any previously reported historic or pre-historic eruption and would have been capable of inducing sudden climatic change by altering the Earth's radiation budget. The climatic response to volcanic loading would have lowered global temperatures by several degrees for a period of 3-5 years. The lack of evidence for a corresponding mass extinction or for an immediate onset of widespread glaciation suggests short-term catastrophic climatic events, such as those resulting from volcanic eruptions, may not, in themselves, bring about long-term regional climatic or biologic changes. There may, however, be locally severe effects which are recorded in the stratigraphic record.
DEFINITION, CLASSIFICATION AND ORIGIN OF CLAY MINERALS.

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In order to communicate as clearly as possible, members of each scientific group adopt definitions of frequently used words. Before considering the definition of clay (rock name) and clay mineral it is appropriate, then, to consider how these words already are defined. For general meanings of words, we consult dictionaries and glossaries, but for more specific definitions of key words in the sciences we turn to definitions their scientists have adopted. For words dealing with chemicals, atomic reactions, states of matter, forces, etc., we turn to chemists and physicists. For organic materials and the biota, we turn to organochemists, biologists, zoologists, etc. For definition of a rock or mineral we turn to a geologist or mineralogist. Any scientist seeking an unequivocal definition turns first of all to the terminology already adopted by the appropriate group of scientists.

Mineralogists have agreed for a long time on the definition of a mineral; similarly, geologists agree on the definition of a rock, and on more specific definitions of all common rocks.

Rocks are distinguished by their mineralogy, grain size or particle size, texture, and various diagnostic structures. Mineralogists have long agreed that no two minerals can be the same chemically and structurally. Before any substance can be assigned a mineral name, proof must be furnished that its atomic composition is significantly different, or that its configuration and bonding of atoms is different. Any rock differing in mineralogy, grain size or texture, regardless of its chemical composition, is a different rock. The Mineralogical Society of America, founded in 1919, requires that the name of every new mineral end with the suffix `ite'. Attempts to use a mineral name for a rock or a group of minerals, like `kaolinite group' or `kaolinites' is confusing and unacceptable because it is inconsistent with accepted definitions.

Words like clay, silt, sand, pebble, etc., pertain to the size of a solid and are consistently used in virtually every science and group of professional engineers. The first widely used grade scale was that of Udden, introduced in 1898; it consisted of 12 grades extending from 3.9 f to 16 mm. Hopkins (1899) pleaded for a slightly different basis for division of particles into grades. He suggested a true geometric scale based on 10^0, but his suggestion was never adopted. The Atterberg scale introduced in 1905 and widely used was based on a unit value of 2 mm and a fixed ratio of 10 for each successive grade. The Wentworth grade scale used by most sedimentary petrologists is a small modification of the Udden scale. The ASTM sieve scale, which decreases the size class interval by 2^{0.5} or 2^{0.25} instead of 2, is used by engineers. Other proposed and widely adopted grade scales are the U.S. Bureau of Soils classification, the Rubey size classification, etc. Krumbein & Pettijohn (1938) summarized the development of these grade scales and reminded that differences between them are small. In all grade scales ever widely used, Clay is the name of the finest size fraction. This fraction of particulates begins at either 0.39µm or 0.2µm and extends down through the nannometer range to a few picometers; the finest clay particles are ~10 picometers across (~0.00001µm).

The earliest published classification of clay minerals is that of Brindley, 1951. Realistically, it included not only silicates but also oxides and hydroxides that are common in many clays. Subsequently, most prominent clay mineralogists have tended to restrict clay minerals to silicates. As special instruments have been developed, additional information about the origin of clay minerals has been gained from which a distinction can be drawn between silicates formed at high temperatures, those formed by hydrous alteration at lower temperatures, and a third major class of clay minerals, those formed by weathering in water-unsaturated zones where much silica has been depleted by weathering or bound in quartz.

A new classification of clay minerals more consistent with current knowledge will be proposed. If time is sufficient, some interactive relationships between clays, ubiquitous organics and a nanno-pico-meter group of clay minerals that is beginning to be recognized will be discussed. It is the fourth class of clay minerals in the new classification.
AN IR AND AFM STUDY OF HYBRID FILMS CONSISTING OF A SINGLE LAYER OF SMECTITE

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The Langmuir-Blodgett method was used to prepare hybrid films consisting of a single layer of smectite and a monolayer of a cationic surfactant. These films were studied using polarized infrared attenuated total reflection (ATR), polarized infrared reflection absorption (IRRAS) spectroscopy and atomic force microscopy (AFM). Based on a quantitative thin-film model, the measured intensities the v(Si-O) bands of SapCa-1 saponite and SWy-1 montmorillonite on both Ge and ZnSe substrates confirmed that a monolayer of smectite was present in the hybrid LB films. This was also supported by the AFM measurements. These spectra represent the first reported IR spectra of clay monolayers functionalized with cationic surfactants. The measured intensity on both substrates corresponds to the calculated intensity of one clay layer (0.96 nm), indicating that a monolayer of clay was formed on ZnSe as well as on Ge. Both the ATR and IRRAS spectra are strongly polarized indicating that the hybrid films are highly oriented. In the case of saponite, a trioctahedral smectite, the measured dichroic ratios of the hydroxyl stretching band the out-of-plane v(Si-O) band were consistent with the nearly perpendicular orientation of these bonds in the film. For SWy-1, a dioctahedral smectite, the v(OH) bands have a dichroic ratio indicating that the structural OH groups are oriented more within the 001 plane. From the polarized IR spectra and AFM, it has been confirmed that the clay particles are highly oriented in the LB monolayer. In addition to the vibrational modes of the smectite, the IR spectra of the cationic surfactants are polarized and perturbed by the clay.
ROM MARTIAN METEORITES TO TERRESTRIAL ANALOGS AND FROM INFRARED TO RAMAN SPECTROSCOPY: IN SEARCH OF HYDROUS PHYLLLOSIONATES ON MARS


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The shergottite-nakhlite-chassignite (SNC) martian meteorites contain traces of preterrestrial alteration mineralogy, including hydrous phyllosilicates such as smectite and illite, and other minerals likely to have precipitated from aqueous fluids. Major geologic features such as valley networks and collapsed chaotic terrain provide evidence of past epochs of an active hydrosphere on Mars, and heat sources in the form of volcanic activity would have caused aqueous alteration of primary rock types. Recently, remotely sensed neutron-spectrometer data from the Mars Odyssey mission have shown substantial concentrations of near-surface hydrogen, presumably coupled in some regions with some form of hydrous mineralogy (Basilevsky et al., 2003). Yet direct and unambiguous detection of hydrous phyllosilicates at the surface of Mars either remotely (orbital) or in-situ (Viking, Pathfinder) remains elusive. In addition to their possible role of sequestering martian water, the phyllosilicates provide evidence of specific surface environments and weathering or hydrothermal processes, and they may play a key role in martian prebiotic or biotic chemistry. Terrestrial analog studies of volcanic terrains that exhibit evidence of aqueous alteration and development of hydrous phyllosilicate clay mineralogy detectable with remote sensing are helping to define strategies for deployment and analysis of future Mars remote sensing. Current and planned mission emphasis is on near- and mid-IR approaches to detection for remote sensing, especially in the range 2.2-2.5 µm (e.g., Bishop et al., 1998). Instability at the very surface of Mars, obscuration by windblown dust or other surface coatings, and low concentrations of phyllosilicates in rock formations, however, pose problems for remote detection. Thus, in-situ approaches for future landed missions are being developed such as laser Raman spectroscopy, which provides fingerprint spectra for the phyllosilicates and can detect phases present in very low concentrations (Wang et al., 2002, 2003), and which could be used to examine samples from below the surface, exposed by abrasion, coring, or impact ejection.

MOLECULAR MODELING OF THE INTERLAYER H-BOND NETWORKS IN LAYERED DOUBLE HYDROXIDES: STRUCTURE AND DYNAMICS

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The molecular scale structure and dynamics in the interlayers of layered double hydroxides, clays and other layered materials is often difficult to investigate due to spatial and temporal disorder, although it plays a dominant role in controlling the swelling and transport properties of these phases. Computational molecular modeling can be an effective tool in investigating interlayers, and we present here the results of a molecular dynamics (MD) study of the effects of hydroxide layer composition and anion on the structure and dynamics of interlayer anions and water molecules in layered double hydroxides (LDHs). These phases develop permanent, positive structural charge by cation substitution such as $\text{Al}^{3+}$ for $\text{Mg}^{2+}$ or $\text{Li}^+$ for vacancy in trioctahedral or dioctahedral hydroxide sheets and incorporate water molecules and a wide variety of anions in the interlayers. Phases studied include the $\text{Cl}^-$ compounds, $\text{[Ca}_2\text{Al(OH)}_6\text{]}\text{Cl} \cdot 2\text{H}_2\text{O}$, $\text{Mg}_3\text{Al(OH)}_8\text{Cl} \cdot 3\text{H}_2\text{O}$, and $\text{LiAl}_2(\text{OH})_6\text{Cl} \cdot \text{H}_2\text{O}$, and the $\text{SO}_4^{2-}$ compound $\text{[Li}_2\text{Al}_4(\text{OH})_{12}\text{]}\text{SO}_4 \cdot n\text{H}_2\text{O}$.

The results show greatly different interlayer structures related to the composition of the hydroxide layer and the anion. These structures are controlled by Coulombic and H-bond interactions among the OH-groups, water molecules, and anions. The nearest neighbor structural environments of the waters and anions are often similar to those in bulk liquid water and aqueous solutions, although the Coulombic interactions reflecting the hydroxide layer structure and composition lead to quite different longer-range structures. The H-atom distributions are highly disordered due to librational hopping of the water molecules. In $\text{LiAl}_2(\text{OH})_6\text{Cl} \cdot \text{H}_2\text{O}$ the waters and $\text{Cl}^-$ occur in a single layer with each water molecule in an H-bond stabilized, distorted tetrahedral coordination very similar to that in bulk liquid water. The average $\text{Cl}^-$ coordination is 6.5 by H-bonds, as in aqueous solutions, and most $\text{Cl}^-$ ions occupy distorted and dynamic octahedral sites. In contrast, the interlayer of $\text{[Li}_2\text{Al}_4(\text{OH})_{12}\text{]}\text{SO}_4 \cdot n\text{H}_2\text{O}$ is much more disordered and the water molecules form two sub-layers. The positions of water molecules are controlled by their H-bonding to the negatively charged O atoms of sulfate. For $n = 3$ or 4, approximately 70% of all $\text{SO}_4^{2-}$ ions have $C_2$ orientation, and 30% have $C_3$ orientation. In $\text{[Ca}_2\text{Al(OH)}_6\text{]}\text{Cl} \cdot 2\text{H}_2\text{O}$ there are two highly ordered sub-layers of water molecules, with the water molecules coordinating their O-atoms to the Ca’s, as in bulk solution. The $\text{Cl}^-$ is at the interlayer center and is in an unusual 10-coordinate site by H-bonds from $\text{H}_2\text{O}$ and $\text{OH}^-$. In $\text{Mg}_3\text{Al(OH)}_8\text{Cl} \cdot 3\text{H}_2\text{O}$ the water molecules and $\text{Cl}^-$ form two sub-layers, and the nearest neighbor $\text{Cl}^-$ environments are very similar to those in bulk solution. Each water molecule has an average of 3.8 H-bonds, significantly higher than the calculated value of 3.2 for bulk liquid water and close to the value of 4.0 for ice.
COMPETITIVE SORPTION OF PHOSPHATE BETWEEN FE- AND AL-OXIDES IN MIXED-MINERAL SYSTEMS

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Historical overapplication of phosphorus in soils has led to deterioration of water quality in many agricultural regions worldwide. Because Fe- and Al-oxides are considered the most important P-sorbing minerals in soils, an understanding of the binding affinity and sorption mechanisms of phosphate on various Fe- and Al-oxide minerals are important for managing the dissolution and discharge of P from soils into water. The objective of our study was to quantify the distribution of phosphate between Fe- and Al-oxide minerals as a function of sorbed P level in mineral mixtures, and thereby provide a measure of the relative binding affinity of PO4 for each mineral.

Phosphate was sorbed on various Fe- and Al-oxide minerals up to their maximum sorption capacities of 560 mmol kg⁻¹ (goethite), 1860 mmol kg⁻¹ (ferrihydrite), 850 mmol kg⁻¹ (boehmite), and 3400 mmol kg⁻¹ (non-crystalline Al-hydroxide) in aqueous suspensions at pH 6 and 22°C. Phosphate was similarly sorbed in suspensions containing physical mixtures (1:1 mass basis) of ferrihydrite/boehmite, goethite/boehmite, or ferrihydrite/non-xl Al-hydroxide. The mixtures showed maximum P sorption capacities intermediate between those of each mineral involved. Phosphorus K-XANES (x-ray absorption near edge structure) analysis was performed on moist samples of the single- and mixed-mineral systems containing sorbed P.

The XANES spectra for PO4 sorbed on any of the Fe-oxide minerals always showed a pre-edge feature at 2146 eV, which we attributed to an electronic transition of a P 1s electron to an Fe 3d (antibonding) orbital. This pre-edge feature indicated that PO4 was bound to Fe-oxides as an inner-sphere surface complex. XANES spectra for PO4 bound to Al-oxides showed no pre-edge feature at 2146 eV, and thus this spectral region provided a basis for distinguishing PO4 associated with Fe- versus Al-oxide minerals in the physical mixtures. Phosphate distribution between Fe- and Al-oxides in the mixtures was quantified using non-linear least squares fitting analysis, using XANES spectra for PO4 sorbed in single-mineral systems as standards. The distribution of PO4 between the Fe- and Al-oxide provided a quantitative estimate of the relative affinity of PO4 for each mineral.

Based on XANES results, all systems showed a preference of PO4 for the Fe-oxide in a mixture at low sorbed P concentrations, and an increasing preference for the Al-oxide mineral with increasing sorbed concentration. However, the sorbed PO4 concentration at which the preference changed depended on the type of oxide minerals in the mixture. Phosphate showed preference for goethite up to 40% of the maximum sorption capacity in goethite/boehmite mixtures and up to 10% of the sorption capacity in ferrihydrite/boehmite and ferrihydride/non-crystalline Al-hydroxide mixtures. The greater preference of PO4 at higher sorbed concentrations was attributed to formation of an Al-phosphate mineral, which caused a disproportionate amount of PO4 association with Al (III). This conclusion was supported by a decrease in the white-line peak of the XANES spectra. We concluded that PO4 distribution and consequently its relative affinity for Fe- or Al-oxide minerals in mineral mixtures may depend on high affinity binding sites in Fe-oxides and possible (surface) precipitation of Al-phosphate.

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THE EVIDENCES FOR MICROBE-MEDIATED SMECTITE-TO-ILLITE TRANSFORMATION

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For the past four decades, smectite-to-illite (S/I) transformation has been a topic of interest among the geoscientists especially, petroleum geologists and clay mineralogists, because the S/I transition is linked to the maturation, migration and trapping of hydrocarbons, the development of pore pressures, growth faults, and pore water chemistry. The degree of S/I transformation is frequently used as an independent geothermometer to allow reconstructions of the thermal and tectonic history of sedimentary basins. Despite the importance of the S/I reaction, considerable ambiguity exists in the literature as to how smectite is converted to illite as a function of geological variables. Numerous studies have been performed in support of one model, or the other emphasizing that temperature, pressure, and time are major variables, but none of them has taken into account the role of microbes. Here, using high resolution transmission electron microscopy (HRTEM), X-ray Diffraction (XRD) and energy dispersive X-ray spectroscopy (EDXS), we demonstrate that microorganisms can promote the nontronite (Fe-rich smectite) to illite transformation via reduction of structural Fe(III) in smectite. This observation is highly significant considering that bacteria can accomplish the task of transforming smectite to illite at room temperature within 21 days, a process that would otherwise require conditions of 300-350°C, 100 mPa, and 4-5 months in abiotic systems. Therefore, these results would drastically change the conventional concept of the S/I transformation models and reaction kinetic with subsequent implications.
THE INFLUENCE OF MICROBIAL FE(III) REDUCTION ON CLAYEY SEDIMENT FLOCCULATION

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The flocculation properties were shown to be greatly enhanced by the addition of the iron-reducing bacterium, *Shewanella oneidensis*. Fe(II) content in bioreduced nontronite measured by Ferrozine method is 5-times higher than in nonreduced control. Micromeritics Sedigraph measured 2.3-µm increase in mean aggregate size and a 30-times faster settling velocity compared with nonreduced nontronite suspensions. The clay aggregate size distribution of bioreduced nontronite suspensions with various incubation times in anaerobic condition is compared with that of aerobically bioreduced nontronite suspensions. Significant changes in physical properties of nontronite suspensions induced by microbial Fe(III) reduction were directly measured using Transmission Electron Microscopy (TEM). Particularly, floc architecture revealed that several domains of nontronite packets are glued by biopolymers secreted by bacteria, and the aspect ratio (thickness/length) of individual nontronite particle increases from 0.11 to 0.18. We suggest that surface chemistry changes induced by microbial Fe(III) reduction more likely to promote the micro-flocculation and then biopolymers bridge microflocs to macroflocs.
Oil sand ores, composed of bitumen, sand, and clay minerals, from Alberta, Canada are beneficiated to produce a feed stock for the production of synthetic crude oil. While the ores contain on average less than ten percent clay, the type of clay minerals determine the processibility of oil sand ores. Therefore, it is critical to fully understand clay mineralogy to control the extraction process from oil sand ores. For a laboratory study clay minerals are usually separated by toluene solvent extraction process while hot water extraction process is employed in industry. Preferentially oriented slides of the separated clay minerals were prepared for x-ray diffraction (XRD) analysis. XRD analysis shows that both swellable and non-swellable clays are present within the oil sand ores. More interestingly, however, it is demonstrated that there are differences in the XRD patterns of samples obtained through the two extraction techniques. It is observed that some XRD peak shifts while other are eliminated in samples prepared by toluene solvent extraction process, compared to similar samples obtained using the hot water extraction technique. This suggests that the extraction process alters the apparent structure of clay minerals, potentially leading to a misinterpretation of the clays present and provides insight into problems observed in ore processing.
At the Shell Creek stratigraphic section, Wilcox County, Alabama, the upper surface of the Maastrichtian Prairie Bluff Chalk is truncated and an impact-related basal sand couplet (consisting of a microtektite-rich sand and an overlying cross-laminated sand unit) rests directly on top. This basal sand couplet comprises the lower two beds of the Paleocene Clayton Formation in this vicinity. At Shell Creek, a sharp contact can be seen between the grey, bioturbated shelfal chalk and an overlying grey, microtektite-rich, coarse to medium sand layer, ~15 to 25 cm thick. The basal few centimeters of this microtektite-rich layer contains significant amounts of hematite in the matrix, but the upper part is mainly cemented by clay and calcite. This layer does not appear to be graded, but is very densely packed with microtektites, which make up as much as 25% of the grains in some parts of the rock. The microtektites are mostly in the size range of 0.5 to 3 mm, averaging about 1 mm. They have many different shapes, including spheres, “dumbbells,” “teardrops,” disks, and others. The most common shapes are spheres and “teardrops” (which may be broken “dumbbells”). Most of the microtektites appear to be altered to smectitic clays and many are encased in a shroud of calcite cement. Colors of microtektites include black, grey, greenish grey, and light grey. In cross-section, some spherical microtektites display an internal structure than includes intact smaller spherical droplets adhered to the inner walls of the microtektite. The medium to coarse sands comprising the microtektite host bed are quartzitic (no shocked grains have been found thus far) and not remarkable except that they are quite coarse, and thus “out of place” within the interpreted shelfal depositional realm of this material. The microtektite host bed also contains some rip-up clasts of chalk and phosphatic molds of fossils (snails, straight cephalopods, and pelecypods), both in the size range of 0.3-0.6 cm. The overlying layers of tan medium to fine quartzose sand (0.3 to 0.5 m) contain no microtektites, and there is a rather sharp, flat contact between the overlying sand and the grey, microtektite layer. At this contact, clasts and molds are strongly aligned. The main features of these upper sands are thin laminations, which are more nearly horizontal near the base and grade upward into hummocky-type cross-laminations near the top. Original relief of irregular sandwave structures (~ 4-8 cm) is preserved on the top of the upper sand bed. Above this upper sand bed, marls of the Clayton Formation are found, signaling a return to normal shelf sedimentation. The Shell Creek microtektites probably represent condensed particles of the vapor cloud or “melt mist” from the Yucatan deep bedrock, which arrived in Alabama in time to fall into the sea and be swept up in some initial tsunami wave effects. Subsequent tsunami waves likely produced the overlying sand unit, perhaps by scouring of the adjacent sandy shoreline.

The microtektites of Shell Creek represent the most easterly occurrence of Chicxulub impact ejecta in the Gulf Coastal Plain of the United States. Microtektites at this level are also known from Moscow Landing, Sumpter County, Alabama (28 km west-northwest of Shell Creek), the Brazos River sections in Texas, Beloc, Haiti, and the Arroyo el Mimbral sections in northeastern Mexico. Basal Clayton sections in Alabama east of Shell Creek do not contain microtektites or other known ejecta (i.e., Mussel Creek and Braggs sections, Lowndes County).
PRODUCTION AND CHARACTERIZATION OF HIGH ASPECT RATIO METAL PLATELETS BY MEDIA MILLING

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New technologies have prompted the U.S. Army to develop engineered aerosol particulates for dispersing in obscurant fogs. By dispersing high aspect ratio metallic flakes with certain refractive and conductive properties in these smoke clouds, the Army soldiers are protected from radiation and thermal imaging by the enemy through radiation scattering, adsorption, and emittance. Army scientists have concluded that the best particles for the targeted frequency range are in the 3-5 μm range with at least one nano- dimension. High aspect ratio metal particles have been manufactured in low yield through solution chemistry and higher yield by media milling. By grinding commercial spherical metal powders in a modified ring mill, we are able to produce flakes with diameters from 1-40 μm and thicknesses on the order of 100nm. The commercial metals that have been used thus far include iron, zinc, and titanium. These particles have been characterized through light scattering, image analysis and SEM techniques. Through further analysis using FTIR, XRD and other techniques, the optimum grinding time, media size, choice of metal will be determined for this application.
SYSTEM 3SnO$_2$-MnTaO$_6$: SYNTHETIC VS. NATURAL SAMPLES

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Prompted by studies of natural samples of cassiterite that contain exsolution of wodginite, synthetic phases in the system 3SnO$_2$ - MnTa$_2$O$_6$ were prepared, and compared to their natural counterparts. The following methods of study were used: X-ray powder diffraction, IR-spectroscopy and microprobe analysis.

Synthetic samples were prepared from pure oxides: SnO$_2$, Ta$_2$O$_5$ and MnO. The oxides were mixed in their required proportions and pressed into pellets that were then fired at high temperatures in air. Two series of samples were sintered, at 1100 deg and 1400 deg. Three different phases were grown: cassiterite SnO$_2$, wodginite MnSnTa$_2$O$_8$-Mn(Mn$_{0.2}$Sn$_{0.4}$Ta$_{0.4}$)Ta$_2$O$_8$ and tantalite MnTa$_2$O$_6$. Two two-phase fields were observed, cassiterite + wodginite and wodginite + tantalite. The first miscibility gap corresponds well to samples from the Annie-Claim pegmatite in Canada, but there are no natural analogues of the second.

Synthetic SnO$_2$ can dissolve up to 25 per cent MnTa$_2$O$_6$ in its structure at 1400 deg, whereas at 1100 deg the solid solution is restricted to a mere 1-2 per cent MnTa$_2$O$_6$. X-ray powder patterns of natural and synthetic samples are very similar, including synthetic cassiterite with high contents of MnTa$_2$O$_6$. In contrast, IR spectra of natural cassiterites are rather different from the IR-spectrum of pure synthetic SnO$_2$. All natural cassiterites, even the pure ones according to microprobe analysis, give IR spectra corresponding to SnO$_2$ that contains MnTa$_2$O$_6$. A natural sample of wodginite corresponds well with synthetic samples. In IR-spectra of both phases, the peak positions are identical, although peaks of natural wodginite are not as sharp as the peaks of the synthetic phase, which is probably due to disorder in the natural sample. Natural tantalite yields X-ray powder data, which are identical to those of synthetic tantalite. However, its IR-spectrum matches the spectrum of synthetic wodginite rather than that of synthetic tantalite. This may be caused by a substitution of some Sn in the structure of natural tantalite.
IMMOBILIZATION OF CESIUM-CONTAMINATED SEDIMENTS THROUGH THE ADDITION OF ILLITE CLAYS

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About 3,000 acres of wetlands on the Department of Energy’s Savannah River Site (SRS) located near Aiken, SC became contaminated with 560 Ci of cesium-137 (Cs) as a result of operations during the 1960’s. The problems of Cs contaminated aquatic systems and their associated risks are heightened at the SRS because Cs is generally more mobile on the site than in other environments. Cs in these kaolinite-dominated sediments is weakly sorbed, that is, it enters into a mobile phase and continues to spread through the environment. An earlier study demonstrated that when illitic minerals were added to contaminated SRS sediments, Cs became immobilized. The objective of this study was to evaluate the use of illites to immobilize Cs and reduce Cs bioavailability under field conditions. Sixteen 3-m diameter mesocosms were established in a Cs-contaminated canal on the SRS with the following treatments: four controls (no amendments), six with low illite application (0.2-cm covering the contaminated lake sediment), and six as a high clay application (2.5-cm coverage). During the initial 4-months of the study, there was a 25 to 30 fold decrease in Cs-water concentrations; a 3 to 5 fold decrease in Cs-plant (duckweed) concentrations; and a 2 to 3 fold decrease in Cs-fish (Gambusia) concentrations. Additionally, there was no evidence of harm to the environment. These encouraging early results suggest that this approach may provide a cost-effective alternative to digging up and then treating the sediment offshore.
Polymer nanocomposites will soon become common in applications that require unique value-added properties not normally possible with traditional fillers, such as reduced permeability, tailored biodegradability, optical clarity, self-passivation, and flammability, oxidation and ablation resistance. The lower loadings (1-5%) facilitate processing and reduce component weight compared to traditional fillers (15-40%). A key element to improved properties is the presence of highly anisotropic inorganic elements, such as layered silicates (LS) or carbon nanotubes, embedded in a filler/matrix interface dominant environment. The challenge to forward the area of nanocomposites is the characterization of the distribution and the spatial-directional control of inorganic nanoelements. Fundamentally, conceptual similarities can be established with the phase behavior of nematic and discotic liquid crystals, articulated by Flory and De Gennes.

Using this framework, the ‘phase’ structure and morphology of LS both quiescent and under external stimuli, such as shear and electric fields will be discussed. In-situ synchrotron experiments of orientation and relaxation behavior reveal many parallels to liquid crystals. Furthermore, dielectrophoreses enables control of LS orientation, providing a means to not only examine local particle dynamics but also tailor properties, such as modulus and thermal expansion, of LS nanocomposites by ‘dialing-in’ of morphology. Finally, examples will be discussed with an outlook to potential applications for these novel materials.
Chemical modification of smectites is often used to tailor smectite properties to suit various purposes. Among the methods used are acid activation, oxidation-reduction (redox), and Li\(^+\) fixation. Acid activation is one of the most common methods for chemical modification of bentonites. It is used in the laboratory as well as in industry for the preparation of adsorbents (bleaching earths), catalysts or their supports, and other products. Acid dissolution of smectites is rather common in nature, occurring, for example, when acid mine waters attack the minerals. In laboratory experiments strong mineral acids, such as HCl or H\(_2\)SO\(_4\), are used; and, typically, the aim is to prepare partly dissolved materials. The process proceeds via exchange of exchangeable cations with protons and partial dissolution of the layers, which yields the partial removal of octahedral cations and any substituted tetrahedral cations from the clay-mineral layers. The product is an amorphous, partly protonated silica phase. The extent of mineral dissolution is commonly followed by the chemical analysis of solid or liquid reaction products, or by various physico-chemical methods, such as infrared or MAS NMR spectroscopies. The process is substantially affected by several variables, including chemical composition of the mineral used and the number of non-swelling layers.

The negative charge on the smectite layer can be manipulated chemically, being increased via reduction of structural Fe(III) to Fe(II) or decreased via fixation of exchangeable Li\(^+\) upon heating. Iron reduction will be illustrated using a unique clay mineral named griffithite. This is a trioctahedral smectite with dioctahedral domains, found in the weathered basic rock from Griffith Park, California. The 0.2-2 \(\mu\)m fraction is brown, very similar to the overall <2-\(\mu\)m fraction; the 0.06-0.2 \(\mu\)m fraction is dark reddish-brown, while the finest fraction is dark yellow. Crystalline admixtures (albite, calcite, quartz and maghemite) are concentrated in the 0.2-2 \(\mu\)m fraction, while the finest fraction contains only trace amounts of other minerals. Griffithite is primarily an iron-rich saponite with negative tetrahedral and positive octahedral charges of \(-1.33\) and \(+0.46\) e per O\(_{20}\)(OH)\(_4\), respectively. The octahedral occupancy is about 91\%, and about 26\% of the octahedra contain trivalent cations, imparting a net positive charge to the octahedral sheet. Medium levels of Fe(III) reduction in griffithite, up to 60\% of total Fe, can be achieved by adding solid sodium dithionite to clay dispersions in a citrate-bicarbonate buffer. By contrast, more than 90\% reduction of Fe(III) to Fe(II) is achieved in nontronites using the same method. The lower reducibility of Fe(III) in griffithite relative to nontronites may be due to structural differences between the two smectites, such as a more negative tetrahedral charge and a positive octahedral charge.

Fixation of exchangeable Li\(^+\) in montmorillonite upon heating at different temperatures up to 300 °C generates a series of chemically relatively stable, very similar materials of different charge derived from the same parent mineral.
Several micas containing different octahedral and interlayer cations were synthesized at different temperatures under conventional- and microwave-hydrothermal conditions and these phases were characterized by powder X-ray diffraction, solid-state magic angle spinning nuclear magnetic resonance (MASNMR) spectroscopy, scanning electron microscopy and Fourier transform infrared spectroscopy. A zinc K-mica with Zn in the octahedral sheets and K in the interlayers was synthesized in the temperature range of 150°-200°C and a novel zinc Rb-mica with Zn in the octahedral sheets and Rb in the interlayers was synthesized at 200°C. On the other hand, the synthesis of either magnesium or cobalt or nickel K-micas was found to be difficult or impossible at these low temperatures. Solid-state $^{29}\text{Si}$ MASNMR revealed that the Al in the tetrahedral sites is disordered with several nearest neighbor Si environments. In general, microwave-assisted hydrothermal conditions led to better crystallization of the zinc K-micas compared to the conventional method.
Microorganisms, while metabolizing nutrients, release respiratory electrons that are ultimately transferred to Terminal Electron Acceptor Processes (TEAP). In aerobic organisms, such as ourselves, oxygen serves as the TEAP, whereas anaerobic life has a much wider range of TEAPs, including nitrates, sulfates and a variety of metal ions. It is possible to harvest this flow of respiratory electrons in a microbial biofuel cell and develop sufficient electrical energy to power external circuits. Such arrangements can employ anaerobic microorganisms with oxygen as the TEAP, since they are “breathing through a wire,” so to speak, and are not exposed directly to the oxygen. Both mediated and non-mediated mechanisms of respiratory electron transfer are supported in this energy harvesting process.

Marine sediments are a useful laboratory to study this process. Here, organic material in the sediment acts as fuel and dissolved oxygen in the seawater acts as an oxidizer for a microbial biofuel cell. A succession of microorganisms utilize a series of TEAPs, starting with oxygen in the uppermost few millimeters of the sediment, and proceeding through nitrate, iron and manganese reduction, to sulfate reduction deep in the sediment. These produce a sequence of chemical horizons within the sediment that can result in as much as 0.75 volt potential difference between graphite electrodes placed within the sediment and in the overlying seawater.

If microorganisms can be used in this way to produce electrical energy, can, under the proper circumstances, the generation of electrical energy be used to indicate the presence of microorganisms, perhaps in an extraterrestrial environment?

Experimental results of several microbial biofuel cells employing marine sediments are presented and various mechanisms of respiratory electron transfer are discussed. These are used as a model to develop an approach for in-situ detection of microbial life beyond the Earth. Important constraints are considered to discriminate between electrical energy developed by microbial biochemistry, and that generated by purely geochemical processes.
ANTIMICROBIAL ACTIVITY OF MODIFIED CLAY MINERALS

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The physical and chemical surface properties of smectite clay minerals can be modified by exchanging the naturally occurring inorganic cations with either transition metal cations or quaternary ammonium cations. By appropriately choosing the exchangeable cation, antimicrobial properties can be imparted to the modified clay mineral. A series of differently modified smectite clay minerals, both natural and synthetic, were examined by a standard microbial assay using activated sewage sludge as a source of microbes. The antimicrobial activity of the transition metal cations studied followed a decreasing order whereby Cu>Mn>Zn>Fe. Of the quaternary ammonium cations, hexadecyltrimethyl ammonium (HDTMA) showed the highest activity, and the activity was directly related to the amount of the cation present on the clay mineral surface. Adsorption of HDTMA in excess of the CEC proved to be particularly effective in killing the sewage sludge microbes. The exchanged clay materials have a wide range of potential applications for imparting antimicrobial activity to medical, industrial, and household applications.
NATURAL ATTENUATION OF URANYL(VI) DURING THE DISSOLUTION OF DIFFERENT CHLORITES IN MIXED-FLOW EXPERIMENTS

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In batch sorption and mixed-flow experiments the sorption of U(VI) was studied on an unaltered rigidolite chlorite (CCa-2) from Flagstaff Hill (El Dorado County, California) and on a hydrothermally altered chlorite from Grimsel (Switzerland). During the dissolution of the unaltered CCa-2 chlorite the major cations Al, Fe, Mg, and Si are released into the aqueous solution leaving an altered chlorite mineral which transformed to vermiculite. Depending on the pH of the solution new Fe-minerals, in particular ferrihydrite, precipitate from solution at pH > 5. Ferrihydrite forms coatings on the chlorite edges as well as colloids in the aqueous solution. Due to its very high specific surface area and its high affinity to bind heavy metals ferrihydrite is an important sorbent for U(VI). In batch sorption and mixed-flow experiments of U(VI) on 0.5 g of the dissolving chlorite U(VI) is sorbed to both chlorite and newly forming ferrihydrite. At pH 6.5 to 7.5 almost 90 % of the initially added uranium (1*10⁻⁶ M) is sorbed to the chlorite. The second chlorite is a hydrothermally altered chlorite from Grimsel, which is relative resistant to weathering and therefore does not tend to form secondary phases. The Grimsel chlorite sorbs distinctively less U(VI) than the CCa-2 chlorite. Under comparable conditions only 70 % of the initially added U(VI) is sorbed.

The higher sorption capacity of the CCa-2 chlorite was attributed to the formation of secondary Fe, and may be Al phases. The newly formed secondary Fe phases, very likely ferrihydrite, provides additional sorption sites to the system. Although all the available reactive sites on the CCa-2 chlorite were occupied U(VI) was continuously sorbed to a minor proportion in our mixed-flow experiments. This indicates that an additional process must have taken place, which can be attributed to newly formed ferrihydrite particles.
POLYSOME-RELATED DEFECTS IN PALLYORKSITE-SEPIOLITE MINERALS: A TRANSMISSION ELECTRON MICROSCOPY (TEM) STUDY.

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Palygorksite-sepiolite minerals consist of 2:1 layer ribbons (polysomes) connected by tetrahedral inversion; this configuration produces zeolite-like channels in the structure. These minerals are beam-sensitive in the transmission electron microscope. Image-capture technology by charge-coupled devices (CCDs) now enables more rapid data acquisition. Consequently, better imaging of palygorskite-sepiolite minerals is possible owing to very short (0.3 to 0.7 s) exposure times.

Sepiolite [approximate composition of Mg8Si12O30(OH)4·12H2O] from Helsinki, Finland and yofortierite [approximate composition of Mn5Si8O28(OH)2(OH2)4·4-5H2O] from Mont St. Hilaire, Ontario, Canada were examined using TEM to determine variations in microstructure. In both samples, defects were observed where polysomes are omitted from the structures. Defects occur in approximately 5 % of both the yofortierite and sepiolite sample material. The number of polysomes omitted in a defect cluster varies from a few to several dozen. These defect clusters are most commonly found in small groups of 2 to 3 in both sepiolite and yofortierite fibers. We believe that these defects may result from variation in the rapidity of crystallization or from the imperfect coalescence of domains.

Such defects may explain variations in physical properties of palygorskite-sepiolite minerals as determined by previous workers such as anomalously high H2O content, and sorption of large cation complexes and organic molecules. The presence or absence of these defects may affect palygorskite-sepiolite commercial applications involving the sorption properties of this mineral group.
BIO/LITHOFACIES OF OCTOPUS SPRING SINTER IN YELLOWSTONE NATIONAL PARK, WYOMING

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Siliceous sinter material (silica-rich deposits formed at the edge of thermal hot springs) was collected from Octopus Spring located in Yellowstone National Park for the purpose of characterizing biological and lithological properties. The sinter deposit was cut cross-sectionally exposing five bio/lithofacies based upon crystal, textural, and chemical components. These five bio/lithofacies include the crust, an altered interior, light/dark, dark laminated with pores, and colloform (structural protrusions into the pool). Using X-ray Diffraction and Fourier Transfer Infrared spectroscopy, opal-A was found to be the dominant mineral, except within the altered region, which is also composed of dioctahedral smectite, quartz, pseudobrookite, hematite, and rutile. The altered region also varies in that it has no textural component, whereas the other regions contain very fine to wavy to concave up laminations. Textural analysis was conducted using light, confocal, and backscatter electron imaging. For chemical analysis, micro-Dumas combustion for C/N analysis showed the greatest percentage of carbon within the dark lamination zone. Electron Probe Microscopy indicated that the elemental ratios of Ca/Mg, Na/K, F/Cl, and Na/Cl are greater than one, which is consistent with the composition of geothermal waters in felsic volcanic rocks found in other parts of the world.

Through study of actively growing sinter deposits, we are able to understand the mechanisms of how sinter deposition is initiated, and how sinters mineralogically and texturally change through time. This work is important because sinters may serve as analogs for the preservation of early life forms in ancient Earth rocks and possibly rocks from nearby planets and moons.
STRUCTURAL CHANGES IN HYDROXYL ION OF TRIOCTAHEDRAL MICA WITH INCREASING TEMPERATURE: IN-SITU NEUTRON POWDER DIFFRACTION

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The objective of this study was to investigate structural changes and the orientation of hydroxyl bond in trioctahedral mica at high temperature. The thermal response of the natural phlogopite-IM, K₂(Mg₅.₃₇₃Fe₀.₃₇₄Al₀.₀₇₉Ti₀.₀₇₀)(Si₅.₇₃₀Al₂.₇₇₀)O₂₀[OH₃.₈₆₄F₀.₁₃₆], Quebec, Canada, was studied by in situ neutron powder diffraction (HANARO reactor, Korea Atomic Energy Research Institute). The in situ temperatures were ranged from 25°C to 600°C. To determine the orientation of the O-H vector accurately, this sample was examined at -263°C. The crystal structure was refined by Rietveld method (FullProf program, Rodriguez-Carvajal, 1998) at 25°C, 150°C, 300°C, 450°C, 600°C and -263°C (R_p=2.35%-2.7%, R_wp=3.01%-3.43%).

At room temperature, a=5.13Å b=9.20Å, c=10.21Å, γ=100.06°, and V(volume)=491.69Å³. The expansion rate of unit cell dimensions and volume was linear. The values for a, b, c and volume were 1.54×10⁻⁵°C⁻¹, 1.04×10⁻⁵°C⁻¹, 1.05×10⁻⁵°C⁻¹ and 3.80×10⁻⁵°C⁻¹. The angle γ, however, decreased in the temperature range of 400°C-600°C to 99.84° and had no significant change below 400°C.

At -263°C, hydroxyl bond length was 1.03Å and an angle of the bond to the (001) plane was 87°. With increasing temperature (25°C-600°C), the bond length decreased from 0.9Å to 0.7Å. The angle also decreased from 87° to 82°. These results were related to an increase in its vibrational amplitude.
LONG-TERM LEACHING OF JEJU ANDISOLS WITH HCl SOLUTION: BUFFER CAPACITY AND ALUMINUM SOLUBILITY CHANGE

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Buffer capacity and aluminum solubility of two Bo horizon soils of Jeju Andisols developed from different parent materials have been investigated. For column leaching test 0.1N HCl solution was injected into the bottom of the acryl column with rate of 0.025ml/min. by peristaltic pump, and the solution extracted from the top of the column was collected at regular intervals for 14 months. For batch test 50ml of different concentrations of HCl solution was added to 5g field-moist soil and they were equilibrated for 1 month.

The titration curves from column leaching test showed that buffering occurred at pH 6.0 and 4.0. The buffer intensity of soil developed from pyroclastic materials (P-soil) is higher than that from basalts (B-soil). From batch test we found that proto-imogolite and/or imogolite might control Al solubility as well as Al(OH)$_3$ in the moderate acid condition. The buffer intensity ($\beta$) of P-soil was plotted on the theoretical buffering curve of Al(OH)$_3$, while $\beta$ of B-soil approached to that of proto-imogolite. These results showed that the dissolution of short-range-order materials control the buffer capacity of P-soils. Buffering at pH 6.0 is attributed to dissolution of some silicate clays and exchange reactions between H$^+$ and base-forming cations.

Considering the amount of annual acid precipitation, aluminum solubility of Jeju Andisols, and the low BS (Base Saturation percentage), it can be predicted that prolonged acid precipitation will reduce the buffer capacity of soils and lead to soil acidification.
THE USE OF INORGANIC PLASTICIZERS FOR TECHNICAL CERAMICS EXTRUSION: CHARACTERIZED USING HIGH PRESSURE SHEAR RHEOMETRY

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High pressure shear rheometry (the High Pressure Annular Shear Cell (HPASC) located at Alfred University) was used to characterize the plasticity changes associated with the substitution of an inorganic plasticizer for polymeric additives in advanced ceramic bodies intended for piston extrusion. While polymeric additives are commonly used for ceramic extrusion, the solubility of these additives can lead to variability in the extrusion character and extrudate quality. In this study, a portion of the organic additives was replaced with inorganic plasticizer, the high pressure rheology measured, and the extrusion performance evaluated. The experiments were conducted using a statistical experimental design methodology that allowed the role of each additive to be deciphered allowing optimum additive levels to be developed. Bentonite was necessary to improve the cohesion of the system (correlating to green strength). The addition of an inorganic plasticizer generally resulted in an increased water level necessary to achieve an extrudable plastic body while reducing extrusion pressures. The extrusion behavior correlated well with cohesion and pressure dependence as measured by the HPASC allowing plasticity limits to be defined for optimum piston extrusion.
STRUCTURAL DISTORTIONS IN Fe SITES AND REVERSIBILITY OF REDOX PROCESSES IN GARFIELD NONTRONITE: A MÖSSBAUER SPECTROSCOPIC STUDY

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The redox state of structural Fe in smectites greatly alters clay surface chemistry. While the exact mechanism(s) for this phenomenon has yet to be identified, links to changes in crystal structure are believed to be important. Previous studies reported that extensive changes occur in structural OH groups and coordination environment of Fe during redox processes. As reduction progresses, these changes become more extensive and reversibility upon reoxidation is degraded. The purpose of the present study was to further probe the changes in the state and environment of Fe at various stages of Fe reduction and reoxidation in order to fill gaps in our knowledge of this subject. The structural Fe of unaltered (oxidized), reduced (0.20 to 0.95 Fe(II)/Total Fe), and reduced-reoxidized Garfield nontronite (API-33a) clay was characterized by Mössbauer spectroscopy at 88 K and ± 4 and ± 12 mm/s, and by chemical analysis for structural Fe(II). The reoxidized form of each reduction level was also analyzed. Areas of spectral components attributable to Fe(II) correlated well with chemical analyses. Only subtle changes, except for a decrease in intensities, were observed in the remaining Fe(III) peaks at the level of reduction increased. Reoxidation restored virtually all of the Fe to the Fe(III) state, but the Fe environment (QS) of the reoxidized samples differed from that of the unaltered (oxidized) sample to increasing degrees depending on the initial level of Fe reduction. Samples reduced to Fe(II)/Total Fe = 0.20, then reoxidized, yielded QS similar to the unaltered sample; but, samples reduced to Fe(II)/Total Fe > 0.2, then reoxidized, gave QS values that increased steadily with the initial reduction level. These differences indicate that the reversibility of the redox process depends on the initial extent of reduction.
SORPTION CHARACTERISTICS OF POLYCYCLIC AROMATIC HYDROCARBONS AND CADMIUM ON ORGANOCLAYS

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The fate and the behavior of polycyclic aromatic hydrocarbons (PAHs) and heavy metals in the environment are mainly controlled by their interactions with various components of soils and sediments. Due to its large surface area and abundance in many soils, montmorillonite may greatly influence the fate and transport of the contaminants in the environment. In our experiment, PAHs (naphthalene, phenanthrene) sorption by hexadecyltrimethylammonium (HDTMA)-modified montmorillonite linearly increased in proportion to the amount of HDTMA added on the clay. However, trimethylammonium (TMA)-modified montmorillonite did not show superiority in its sorption of PAH compared with the HDTMA-montmorillonite or dodecyltrimethylammonium (DTMA)-montmorillonite. Meanwhile, the montmorillonites modified with the same cationic surfactants adsorbed Cd$^{2+}$ (heavy metal) significantly from water at low surfactant loading level, but the Cd$^{2+}$ adsorption linearly decreased as the loading of surfactant increased. The result shows that the sorption tendency of organoclays for organic or inorganic contaminants was significantly influenced by the amount and size of the surfactants added on the clay. It means that the stabilization and configuration of cationic surfactant formed on the clay interlayer according to the loading amount of each surfactant of different sizes may be an important factor in effectively sorbing the environmental pollutants.
LIQUID-SOLID TRANSITIONS OF LAPONITE SUSPENSIONS: STRUCTURE, STABILITY AND JAMMING

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In recent years, aqueous suspensions of charged plate-like colloids and more especially clay particles have been the subject of intense investigation. Systems such as Laponite, a synthetic clay, undergoes puzzling liquid-solid transitions at low concentrations. The status and the origin of these transitions (Wigner glass, frustrated nemat transition, gelation) are under strong debate. In the first part of this talk, we propose a direct and quantitative inspection of the particle morphology by atomic force microscopy(1). In the second part, we show that a liquid-solid transition is observed at very low ionic strength. Such a structural transition involves a long-range electrostatic stabilization and/or jamming which is compatible with a Wigner glass transition(2). Close inspection of ultra small angle X ray scattering experiments reveals that particles are not homogeneously distributed in space. A similar observation is done at higher ionic strength, using magnetic colloidal particles as probes for the determination of laponite suspensions structure (3). In the third part, we present some recent field cycling NMR relaxometry experiments allowing to follow the particle and the solvent dynamics during the solid-liquid and/or the glass transition. Finally, a simple stability analysis of this colloidal system is discussed (4,5,6), raising interesting questions about long term stabilization and/or coagulation, (very) slow structural relaxation and nematic defects generally observed for these colloidal suspensions at relatively high ionic strengths.

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The uses of fossils and minerals for healing date back thousands of years. Peoples all over the world have applied these geologic materials in various forms to soothe, and cure. While modern day mainstream America uses a few common minerals such as clay and calcite for medical purposes, other countries manufacture tons of pharmaceuticals with a multitude of rocks and fossils incorporated as part of their ingredients. Homeopathy, some manual therapies, and various medical disciplines take advantage of these earth materials. Little research exists as to what the healing effects of minerals and fossils might be.

Over 100 minerals have been used for medicinal purposes. Besides quartz and its various forms, sapphire, amber, topaz, emerald, and hematite are at the top of the list, followed by malachite, jade, diamond, and fossil bone.

These rocks are used for a wide range of maladies such as malachite for rheumatic conditions and tumors; peridot for ulcers and gastro-intestinal problems; amber for diseases of the brain, asthma, and pain; sapphire for gout, eyes, and skin problems; and fossilized bones for high blood pressure, diarrhea, and sexual dysfunction.

The most common forms of use are the direct application of the whole compound to the body, the essence of the rock in either drops or tea, and ground up minerals mixed with a fluid to make a paste.
TIME-RESOLVED STRUCTURAL ANALYSIS OF CATION EXCHANGE REACTIONS IN BIRNESSITE USING SYNCHROTRON XRD

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Birnessite ((Na,Ca,Mn2+)Mn7O14·2.8H2O) is an abundant phase in soils, desert varnishes, and ocean nodules, and it plays a significant role in soil and groundwater chemistry. As part of a broad-based study to examine cation substitution in the interlayer sites of birnessite, we have monitored K- and Ba-cation exchange reactions in Na-birnessite by time-resolved X-ray powder diffraction with a simple flow-through cell at the National Synchrotron Light Source. A series of synthetic Na-birnessite samples were saturated with chloride solutions containing dissolved K+ and Ba2+ ranging from 0.1M to 0.001M. Powder X-ray diffraction patterns were collected every ~ 3 minutes. Rietveld analysis of the synchrotron data revealed that complete cation exchange occurred within four hours. Based on Post et al.’s (2002) re-evaluation of Na-birnessite with triclinic symmetry, we refined the fully exchanged K end-member in both monoclinic and triclinic settings. These analyses demonstrated that K-birnessite is triclinic. The final $\chi^2$ for a monoclinic cell was 2.60 in comparison with a value of 1.78 for a triclinic cell. In addition, splitting of the -102 and the 012 peaks was evident in the observed X-ray diffraction pattern. The improvement of the triclinic over the monoclinic refinement for the Ba-exchanged birnessite was even more significant. The rate of change of the axial parameters was discontinuous for both K- and Ba-exchange. The linear volume contraction coefficient was 7.80 x 10^{-6} sec^{-1} for the first 22 minutes of K-exchange. This coefficient decreased to 2.45 x 10^{-7} sec^{-1} for the remainder of the experiment. The volume contraction was driven by decreases in the a, c, and $\beta$ cell parameters. In comparison, Ba-substitution induced a much smaller change in unit cell volume. The linear volume contraction coefficient was 1.96 x 10^{-6} sec^{-1} for the first 36 min of exchange and this diminished to 1.72 x 10^{-7} sec^{-1} thereafter. Fourier electron difference syntheses revealed that the structural changes were a function of the configuration of the interlayer species. Split electron density maxima with centroids at (0 0.5 0.5) were present in both Na and K end-members. However, with increased substitution of K for Na, the axis connecting the split-site maxima rotated from an orientation parallel to $b$ to $a$. A similar rearrangement occurred during Ba-substitution, but this rotation was accompanied by a displacement of the centroid to (0 0.5 0.5).
**SURFACE MODIFIED KAOLINITE AS FILLER IN NATURAL RUBBER**

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Kaolinite from Kundara, Kerala has been used as filler in natural rubber after thermal and chemical modifications. The mineralogical, structural, morphological and chemical evaluation of raw and metakaolinized clays (600°C and 900°C), was undertaken by X- ray diffraction analysis (XRD), Fourier Transform Infrared Spectra (FTIR), Scanning Electron Microscopic (SEM) and chemical characterization. Calcined and uncalcined kaolinites were hydrob Hobized by surface modification using the coupling agent- triethoxyvinyl silane by dry mixing. The extent of hydrophobicity of this organic-inorganic hybrids were analysed by Diffuse reflectance infrared spectra, Contact angle measurements, Rheological studies and Thermal analysis. Incorporation of these aluminosilicates as filler into natural rubber matrix results in the composites, which show improved mechanical, curing, swelling and thermal properties. Vulcanized samples with calcined and silylated kaolinite fillers show better compatibility, thereby giving higher density, lower curing temperature, higher thermal stability, higher break stress, break strain and modulus at 100% and 300%. The improvement in properties results from higher cross-linking of these rubber- kaolinite composites.

Key words: Kaolinite, Metakaolinite, Surface modified clays (SMCS), Silane, Triethoxyvinyl silane, Polymer composite, Filler, Natural Rubber, Cross- linking, Inorganic-organic hybrids, Mechanical strength, Swelling, Thermal properties
NUCLEATION AND GROWTH OF Fe(III) AND Al(III) COLLOIDS IN THE PRESENCE OF COMPLEXING ORGANIC AND INORGANIC LIGANDS

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Colloidal species play a major role in contaminant transport. Their high reactivity confers them the ability to bind organic as well as inorganic pollutants. The transport of contaminants can be either facilitated by the small size of the colloidal species or hindered by the formation of large aggregates. A better understanding of the contaminant transport mechanism therefore requires a detailed knowledge of the formation and aggregation mechanisms of the colloids. Here the focus will be on the colloids formed with aluminum(III) and iron(III), two major elements of the earth's crust. The aqueous chemistry of these two metal cations is characterized by the fact that they undergo hydrolysis, which leads to the formation of well crystallized minerals. For these two cations, the nucleation and growth pathways (i.e. the first steps of the hydrolysis) in the absence of complexing ligands have been clearly identified over the past two decades. We show in the present study that these nucleation mechanisms are deeply modified by the presence of complexing ligands such small organic acids, natural organic matter or phosphate ions.

The presence of organic ligands modifies deeply the nucleation of Al(III). The formation of the characteristic Al₁₃ polymer is strongly inhibited. In the precipitated phases, the aluminum is predominantly in the form of monomers. The small amounts of Al₁₃ initially present are depolymerized by the organic ligands within the two first hours of aging. The aggregates display high fractal dimensions (>2.2), the highest values being obtained with bridging ligands. The coagulation of natural organic matter (NOM) by Al(III) or Fe(III) salts leads to the formation of large sized flocs. There is a selectivity of the coagulants towards certain types of biopolymers constituting the NOM. Iron preferentially binds polyhydroxy-aromatic compounds whereas aluminum binds polysaccharides. The speciation of aluminum within the flocs resembles that described above: monomers are the predominant species and larger Al polymers are depolymerized with time. The speciation of iron consist of small oligomers (mainly Fe dimers and trimers) demonstrating the detrimental effect of the ligands on the Fe polymerization. For both metal cations, the obtained flocs are dense and the evolution of the fractal dimension with pH shows that the ligands control the structure.

The hydrolysis of Fe in the presence of PO₄ ligands results in the formation of small aggregates (approx. 100 Å) or a gel phase, depending on the PO₄ concentration. The largest Fe polymer observed in these system is the Fe edge sharing dimer. As with the organic ligands, the fractal dimension of the resulting solids is high and the evolution of the structure is controlled by the PO₄ ions.
FOSSILIZATION OF MICROORGANISMS ON AN ANNUAL TIMESCALE IN AN ANAEROBIC AQUIFER: GEOCHEMICAL CONTROLS AND IMPLICATIONS FOR PRESERVATION OF EVIDENCE OF EXTRATERRESTRIAL LIFE

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We report Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometry (EDS) evidence of carbonate mineralization of microbes in a highly reducing contaminated aquifer environment. Mineralogical and textural consequences of mineral exposure to an anoxic contaminant plume in a glacial aeolian/outwash-sand aquifer were examined experimentally using in-situ microcosms. Crushed and euhedral grains of almandine garnet were placed into the aquifer at a single multi-level well at depths of 25, 28, 32 and 37 feet below land surface and removed after a period of eleven months. Prior to and during the eleven-month incubation period, the geochemical conditions of the plume were monitored. The microcosms placed at depths 25 and 28 feet interacted with more contaminated reduced water than those placed at the 32 and 37-foot depths. In addition, during the bulk of the eleven-month incubation period, the well was exposed to unique biogeochemical conditions as a result of a test flow-through bioreactor system located approximately 270 feet upgradient from the test well. Organic matter was removed from experimentally exposed garnets by standard soil-chemical techniques and the exposed grains were analyzed by SEM-EDS.

Precipitates, typically individual rugose rodlike forms or clusters of ellipsoidal bodies 1-20 microns in long dimension, were discovered on both crushed and euhedral garnet grains from depths corresponding to the most reduced groundwater, but not at greater depths. Precipitates are most likely calcite. EDS indicates the precipitates contain Ca, C, and O. Sand above the water table is depleted of sand-size carbonate fragments, whereas sand below the water table is up to ~15% carbonate; and groundwater is near equilibrium with respect to calcite. Precipitates strongly resemble encrusted microorganisms; many have filamentous protrusions morphologically resembling extracellular polysaccharides that connect to the mineral surfaces. Some cell-shaped precipitates are demonstrably hollow, consistent with mineralization of a sheath around microbes, followed by removal of organic material. Precipitates on crushed garnets are randomly distributed, whereas on euhedral grain surfaces the precipitates occur along growth steps and within pits. Cell counts and 16S rRNA indicate that a diverse but variable microbial assemblage was present before and during the experiment, but no precipitates were observed on pre-experiment aquifer sand.

Fossilization of microorganisms took place in less than a year under well-documented unique geochemical conditions. The biogeochemical conditions in the system described here are similar to some of the conditions believed to exist in other settings of astrobiological significance. Our findings suggest that mineral microfossils can form rapidly under astrobiologically relevant conditions.
Nuclear waste disposal in geological environments necessitates a profound knowledge of the evolution of the natural rock barrier during long term storage. Therefore, thermal alteration of geological barriers is one of the parameters to take into account. The aim of this work is to study the effects of thermally-induced clay-organic matter interactions on each component by aqueous pyrolysis, as encountered in the Callovo-Oxfordian claystone of the underground laboratory of ANDRA (Bure, France). In a preliminary step, which results are presented here, experimental simulations on mixtures of appropriate organic and clay model components were conducted.

The experimental material, which was chosen, consists of two standard clay fractions (Volclay bentonite and natural Illite from Le Puy, France) and of pure immature-type II kerogen from the Toarcian unit of the Paris Basin. Several sets of confined pyrolysis experiments in gold cells were conducted on mixtures of clays, kerogen and water (water/sample ratio of 1, organic/mineral ratio of 1/10). The experimental conditions include steps of increasing temperature (200 to 365°C) over short periods (72 hours) at a pressure of 300 bars.

The soluble organic compounds were quantified after pyrolysis; they were fractionated. Polar compounds and hydrocarbons were analysed by µFTIR and GC-MS respectively. The mineralogical content was studied by DRX, MET, ICP-MS, ICP-AES. Sequential leaching experiments were realised with distilled water and dilute acid solutions in order to compare the structural chemical elements of the clays to the soluble free and sorbed ones.

The organic extracts obtained show that a fraction of the kerogen-generated bitumen is trapped by the clays. Quantification and composition of the extractable materials reveal that the trapped material are mainly polar compounds. Also, the amounts of inorganic elements collected after water leaching of the pyrolyzed samples decrease significantly when the experiments are conducted in the presence of kerogen. On the basis of this result, the observed retention effects induced by artificial maturation suggest either a physical interaction or a chemical binding. This will have to be determined more precisely, since it is one of the required information in terms of the elemental adsorption/complexation capabilities of geological barriers.
Swelling clay minerals exhibit at low concentration a sol-gel transition whose origin remains debated. Most recent work has been carried out on synthetic laponite which exhibits a concentration/ionic strength phase diagram with a negative slope, i.e. an increase in ionic strength favors gel formation. Various models have been invoked to explain this transition and the resulting structure of the gel: “house of cards” structure, frustrated Onsager transition, glass transition, retarded aggregation. However, due to its very small particle size (25 nm), laponite does represent a very particular case and is not truly representative of most natural swelling clay minerals which elementary particles are much larger and much more polydisperse. For this reason, we studied the phase behavior of Wyoming sodium montmorillonite. The osmotic pressure curves exhibit, as in the case of laponite, a pseudo-plateau whose position depends on ionic strength. The combination of rheological measurements and optical microscopy observations allows to build a phase diagram. As in the case of laponite, two types of gels an isotropic one and a birefringent one are observed. The transition between sol/isotropic gel and isotropic gel/birefringent gel exhibit a slight positive slope. In order to investigate size-effects, a size separation in three fractions was carried out by centrifugation. Cation exchange capacity measurements show that layer charge does not depend on size. As a consequence, this system is well suited to study the influence of particle anisotropy on the phase diagrams of Wyoming montmorillonite. Osmotic pressure measurements reveal a strong influence of particle size, smaller particles yielding higher osmotic pressures. In parallel, rheology experiments in oscillatory mode show that the sol-gel transition is positively linearly correlated to the mean particle size, smaller particles presenting a sol-gel transition shifted towards lower solid contents whatever the ionic strength. Optical observation of the samples in polarized light reveal the birefringent character of the suspensions indicating the presence of long range order in the gels. In the case of the smallest particles, the appearance of “permanent” birefringence is nearly superimposed on the sol-gel transition and in this case, no isotropic gel can be observed. The consequences of these findings on the possible mechanisms for gel formation will be discussed.
QUANTIFYING CHANGES IN WATER CONTENT OF MONTMORILLONITE USING REFLECTANCE SPECTROSCOPY

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Understanding the role of water in surface and atmospheric processes on Mars will be an important goal of future planetary missions. Upcoming missions such as NASA’s Mars Reconnaissance Orbiter and ESA’s Mars Express will carry VIS-NIR spectrometers (CRISM and OMEGA, respectively) capable of retrieving spectral data at wavelengths of 0.4-4.0 µm [1]. Characteristic water and hydroxyl absorptions at 1.4, 1.9, 2.2, and ~3 µm will make it possible for these instruments to detect aqueous or hydrothermally altered surface materials as well as seasonal variability of water in the near-surface. Previous work by Yen et al. [2] showed that there exists a correlation between percent water and apparent absorbance, but the percent water determined by a given absorbance may differ by as much as 2% for different mineral compositions. Small amounts (or changes in) adsorbed water would not be well constrained by this method since the total H₂O content of the martian soil is ~2 wt. %. We use a spectral time-series of montmorillonite (SWy-1) in a purged environment to model the loss of readily exchanged interlayer water as a function of the scattering efficiency (Qₛ) and absorption efficiency (Qₘ) of water relative to a “dry” montmorillonite sample. This method is capable of detecting and modeling changes in reflectance spectra due to changes of < 0.1 wt. % of interlayer water.

Reflectance spectra measurements taken under purged conditions at time-steps of 1, 2, 3, 4, 6, 9, and 12 hours allow us to track spectral changes due to loss of interlayer water. Replicate samples were removed from the purging chamber at each time-step to determine the wt. % loss H₂O that corresponds to each spectrum. The 1.9 and ~3 µm absorption regions change due to the loss of interlayer water during purging whereas the 2.2 µm bound H₂O absorption does not, suggesting changes are due only to the loss of interlayer H₂O. We model these changes using the optical constants for water [real (n) and imaginary (k) indices of refraction], where all reflectance spectra are converted to single-scattering albedo (w) using relationships described by Hapke [3]. Hapke also shows that for certain cases, Qₛ ≈ w. If the montmorillonite is considered a two-component system (water and “dry” montmorillonite), then w at any time t may simply be the combination of the scattering efficiencies of the two components:

\[ w = \frac{Qₛ}{Qₛ + Qₘ} \]  (1).

To determine water losses relative to the final weight, we consider our driest spectrum (12 h purge) to represent the “dry” montmorillonite. Substituting \( w_{12} \) for \( Qₛ \), and dividing both sides of (1) by \( w_{12} \) gives:

\[ \frac{1}{w_{12}} = \frac{Qₛ}{w_{12} Qₘ} + 1 \]  (2).

Using theories outlined by Hapke [3], values of \( Qₛ \) as determined from (2) can be modeled using the optical constants of water and an internal-scattering model. The two variables in this model are the optical path length (d) and the near-surface scattering coefficient (s). The value of d decreases as water is lost and follows a power-law relationship when plotted against wt. % loss H₂O. This relationship can be used to estimate changes of < 0.1 wt % in the interlayer water content of montmorillonite.

Weathered basaltic materials near the summit of Mauna Kea Volcano on the Island of Hawaii are spectral and magnetic analogues for the ferric-rich materials that dominate bright Martian surface regions. Based on laboratory studies of samples collected in the field, three types of alteration processes influence the mineralogical composition of Mauna Kea summit cones: 1) hydrolytic, low temperature alteration of basaltic tephra to palagonite and nanophase ferric oxides; 2) hydrothermal, hydrolytic/acid sulfate alterations to sulfates (jarosite and alunite) and phyllosilicates (kaolinite and smectites), and 3) tephra altered by dry heat to form hematite-rich material. Zeolites (phillipsite and erionite) are also occasionally present. We are using AVIRIS (Airborne Visible Infrared Imaging Spectrometer) remote sensing observations to both map the spatial distribution of the alteration products and to simulate observations that are planned by the CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) instrument as a part of the 2005 Mars Reconnaissance Orbiter payload. AVIRIS is a hyperspectral imaging instrument that covers the wavelength range from about 0.4 to 2.5 μm in 224 bands, with a band spacing of 10 nm and average bandwidth of 10 nm. CRISM is also a hyperspectral imaging instrument with a wavelength range between 0.4 and 4.0 μm and a band spacing of ~8 nm. AVIRIS data (taken from about 20 km altitude) for Mauna Kea suggest three spectrally distinct hematite units, three phyllosilicate units (i.e., montmorillonite, saponite, and kaolinite units), a palagonite unit, and scattered jarosite units. Palagonitic tephra (a poorly ordered material) is widespread on the lower slopes of summit cones. Thus, we expect to be able to detect and map hydrothermal alteration and alteration products on Mars if they exist at the spatial scales found on Mauna Kea Volcano.
INTEGRATING RESEARCH AND EDUCATION IN MINERALOGY

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The goals of a modern mineralogy course may include: mastery of content, skill development, and instilling values essential to Science. An important outcome of any mineralogy course is the transformation of novice students in their quest to become contributing professionals. Effective integration of research and education addresses all of these goals. Instructional strategies to integrate research and education should involve some level of discovery and inquiry. It is particularly important to encourage students to do science--to practice the process of science (e.g. observation, hypothesis formation, measurement, analysis, interpretation, data manipulation and presentation, communication), and to begin to make contributions to the products of science. Examples include:

- (Re)Discovery of fundamental principles--design activities where students explore fundamental relations to discover for themselves the underlying principles (e.g. ball and stick models to reveal Pauling's Rules);
- Replication or simulation of classical experiments--where the outcomes are known to the instructor, but students reproduce the steps towards the expected conclusion.
- Modeling is an increasingly important approach to understanding complex geological systems, and a mineralogy course is not too soon to introduce graphical, physical, or computational.
- Use of real-time or archived data--students should have the opportunity to work with data in all its facets from sample collection to reports of outcomes. data see http://serc.carleton.edu/research_education/usingdata/index.html
- Critical review of the literature--have students encounter the literature early and often, seeking information about topics of interest
- Training in instrumentation and software--it matters less which instrument, but if possible, students should have access to instrumentation if at all possible (XRD, SEM/EDS, water chemistry…).
- Field methods--although fewer and fewer geoscientists will find careers in field work, this is still an essential component of training, particularly in preparing students to understand 3- and 4-dimensional relations.
- Encourage students to engage in true research, or at least research-like experiences.

Discovery is essential to both our research and teaching missions. Through discovery we must engage creative thinking, seeing relations in a new light; apply first principles, the basic knowledge of science; work in a meaningful contexts and build on the work of our predecessors; and agree upon use of a common language for effective communication. This is true for master geoscientists who now set the standard in research and teaching, and it is important that we train our students to develop the same practices and scientific "habits of the mind".
CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF QUARTZ EXTRACTED FROM BENTONITE

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Toxicological studies of quartz generally presume that all quartz is identical to crushed single crystal quartz and thus will have identical biological aggressiveness. This assumption results from the seeming impossibility of obtaining respirable quartz without crushing. This work did succeed in concentrating respirable size quartz from sodium bentonite (here termed “quartz isolate”) by exhaustive centrifugation, and compared it a crushed quartz, DQ12.

Comprehensive mineralogical characterization showed the two types of quartz are much different. XRD peak profile analysis shows DQ 12 has a crystallite or diffraction domain size typical of single crystal fragments. The domain size of the quartz isolate, in contrast, is very much smaller, suggesting polycrystalline aggregates. Electron microscopy confirms the morphology of DQ 12 as single crystal fragments, and the morphology of the quartz isolate as particles composed of aggregates. The chemical inhomogeneity of individual quartz isolate particles shows they are polymineralic, with quartz by far the dominant mineral, as well as are polycrystalline. A comparison of BET and EGME specific surface area measurements indicates that the DQ 12 surface area is mostly external, whereas the quartz isolate has a very large internal surface area characteristic of complex, aggregated particles. Differential scanning calorimetry detects $\alpha \rightarrow \beta$ quartz transition at 573 °C transition for DQ12 but not for the quartz isolate. Nevertheless, high temperature XRD shows both DQ 12 and the quartz isolate undergo this transition. The lack of the $\alpha \rightarrow \beta$ thermal signature is indicative of very small domain sizes, internal structural disorder, and high grain boundary energy.

An in vivo experiment with Wistar rats, for 3 and 24 days, shows significantly different biological effects with the two types of quartz. No systemic toxicity was detected. The quartz isolate showed moderate inflammatory effects on day 3, and no significant change by day 28. DQ12, however, showed a high acute inflammatory response by quartz on day 3, which persisted through day 28. Lung inflammation at day 28 was most pronounced for DQ12, and was significantly lower for the quartz isolate. Significantly lower toxicity of the quartz isolate was evident by the absence of alveolar proteinosis, in contrast to the DQ12 control.

This study confirms that a detailed mineralogical characterization absolutely must supplement any toxicological evaluation of quartz-containing particles for a valid toxicological assessment.
The objectives of this study were to investigate mineral precipitates, which derived from the zero valent iron (ZVI) corrosion during TCE dechlorination and to find the controlling factors and the stability of mineral precipitates. A series of column experiments were conducted to evaluate the location of ZVI and the effects of electrode arrangements in electro-enhanced permeable reactive barrier (E2PRB) systems. Based on mineralogical characterization, ZVI samples near the influent port had more lepidocrocite, ferrihydrite or Fe (oxy)hydroxide, and (phospho)siderite while backward samples had more akaganeite, magnetite/maghemite, and green rust (GR) I and GR II. A suite of mineral distribution was preferably related to the dissolved oxygen and the increased pH.

Amorphous iron hydroxides, maghemite, lepidocrocite, and GR I were found to be controlling mineral phases of the pFe$^{3+}$. Considering pFe$^{3+}$ with anions, chloride form GR I was well fitted in the range of measurement data. Akaganeite was dominantly found in ZVI portion and the formation of akaganeite may be related to a relatively high concentration of chloride formed via TCE dechlorination in the E2PRB system. The pFe$^{2+}$ also showed relationship with the pH change as treated pore volumes increased, and might be controlled by the formation of chloride form GR I.

Columns showing the trend of slow decrease of $\Sigma$(SI) of iron containing minerals or almost identical during the column experiment indicate the possibility that the production of ferrous and ferric ions prevailed over the other columns, and these columns might be more efficient in dechlorination of TCE. Conclusively, TCE removal efficiency considering precipitation is more related to the electrode arrangements, basically cathode with ZVI. However, it’s not clear to identify either of ZVI-permeable reactive barrier (PRB) with or without direct current has more removal efficiency of TCE based on the result of geochemical modeling. Controlling factors of E2PRB system were found to be (1) pH, (2) dissolved oxygen, (3) the types of Fe intermediates, and (4) anionic species to form mineral precipitates strongly.
Industrial demands for clay mineral extenders and pigments with controlled optical and physical properties have significantly changed the type and quality of clay products available to the paper, paint, plastics, ceramic, and other industries. Equipment available for processing clays is much more sophisticated and controllable than in the past. Better understanding of the mineralogy and fundamental properties of clay minerals in addition to improved processing equipment has permitted the clay companies to produce engineered or tailored products that meet special needs of a particular user. Particle size and shape, brightness, gloss, opacity, and viscosity can be altered and controlled to meet specific requirements of a particular paper coater. Examples of engineered products available for the paper, paint, and other industries are described.
THE ROLE OF NATURAL ORGANIC MATTER IN CINNABAR (HGS) DISSOLUTION

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Cinnabar (HgS) dissolution rates were measured in batch experiments in the presence of twelve different natural dissolved organic matter (DOM) isolates including humic, fulvic, and hydrophobic acid fractions. Initial dissolution rates varied by 1.3 orders of magnitude from 2.31 × 10⁻¹³ to 7.16 × 10⁻¹² mol Hg (mg C)^⁻¹ m² s⁻¹. Rates correlate positively with three DOM chemical characteristics: specific ultraviolet absorbance (R² = 0.88), aromaticity (R² = 0.80), and molecular weight (R² = 0.76). Dissolution was controlled by an interaction of DOM with the cinnabar surface as demonstrated by linear rates of dissolution with time, significantly reduced rates when DOM was physically separated from the surface by dialysis membranes, and rates that were independent of DOM concentrations greater than those required for monolayer surface coverage. Dissolution rates correlate inversely with sorbed DOM concentrations, indicating the presence of a DOM component that inhibits dissolution. When two hydrophobic acid isolates that enhanced dissolution to different extents were mixed equally, a 20% reduction in rate occurred compared to the rate with the more dissolution-enhancing isolate alone. Rates in the presence of the more dissolution-enhancing isolate were reduced by 58 to 60% when cinnabar was pre-reacted with the isolate that contained a high percentage of dissolution-inhibiting component. Rates in the presence of these two isolates were modeled assuming competitive sorption of the two end-member DOM components.
LIQUID CRYSTALLINE NATURE OF NIOBIUM OXIDE NANOSHEET SOLS PREPARED BY EXFOLIATION OF LAYERED NIOBATE $K_4Nb_6O_{17}$

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Inorganic nanosheets prepared by exfoliation of layered materials have recently attracted attention as modules for constructing novel nanoassemblies. However, there is a very little knowledge of colloidal properties of the nanosheets. We have very recently found that sols of exfoliated $K_4Nb_6O_{17}$, which is a layered niobium oxide possessing intercalating capability, exhibit peculiar liquid crystallinity. Here we report detailed results of the liquid crystalline nature of the niobate nanosheet colloids.

We prepared colloids of niobium oxide nanosheets with the thickness of 1.8 nm and mean lateral size of 0.15-7.8 µm and investigated their liquid crystalline nature. The nanosheet colloids were obtained by exfoliation of single crystals of $K_4Nb_6O_{17}$. $K_4Nb_6O_{17}$ was intercalated with propylammonium ions and subsequently dispersed in water to form sols of [Nb$_6$O$_{17}$]$_4^-$.

The as-prepared sols were subjected to ultrasonication, which broke down the colloidal dispersed niobate particles to yield the nanosheets with small lateral sizes. The colloids were observed with naked eyes or optical microscope by using crossed polarizers to clarify liquid crystallinity.

Observation of the niobate nanosheet sols between crossed polarizers revealed that all the colloids with any lateral size were birefringent at certain concentrations, indicating formation of liquid crystalline phases, whereas the liquid crystallinity depended on the lateral size and concentration of the nanosheets. The sols of larger nanosheets exhibited higher liquid crystallinity at a fixed concentration, and the colloids with the same lateral size of the nanosheets showed weaker birefringence at lower concentration.

All the nanosheet sols varied from isotropic to biphasic, and finally to liquid crystalline as the concentration increased. The weakly liquid crystalline colloids with rather small lateral size and low concentration were found to be biphasic mixtures of liquid crystalline and isotropic phases under static conditions. The sols were separated into two phases within a day after preparation: the birefringent liquid crystalline phase and isotropic phase. The colloids of larger nanosheets also exhibited essentially the same phase behavior, although sedimentation of the large nanosheets gave somewhat complicated behavior.

We determined the phase transition concentrations (isotropic-biphasic and biphasic-liquid crystalline) of the colloids from the relationships between the concentration of nanosheets and volume fraction of the liquid crystalline phase in the biphasic mixture. A plot of the transition concentration against the lateral size of the nanosheets indicates that the phase transition concentration decreases with increasing the lateral size. This behavior is in accordance with the prediction by Onsager theory, indicating that the liquid crystallinity is explained by excluded volume effect between the nanosheets. However, a notable feature of the present system was observed for the sols with large lateral sizes (> 6.2 µm); they kept liquid crystalline state even at the very low concentration (0.00051 vol.-%), which was much lower than that expected from the theory.

STRUCTURAL CONSIDERATIONS IN THE SURFACE CHARGE OF KAOLINITE AS DETERMINED BY AFM FORCE MEASUREMENTS

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The consideration of surface charge in the control of kaolinite suspension stability is recognized to be of significant importance in the processing and utilization of this unique mineral resource. Detailed examination of the anisotropic surface charge features of the kaolinite structure by AFM force measurements provides additional fundamental information, which may allow for further advances in technology.
CHALLENGES OF STIMULATING IN-SITU BIODEGRADATION OF PERCHLORATE IN CLAY-RICH SOILS

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Perchlorate salts and acids are used in many commercial and military applications. The main use of perchlorate is as an oxygen-adding component in propellants for rockets, missiles, explosives, pyrotechnics, fireworks, and is an impurity in some fertilizers. The most widely used form of perchlorate in rockets and missiles is ammonium perchlorate (NH4ClO4). Perchlorate (ClO4-) contamination is an emerging and growing environmental problem. Perchlorate is a highly water-soluble and a potentially toxic oxy-anion. Perchlorate-contaminated soils are often the source of long-term aqueous phase perchlorate contamination and must be remediated to ensure groundwater security. Although research has shown that perchlorate-reducing microorganisms are ubiquitous in soils, natural attenuation of this compound is limited in most soils due to lack of suitable electron and carbon sources and/or the presence of aerobic conditions.

A series of bench-scale tests were conducted to evaluate the type and amount of nutrient amendment needed to biostimulate the removal of perchlorate from clay-rich soils. The greatest engineering challenge was the infiltration of water and dissolved carbon and electron sources through the tight soils. Several organic amendments were evaluated in static batch slurry and column tests and pilot tested at a field site. The biosolids tested included poultry and cow/horse manure, mushroom compost and cotton waste, and the liquid carbon sources included acetate, ethanol, molasses, and methanol. The biostimulation of perchlorate degradation in the soils was indirectly confirmed by measuring the total organic and inorganic carbon (TOC and TIC) and perchlorate concentrations. For batch test, the highest biodegradation rates for perchlorate were observed in acetate-amended soils after a lag time of about 7 days. The different amendments generally stimulated the biodegradation of perchlorate in contaminated soils, with cotton waste being the least effective carbon source tested. Although the biosolids generally improved the infiltration rate of water through the packed soil columns, ethanol partitioned least to the soils and produced the highest DOC concentration in the column effluent.

Based on the results of the laboratory tests, three carbon sources (ethanol, horse and chicken manure) were selected for pilot testing at a field site. It was observed that the application of suitable nutrient amendments and mobilization with water can biostimulate and achieve rapid in-situ bioremediation of perchlorate-contaminated soils. The removal of perchlorate from the silty clay soils was influenced by the following two factors: 1) the length of time the soils remained wet within the treatment depth, and 2) the form in which the carbon source was applied: solid vs. liquid. The data collected to date suggests that the right combination of biosolids and liquid electron sources improves the soil field capacity, increases the infiltration rate and achieves rapid in-situ bioremediation of clayey soils.
EVALUATION AND ENHANCEMENT OF NATURAL ATTENUATION OF CHLORINATED ORGANICS IN AQUIFER SOLIDS

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Chlorinated organic solvents including perchloroethene (PCE) and trichloroethylene (TCE) are among the most common chlorinated organic chemicals found at hazardous waste sites. While PCE and TCE are suspected carcinogens, their anaerobic degradation products are known carcinogens (i.e., vinyl chloride and dichloroethenes). Often, the accumulation of VC, cis-1,2-DCE, and TCE down gradient of source areas at field sites suggests limited in-situ biodegradation. This study examines the limitations to natural attenuation of chlorinated alkenes in aquifer sediments within a plume and evaluates the use of artificial electron sources to enhance natural attenuation in the aquifer solids.

The natural attenuation of PCE, TCE, and dichloroethene (DCE) in aquifer materials obtained from soil cores was investigated in laboratory microcosms and completely stirred batch bioreactors mounted with probes. The concentrations of the parent compounds, products formed, DO, CO2, TOC, TIC, and methane were measured throughout the experiments. The attenuation of the chloroethenes was observed to be primarily due to sorption and anaerobic biodegradation. Based on the spatial and vertical variability in biodegradation activity observed, three broad reaction zones were identified. Rapid and complete biodegradation was observed in the surface layer (0-14 ft) with halorespiration responsible for biodegradation in the source area sediments (Zone I) and co-metabolic processes responsible for degradation in the non-source area organic-rich sediments (Zone II). Sorption was an important removal mechanism in the organic rich sediments (foc > 2.5%) of Zone II. The lack of organic carbon (<1%) in the deep sediments (Zone III) limited biodegradation and sorption of PCE and enhanced transport. Biodegradation of PCE was incomplete in the deep aquifer materials leading to the accumulation of cis-DCE in laboratory microcosms, which was in agreement with the accumulation of detectable concentrations of DCE and VC in groundwater at the field site.

The PCE, TCE, and DCE were observed to completely biodegrade to ethene, ethane, and mineralized to CO2 in the site sediment amended with various carbon sources. Dechlorination of PCE to VC and ethene occurred in the deep sediment only after the addition of different electron (carbon sources). The aquifer sediment showed a wide range of substrate specificity and responded favorably to all amendments. Reductive dechlorination was more rapid and complete in experiments where methane production was greater than 100 μM than in experiments where methane production was less than 1 μM. The role of TOC and DOC in determining the mechanisms of in-situ bioremediation of contaminated aquifer sediments will be emphasized.
In 1990, I read two books by Tobias that significantly changed the way I teach: *They're Not Dumb They're Different*, and *Revitalizing Undergraduate Education*. Since then I have had many conversations with colleagues about teaching and how best to do it, and the consensus is always the same: to learn well, students must be engaged and active learners.

Experts on teaching have long pointed out that a high quality education depends on a high quality learning process. Instead of just delivering knowledge and expecting students to learn, teachers must ensure that students are involved and actively engaged. Successful teaching is student oriented (aimed at developing a student’s cognitive and intellectual development) rather than discipline oriented (aimed at coverage of material). These ideas were well reviewed in National Science Educational Standards (NRC 1996), Shaping the Future (NSF 1996), and Science for All Americans (AAAS 1990). Still, today most college science courses focus nearly entirely on content, not on process.

In 1996 the National Science Foundation funded a Teaching Mineralogy Workshop at Smith College. In the Summer 2003, there will be a similar Teaching Petrology Workshop at Montana State University. Besides such group undertakings, many individuals are working to improve teaching and learning in mineralogy and petrology.

Recent articles in the Journal of Geoscience Education, for example, advocate starting with questions about nature and things students are familiar with, getting students involved in scientific inquiry, concentrating on collection of evidence and letting students create their own knowledge, de-emphasizing dogma and vocabulary, emphasizing interdisciplinary connections and applications, welcoming curiosity and creativity, and extending learning beyond the classroom.

Specific innovative approaches to teaching mineralogy and petrology include urban field trips, interactive games, use of real-time data sets, computer modeling and virtual field trips. Some instructors now emphasize studies of disasters, minerals in everyday life, or the connections between the fine arts or social sciences and geology. Perhaps more significant is that more instructors are getting students involved in basic scientific research – research with no certain outcomes or expectations. The amount of time that students sit passively and pretend to listen to a lecture will continue to decrease if we are serious about promoting learning.

The activities and approaches summarized above cover a broad spectrum but have two commonalities: all involve active learning and all have been shown to work in the classroom. Of course, the success of these new approaches may be due in part to the enthusiasm of the instructors. Successful teaching and learning is thus a synergy between teachers and students, and everyone benefits.
URANIUM RETENTION IN SHALE SAPROLITE ON THE NABIR FRC SITE-
RELATIONSHIPS WITH PHOSPHORUS, SULFUR, AND Fe, Mn AND Al OXIDES

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The Natural and Accelerated Bioremediation Research Program (NABIR) has a Field Research Center (FRC) on the Oak Ridge Reservation in Oak Ridge, Tennessee that is used as a site for in situ bioremediation studies. Cores of the geological material were collected at the site from 2 areas around four buried unlined ponds where nitric acid wastes containing uranium and other contaminants were deposited. The objective of this study was to examine uranium retention in the core material in relation to the presence of total P, total S, and Fe, Mn and Al oxides. Cores from area 1 (~150 m south of the ponds) are predominately Nolichucky shale saprolite that is weathered along seams. Cores from area 3 are closer to the ponds (~60 m west) and are along a strike where the flow of the acidic U contaminated ground water is greatest due to higher permeability of heterogeneous interbedded shale and sandstone saprolite. This has resulted in greater weathering of the geological material from area 3 compared to area 1. In area 1, U is highest (239-375 mg/kg) in thin (2.5-25 cm) very highly weathered clay rich seams within the saprolite collected at 10-20 ft. In these clayey zones, the mineralogy is illite>> vermiculite plus hydroxy-interlayered vermiculite (HIV)>kaolinite> goethite>quartz, and free Fe, Al and Mn oxides are 5.6-9%, 0.1-0.7%, and 0.15-0.85%, respectively. Uranium in ground water from area 1 is as high as 7 mg/L in the zone where the cores were taken. Uranium is generally ~50 mg/kg in the shale saprolite from area 1 where the free Fe, Al and Mn oxides are 1-3.5%, 0.05-0.23%, 0.05-0.45%, respectively. In cores from area 3, U retention is greatest (200-800 mg/kg) at 36-48 ft, while the rest of the cores generally have U concentrations between 10-70 mg/kg. The mineralogy of these cores is similar to those from area 1, except for an increase in kaolinite and quartz. Free Fe, Al and Mn oxides are 0.4-2.9%, 0.16-0.54%, 0.004-0.76%, respectively, in cores from area 3. Ground water U contents rise sharply from 7 mg/L at 30 ft to 53 mg/L at 40 ft in area 3. In all of the cores, most of the Fe and Al oxides are crystalline, while most of the Mn oxides are amorphous. Scanning-electron microscopy with backscatter analysis of a thin section of material from the high U zone at 45 ft (U -800 mg/kg) in area 3 shows U associated with P and S, and coating a Mn oxide mineral. Total P ranges from 0.03-0.2 % and total S ranges from 0.0-0.09% in all of the core samples. There is a much higher correlation between U and free Fe and Al oxides in the shaley core material area 1 compared to interbedded shale and sandstone core material from area 3. Also, there is a higher correlation between U and total P and S in core material from area 1 compared to the core material from area 3. In area 1, linear regression analysis of U and total P, total S, free Fe and free Al give $r^2$ values of 0.76, 0.69, 0.85 and 0.76, respectively. In area 3, linear regression analysis of U and total P, total S, free Fe and free Al give $r^2$ values of 0.67, 0.5, 0.33 and 0.24, respectively.
MINERALOGY OF SEDIMENTS AND FOSSIL REMAINS AT A NEOGENE AGE FOSSIL SITE IN NORTHEAST TENNESSEE

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At the Gray Fossil Site in Washington, Co. Tennessee, a series of highly weathered and truncated paleosols are present in alluvial sediments that overlie laminated, organic-rich, fossiliferous sotano sediments of Neogene age (4.5-5,000,000,000 BP). The objectives of this study were to determine the mineralogy of the sediments and fossil remains through X-ray diffraction, scanning-electron microscopy-with energy dispersive X-ray analysis, micromorphology, and chemical analyses. The acidic (pH = 3.5 - 4) alluvial sediments are rich in dolomitic chert and mica. The clay fraction is dominated by kaolinite and a very fine sand fraction is dominated by quartz in the sediment. Other minerals in the clay fraction of these sediments are illite, vermiculite, quartz, and Ca feldspars. Vermiculite, opaque minerals, orthoclase, biotite and microcline are also present in the very fine sand fraction of these highly weathered sediments. Fe and Mn oxide precipitates are present in the form of Fe pans, concretions/nodules, and coatings on ped surfaces. Crystalline and amorphous oxides average about 1% for Fe and about 0.01% for Mn in these sediments. The underlying alkaline (pH = 6 - 8) gray and black sotano deposits have a similar mineralogy, except for the presence of smectite in the clay fraction and the presence of calcite and a drastic increase in vermiculite in the very fine sand fraction. Additionally, a large calcite formation (3 ft wide X 6 ft long) was observed in the black deposits. Exchangeable Ca, Mn, and K drastically increase in the gray and black deposits compared to the overlying acidic deposits. Total carbon increases from less than 1% in the acidic deposits to 5 - 10% in the black sotano deposits. Although the animal fossils appear to be fairly well preserved in the gray sediments, the plant remains are disintegrating and Fe is replacing this material in places. Some vertebrate fossils in the sotano are coated with goethite and gypsum, while the bone material is composed of anhydrite, siderite and Fe phosphate. The Fe oxide coatings on the animal fossils may be contributed to the preservation of the bones. Anaerobic and alkaline conditions in the sotano deposits are responsible for the presence of smectite and also contribute to the preservation of the fossilized bone and plant fragments.
Soil colloid dispersion is an important phenomenon, which influences soil erosion, toxin and nutrient transport, crusting of surface soils, and siltation in rivers and lakes. The mechanisms governing colloidal dispersion behavior are associated with both interlayer expansion (crystalline swelling) and double layer swelling of expandable clays. The classical DLVO theory predicts that high ionic strength compresses the electric double layer associated with colloidal surfaces inducing flocculation. With increasing monovalent cation concentration ratios, the DLVO predicts an increase in osmotic pressure in the electric double layer, hence soil colloid dispersion. However, DLVO theory does not predict the formation and destruction of smectite quasicrystals. Our results indicate that the 1.4 nm XRD peaks both broaden and decrease in intensity with increasing monovalent cation concentration ratio (CRx), suggesting that Ca-quasicrystals are becoming smaller. At high CRx, broad and low-intensity 1.2 nm XRD peaks start to appear, suggesting the formation of potassium- or ammonium-quasicrystals. Results of the study indicate that soil colloid dispersion is influenced by both DLVO phenomena and quasicrystal formation and destruction.
THE IDENTIFICATION AND COMPOSITION OF AMPHIBOLES WITH THE AID OF INFRA-RED SPECTROSCOPY

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Field portable infrared equipment is available for identifying accessible minerals, and these have been correlated with remote-sensing units. The data results are verified with XRD and XRF data results. Amphiboles comprise one of the most common hydrous mineral groups, which include asbestos minerals.

Amphibole asbestos minerals were mined in California for about 70 years, and the mine and mineral descriptions were often incorrect. The Coffee Creek anthophyllite was actually richterite. The Sylvester and Loma Blanca anthophyllite was tremolite, and the Morgan Mine tremolite was eckermannite. The NIR spectral bands of eckermannite, at 4322, 4207, and 4126 cm\textsuperscript{-1} are similar to those of richterite at 4324, 4211, and 4132 cm\textsuperscript{-1}.

Biopyriboles comprise a closely related family of minerals, but the correlation of hornblende and phlogopite NIR combination bands only extend to their Mg-OH bands. The 4445 cm\textsuperscript{-1} phlogopite band is related to the octahedral Al content whereas the 4445 cm\textsuperscript{-1} Ca-amphibole band is related to its octahedral Fe\textsuperscript{2+} content. The amphibole minerals appear green, rather than white, when there is Al substitution for Si in their tetrahedral sites but this is not so for micas.

Alkali amphiboles such as glaucophane and magnesio-riebeckite are not readily differentiated by their OH combination bands but are by their fundamental OH bands.

Whole-rock scans of specimens from an ophiolite structure, which contains intermixed amphibole and feldspar were useful in studying a newly found deposit of anthophyllite. The mineral contains combination bands at 4345, 4322, and 4186 cm\textsuperscript{-1}, with fundamental OH bands at 3668, 3654, and 3638 cm\textsuperscript{-1}. The two dominant XRD peaks are 8.42\AA\ (110) and 3.042 \AA\ (310).

This kind of work was made possible by the initial investigations of NIR spectra by Graham Hunt, the fundamental OH spectral assignments by R.G.J. Strens, and the others who followed them.
SYNCHROTRON POWDER X-RAY DIFFRACTION STUDY OF SEPIOLITE

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Sepiolite is a hydrous Mg silicate clay mineral with a fibrous-like morphology that typically occurs as fine-grained, poorly crystalline masses. It is found in a wide variety of geological environments and has been mined for centuries because of its many useful properties, e.g. in the pharmaceutical, fertilizer, and pesticide industries and as supports for catalysts, or as molecular sieves.

The sepiolite structure was first deduced by Brauner and Preisinger (1956) and is orthorhombic with space group Pnan. Sepiolite is a layer structure built up of ribbons of 2:1 phyllosilicate modules that are themselves constructed of linked triple silicate chains that sandwich (Mg,Al)-(O,OH) octahedral strips. The structures have large tunnels parallel to the phyllosilicate ribbons that are partially occupied by water molecules.

Because of the fine-grained and typically poorly crystalline nature of sepiolite, it has not been possible to study its crystal structure using single crystal diffraction methods, and consequently many details of the structures are still not well known. We have used synchrotron powder X-ray diffraction data and the Rietveld method to refine the hydrated and partially dehydrated room temperature sepiolite structures. The data were collected at beamline X7B at the National Synchrotron Light Source in air (hydrated) and under vacuum (partially dehydrated) from an unusually well crystalline sepiolite sample from Durango, Mexico. Only the structure framework was included in the initial stages of the refinements, and difference Fourier maps were calculated to locate water positions. We located four zeolitic water positions in the fully hydrated sample, three of which matched reasonably well with those proposed by Brauner and Preisinger (1956). Two of the water sites are fully occupied and two are ~1/2 filled, totaling ~16 zeolitic water molecules per unit cell. The refinement for the sample under vacuum, on the other hand, showed one zeolitic water molecule in a single partially filled water site. The structural water site, coordinated to Mg, remained fully occupied. The refined unit-cell parameters in air: \( a = 13.405(1) \), \( b = 27.018(1) \), and \( c = 5.2754(2) \), compared to those in vacuum: \( a = 13.249(1) \), \( b = 27.051(1) \), and \( c = 5.2611(2) \), reveal that the most significant change is a slight decrease in \( a \) as a result of dehydration.
THE LARGEST GEORGIA TEKTITES

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The first Georgia tektite was found by Dewey Horne near DuBois Georgia in 1938. The specimen was identified by the Smithsonian as a “probable tektite.” Until 1959, about 12 tektites had been found near Dodge County, Georgia (1).

In the 1960’s, William Hambrick of Eastman, Georgia found a beautiful 36 gm tektite that was shaped like a silver dollar. It was the largest tektite found, and was donated to the Smithsonian Institution where it is on display today.

In October 1975, I was informed that a very large tektite had been found near Plainfield, Georgia. I immediately made a trip to Dodge County to authenticate this new specimen. It was a thrill to view this new world record tektite. It was shaped like the typical “Apollo Module,” blunt front ablative end and with the back somewhat resembling a sombrero. It has the dimensions of 63 X 48 X 31 mm and it’s weight is approximately 70.5 gm. The color is the typical drab olive green, and there are no visible inclusions or bubbles. Usually there are small chips caused by farm implements but with one tiny exception, the deep ridges are in pristine condition. The soil that the tektite was found in was the typical gray-tan Hawthorn gravel outwash that covers the area. No other specimens were found nearby.

In about 1980, a large tektite was brought in and I purchased it. It was found in the Cochran area in Bleckley County. It is shaped like a half disk and has a weight of approximately 57.0 gm. The dimensions are 71 X 45 X 11 mm.

In October 2002, J. Dykes found a large tektite in northern Dodge County. It was not recognized as a tektite for several months. This elongated disk measures approximately 74.0 X 47.5 X 19.0 mm. It weighs approximately 86.37 gms and shows no obvious bubbles or inclusions. It is the typical drab-olive green and shows no chips from the plow. The find site was on a hilltop west of Chester, Georgia. The soil appeared to be the typical Altamaha yellow-tan gravel with many plinthite pebbles.

The largest tektite found in the Georgia strewn field was the 130.06 gm Muong Nong-type, or layered specimen, found by Robert Strange on July 31, 1993. This unique specimen was found near Riddleville in Washington County. This specimen has been thoroughly studied and has been the Rosetta Stone for our understanding of the North American strewn field (2).

Today, there about 2000 Georgia tektites known. They are found in approximately 17 counties. The average weight of a specimen is approximately 9 gm. Georgia tektites larger than 50 gm are exceedingly rare. There are always rumors of large tektites being found, but these are the only ones that are well documented.

Since 1970, one hundred and ninety two field expeditions have been made to east central Georgia in an effort to determine the parent formation and distribution of the Georgia tektites by locating new specimens. These have been given the name, georgiaites. About 100 new specimens have been recovered, they represent about five percent of the known Georgia tektites. The primary area is a fan shaped region approximately 30 by 72 kilometers. The total area of distribution appears to extend to the ENE towards Augusta. It is likely that the tektites have been transported by water from the parent formation (1). The parent formation has been identified as the Tobacco Road Sand (2). No correlation has been found between size, shape, soil type, elevation and tektite location.

The first Georgia tektite was found by Dewey Horne in 1938 near Dubois in Dodge Co. By 2003, approximately 2000 Georgia tektites have been found covering an area of 6934 sq. miles and 17 counties as shown in Fig. 1.

The greatest concentration has been found within the rough triangle formed by the towns of Empire, Chester and Plainfield in northern Dodge Co. Approximately 90 percent of all georgiaites have been found in Dodge and Bleckley counties (3).

Several georgiaites found outside of the 90 percent area should be mentioned because some of them are unique specimens. To the south, one large 17.8 gm thin, disk shaped georgiaite was found in Irwin County near Osierfield. To the west, a large disk shaped tektite was found 3 km southwest of Hawkinsville in Pulaski Co. In June, 1994, a 10 g georgiaite was found near the southwest border of Pulaski County suggesting that the neighboring counties of Dooly, Crisp and Wilcox should also contain tektites. To the northeast, 32 georgiaites have been found in Washington Co. including the first Muong Nong-type georgiaite (4). In 1984, the first tektite was found in Montgomery Co. Six georgiaites have been found in Johnson Co. and two specimens have been found in the western part of Jefferson Co. Four tektites have been found in Wheeler Co. and three from Treuten Co. In 1992, four tektites were found in western Emanuel Co. along the Ohooppee River. One tektite has been found in Jenkins Co. and more recently one tektite has been found in Richmond County in the Savannah River. From this trend, it is very likely that tektites will be found in South Carolina.

Much more field work needs to be done especially in the northeast. This is important with the announcement of the 90 km crater found under Chesapeake Bay (5). If this were the source of the North American tektites, then tektites should be found near the source crater.

CLAY MINERAL GENESIS RATES FROM THE COWEETA HYDROLOGIC LABORATORY, NORTH CAROLINA, USA, AND THE RESPONSE TIMES OF CLAY MINERALS TO CHANGES IN CLIMATE

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The weathering of silicate rocks is typically incongruent and the clays that form may be eroded and accumulate in sedimentary basins. These clays will serve as direct evidence of continental silicate weathering and are diagnostic for certain types of climatic environments. However, Thiry (2000) suggests that the best temporal resolution of the paleoclimatic record in clay-rich sediments and mudrocks is 1 or 2 My.

Watershed flux-based mass balance calculations of clay genesis rates have been performed for three watersheds at the Coweeta Hydrological Laboratory, located in the eastern Blue Ridge Province of North Carolina. The Coweeta clay genesis rates have been used to calculate the time required achieve a 5% (or 50 g kg⁻¹) relative change in regolith clay mineral abundance in response to changes in climate. We term this period the “response time”. The choice of 5% reflects the minimum changes in relative clay abundance that can be detected by changes in XRD peak intensities. Based on the present-day clay genesis rates for the three Coweeta watersheds, the response times for kaolin, gibbsite, and vermiculite occur on timescales of tens of thousands to hundreds of thousands of years. In the coolest and wettest watershed (Watershed 27) kaolin is being consumed at a relatively low rate, requiring over 2 My to consume 50 g kg⁻¹ of kaolin.

The present-day clay genesis rates calculated for the three Coweeta watersheds have also been used to calculate the time needed to form measured clay abundances in regolith of the eastern Blue Ridge and Inner Piedmont Provinces; we have termed this time period the “production time”. The eastern Blue Ridge and Inner Piedmont Provinces have similar bedrock geology, regolith, and geomorphic history, and together form the Piedmont Terrane. Production times of Piedmont Terrane clay mineral assemblages range from 2 Ky to 3 My, with mean values ranging from 40 Ky to 800 Ky. Kaolinite has been identified in the regolith of Watershed 27 despite the kaolin reaction rate for Watershed 27 reflecting dissolution. This kaolinite is likely relict from an earlier climatic period and has not yet completely dissolved in the present weathering regime. The “destruction” time indicates that an average modern kaolin abundance in the southern Appalachians would take approximately 10 My to be completely destroyed at the present-day kaolin dissolution rate calculated for Watershed 27. This destruction time may be as high as 30 My for larger abundances of kaolin.

The conclusions of this study are consistent with those of Thiry (2000); the best temporal resolution of the paleoclimatic record in the regolith source of clay-rich sediments and mudrocks is 1 or 2 My. Clay mineral assemblages in the sedimentary record reflect long-term (tens of thousands to millions of years) average climatic conditions.

KAOLIN PROCESS EVOLUTION AND ITS IMPACT ON KAOLIN RESOURCES AND PRODUCTS

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The kaolin industry is a pioneer in process development for engineering micro- and nano-particle size systems. Major process technology developments have come from the Georgia kaolin industry in response to (1) a diverse suite of kaolin ore types, (2) market requirements for clay performance and (3) operations efficiency. Much of the early process development by the Georgia kaolin industry focused on efficient materials handling systems. Process development since 1930 has focused on engineering color properties and particle geometry in response to market demand for kaolin as a paper coating pigment. This paper will review two patented technologies as examples of recent approaches to engineering color and particle geometry for enhanced pigment performance and for improved operations efficiency.

Selective flocculation is a process used to remove anatase from kaolin to engineer higher brightness and higher whiteness pigments. The standard selective flocculation process used by the Georgia kaolin industry (Maynard, 1974) has a dispersed clay slurry dosed with an ionic inorganic salt followed by a high molecular weight polymer to flocculate anatase particles and effect a separation from dispersed kaolinite particles. An example of an optimized process chemistry for selective flocculation (Garforth et al., 2000) has a dispersant added with the high molecular weight polymer to effect improved separation. This optimized process chemistry enables higher recovery of product, higher brightness product, or both.

Shape engineered pigments were developed in the 1990’s to enhance the paper coating properties of kaolin pigments relative to standard kaolin pigment grades such as #1 (90 wt.% < 2 um) and fine #1 (95 wt.% <2 um) kaolin. Shape engineering involves crude characterization, crude selection, and selective processing to yield a kaolin pigment that delivers improved physical properties to the end-use application. Pruett et al. (2001) describes a shape engineered pigment where 1 to 5 um kaolinite stacks are designed into a pigment to gain a higher fluidity clay-water slurry and improved paper coating characteristics relative to standard kaolin grades.

Titania minerals such as anatase (TiO₂) are very common accessory minerals in sedimentary kaolin deposits. Titania is considered immobile in weathering environments and therefore titania minerals offer possible clues to the provenance of the sediments contained in sedimentary kaolin. Analytical electron microscopy shows particle geometry and trace element content are similar for titania minerals examined in Georgia sedimentary kaolin and in primary kaolin weathered from metamorphic source rocks of the Piedmont province. The titania minerals appear to be the weathered products from ilmenite and trioctahedral mica. The strong association between kaolinite and anatase during commercial wet processing indicate the kaolinite and the clay-sized (<2 µm) titania particles are hydraulically transported together as aggregates that were deposited in fluvial to transitional marine environments. Surprisingly, the iron content of anatase in sedimentary kaolin deposits is proportional to the iron content of the associated kaolinite. The related iron content of anatase and kaolinite favors trioctahedral mica weathering as the source of titania minerals in sedimentary kaolin, indicates a significant post-depositional kaolin alteration event, or both. The observations taken together support theories for the origin of Georgia kaolin that include the components of provenance, depositional environment and mineral alteration.
SELECTIVE ADSORPTION OF N-NITROSA MINES BY SODIUM EXCHANGED CLAYS AND ORGANOCLAYS

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Volatile n-nitrosamines and tobacco specific n-nitrosamines are among the most toxic compounds in tobacco smoke. These compounds can reach the respiratory tract, lungs and alveolar tissue within the lungs. The high incidence of cancer among tobacco smokers is proof enough that these compounds are not trapped by the common cigarette filter. The goal of this research is to study the adsorption of n-nitrosamines onto sodium exchanged clays and organoclays.

Clays and organoclays were used as adsorbent materials in order to trap/sorb the carcinogenic n-nitrosamines. Clays were selected because of their high surface area, their known potential to adsorb contaminants, and ease of modification. In addition, because clays are naturally charged particles, this characteristic can be a contributing factor for adsorbing n-nitrosamines. For these reason, three smectite clays of differing cation exchange capacities were used (SAz-1, STx-1, and SHCa-1). As an alternative sorption mechanism, these clays were also modified with different types of tetraalkylammonium cations, in order to study the alternate interaction between these clays and the n-nitrosamines. These modifications resulted in changes to the sodium clay. The changes in surface area and basal spacing indicate the presence of porous materials. Hence, the proposed model is size exclusion and selective adsorption of the n-nitrosamines with the porous clay materials.

Sodium exchanged clays and organoclays were characterized in order to correlate their structural and chemical properties to the adsorption of n-nitrosamines. These clays were characterized by specific surface area, x-ray diffraction, thermogravimetry, infrared spectroscopy, and carbon/nitrogen elemental analysis. More importantly, adsorption studies of volatile n-nitrosamines onto clays and organo-clays were characterized by Infinite Dilution Gas Chromatography. With this technique the heats of adsorption, entropy, and Gibbs free energy are calculated for the interaction of the n-nitrosamines with our clays and organo-clays. The enthalpy of adsorption range for the sodium exchanged clays is -41 to -87 kJ/mol and for the organoclays is -60 to -90 kJ/mol. These experimental results indicate that clays are very effective in trapping and adsorbing carcinogenic compounds such as the n-nitrosamines and that the adsorption of these compounds is enhanced when organo-clays are used as the adsorbent material.
PESTICIDE DEGRADATION BY REDOX-MODIFIED SMECTITES: EFFECTS OF pH AND EXTENT OF Fe REDUCTION

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Recent studies discovered that the redox state of Fe in the structure of clay minerals profoundly affects the fate of agrichemicals, including the pesticide oxamyl. Oxamyl can degrade either by a redox pathway to produce N, N-dimethyl-1-cyanoformamide (DCMF), or by a base catalyzed hydrolysis pathway to produce oxamyl oxime. An earlier study reported that oxamyl, in the presence of reduced reference clay (SWa-1), degraded rapidly, completely, and exclusively to oxamyl oxime (base hydrolysis pathway). This result was surprising because the reduced smectite presumably has a high reduction potential, which a priori predicts the redox pathway and production of DCMF. The objectives of this study were, therefore, to understand better the basis for the observed degradation mechanism of oxamyl in the presence of reduced smectite, and to determine the potential for such degradation reactions to occur in nature. The hypotheses tested were: (1) neutralization of the Brønsted basicity of the reduced smectite precludes the hydrolysis degradation pathway and invokes the redox pathway, (2) degradation depends on the smectite Fe (II) content and redox cycle, and (3) oxamyl degradation occurs in soil clays reduced under natural conditions. Results revealed that both reference and soil clays, reduced to varying degrees at circum-neutral pH, degrade oxamyl to oxamyl oxime (base hydrolysis pathway). As solution pH decreased, the surface Brønsted basicity is neutralized, increasingly yielding DCMF (redox pathway). At pH 2.5 DCMF is the only product. Reoxidation of the smectites restored some, but not all, of the clay properties and behavior observed in the unaltered state.
INFLUENCE OF NITRATE ON IRON REDOX CYCLING AND MINERALOGY IN FRESHWATER SEDIMENTS

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Competitive interactions between nitrate- and Fe(III) oxide-reducing bacteria, together with the recently discovered capacity for bacteria to couple enzymatic oxidation of Fe(II) to reduction of nitrate, have broad implications for the formation and destruction of Fe-bearing minerals in anaerobic soil and sedimentary environments. We have investigated N-Fe redox interactions in anaerobic freshwater wetland and shallow coastal plain aquifer sediments. Slurry systems containing synthetic or natural α-FeOOH (goethite) and undergoing sequential shifts in redox conditions (from NO₃⁻ reduction to Fe(III) reduction to NO₃⁻-dependent Fe(II) oxidation) were employed to examine the role of NO₃⁻-dependent Fe(II) oxidation in the biogeochemical cycling of nitrate and Fe. NO₃⁻ reduction preceded Fe(III) oxide reduction in the slurries, and resulted in transient accumulation of NO₂⁻ and production of mixed reduced N end-products including NH₄⁺. Fe(III) oxide reduction commenced once NO₃⁻ concentrations decreased to below ca. 0.5 mM, and continued until the electron donor (acetate) was depleted. Nitrate (3 mM) was added to the reduced slurry once Fe(III) oxide reduction ceased. The NO₃⁻ amendment induced rapid oxidation of both aqueous and solid-phase Fe(II), resulting in the production of primarily crystalline Fe(III) oxide phases similar to those originally present in the slurries. No significant NO₃⁻ reduction or Fe(II) oxidation occurred in pasteurized control cultures. Molecular analysis of PCR-amplified 16s rRNA gene fragments suggested that the microbial community associated with the initial, organotrophic NO₃⁻ reduction phase was distinct from the community present during the latter stages of the experiment, but that similar microbial communities were active during Fe(III) reduction and NO₃⁻-dependent Fe(II) oxidation. These results demonstrate the potential for development of microbial communities capable of both dissimilatory Fe(III) oxide reduction and oxidation of Fe(II) coupled to dissimilatory NO₃⁻ reduction in surface and subsurface anaerobic sediments. Our findings provide a quantitative basis for numerical simulation of the influence of N redox metabolism on Fe cycling and mineralogy at the interface between NO₃⁻ and Fe(III) reduction zones in sedimentary environments.
Principal component analysis (PCA) of published bulk compositions (SiO$_2$, Al$_2$O$_3$, FeO, CaO, MgO, TiO$_2$, Na$_2$O, K$_2$O) of 290 tektites and microtektites from eastern North America is consistent with an origin for the glasses from a single impact. The first two principal components account for approximately 75% of the compositional variation in the impact glasses. PCA axis 1 largely reflects the importance of a silica-rich parent lithology in these tektites; PCA axis 2 is loaded most heavily by K$_2$O and Na$_2$O. When sample scores are plotted against axes 1 and 2, the tektites and microtektites define a pinwheel pattern characterized by geographically defined clusters of tektites and microtektites; however, all groups overlap in the center of the pinwheel pattern where the bulk of georgiaites, glasses from Barbados and the tektite from Martha’s Vineyard plot. This leads us to conclude that the analysis provides permissive evidence for a single impact crater (such as the Chesapeake Bay structure) as the source for the Eocene impact glasses. Nonetheless most geographic groups of glasses have individual glasses that range to relatively unique compositions. For example, most bediasites define one arm of the pinwheel pattern where only a few georgiaites, glasses from Barbados and the Cuban tektite plot. Likewise, analyses from the heterogeneous Muong Nong tektite from Georgia define another arm of the pinwheel, but the curvilinear array defined by these analyses passes through the center of the pinwheel as well. Glasses from the New Jersey continental slope and the Caribbean define a third, diffuse arm of the pinwheel array.
THE INFLUENCE OF MANGANESE ION ON IRON BIOMINERALIZATION BY
SHewanella alga AT 25 ºC AND Thermoanaerobacter ethanolicus AT
60 ºC

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Biomineralization may play an important role in biogeochemical cycling of metals and
carbon in diverse subsurface environments. The objective of this study is to examine the
influence of Mn-concentration on the biomineralization products formed and to identify
biogeochemical factors determining phase distribution of Mn2+ during iron biomineralization.
The reductive biotransformation of a Mn-substituted (2 – 20 mol %) akaganeite (Fe1-xMnxO2OH)
by Shewanella alga (PV-4, 25 ºC) and Thermoanaerobacter ethanolicus (TOR-39, 60 ºC) was
investigated under anaerobic conditions at circumneutral pH (pH = 7 – 8). No exogeneous
electron carrier substance (i.e., anthraquinone disulfonate) or reducing agent (i.e., cysteine) was
added to the anaerobic medium. Incubations with both of the iron-reducing bacteria and Mn-
substituted akaganeite were sampled after 30 days, after which the aqueous chemistry and solid
phases were characterized. By comparison of iron minerals formed by S. alga and T. ethanolicus
using Mn-substituted akaganeite, it was shown that S. alga formed siderite (FeCO3), green rust
[Fe2+Fe3+(OH)16CO3•4H2O], and magnetite at 25 ºC, whereas T. ethanolicus formed mainly
magnetite at 60 ºC. The presence of Mn in the magnetite formed by T. ethanolicus was revealed
by energy dispersive X-ray analysis (EDX) is indicative of Mn substitution into magnetite
crystals. EDX analysis of iron minerals formed by S. alga showed that Mn was preferentially
concentrated in the siderite and green rust. These results demonstrate that coprecipitated/sorbed
Mn induced microbial formation of siderite and green rust by S. alga, but the formation of Mn-
substituted magnetite proceeded by T. ethanolicus.
DEHYDROXYLATION OF BAXITE CHARACTERIZED BY FOURIER TRANSFORM INFRARED SPECTROSCOPY AND X-RAY DIFFRACTION

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An important step in the industrial production of alumina by the Bayer process is the calcination of the bauxite ore to convert crystalline Al-hydroxide minerals into disordered or poorly crystalline transition alumina phases. Optimization of this “activation” step can increase the yield of alumina and reduce refining costs. Bauxite from Weipa, north Queensland, Australia was activated by heating it in air to various temperatures between 250 and 800° C for 30 minutes. The dehydroxylation pathways of both the Al-hydroxides and the impurities were studied using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Gibbsite, the most abundant mineral in bauxite, completely decomposed at 250° C, followed by boehmite and kaolinite at 500° C. No phase transformations were observed for hematite, anatase, rutile or quartz. Small amounts of gibbsite transformed to boehmite but the majority transformed to chi alumina, a disordered transition alumina phase, after dehydroxylation at 250° C. The dehydroxylation pathways of crystalline gibbsite follow the orders: (a) gibbsite (<250° C) to boehmite (250-450° C) to gamma alumina (500-800° C); or (b) gibbsite (<250° C) to chi alumina (250-800° C) to chi + kappa alumina (700-800° C). Boehmite completely altered to gamma alumina, while kaolinite altered to metakaolinite at 500° C.
USING HUMOROUS CARTOONS TO REINFORCE LEARNING IN MINERALOGY

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Cornett (1986, 2001) lists many reasons for incorporating humor in teaching. Starting a lesson with a joke, cartoon, or riddle is a good way to focus students on a lesson topic. Humorous riddles attract attention as students try to figure out the punch line. Students practice critical thinking skills as they unravel the connections and incongruities in a joke. Humor offers novelty - a different way of viewing a situation - and one of the components of creative thinking. Laughing at funny situations and sharing jokes is a pleasurable social activity that promotes a sense of group unity. Laughter relaxes people and relieves tension. Physiologically, this amusement increases blood oxygen, exercises lung, facial, and other muscles, and produces endorphins, while decreasing stress hormones. Students find humor an attractive teacher trait. Teachers who smile and "kid around" create a positive classroom atmosphere. People involved in devising and enjoying humor are viewed as more intelligent and creative. Laughter motivates and energizes students. During laughter, the brain produces a substance called catecholamine that boosts alertness.

Sixty humorous cartoons featuring minerals as characters were used to review physical properties of minerals in an undergraduate Petrology class. Students reported that they learned many new mineral terms and that the presentation clarified and reinforced concepts with which they were already familiar. Students mentioned that they appreciated the lighter side of mineral study, that the cartoons made the topic "more humorous and less overwhelming." Students thought that the mineral cartoons provide an effective teaching tool because they "integrate humor into a very technical and serious topic," and they facilitate memory - "a good way to get things stuck in your head." Below are two of the cartoons identified as the best by students.

USING POETRY IN TEACHING ABOUT MINERALS

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Incorporating poetry in teaching about minerals has many benefits. Poets, like scientists, use metaphors to express abstract ideas. The condensed, rich language of poetry may touch students at levels not easily articulated. Poetry allows students to expand their concepts of minerals, linking these concepts with other related ideas. Connections made between science class topics and the outside world enriches the educational experience (Walders, 2000; Abisdris and Casuga, 2001). Using poetry in teaching science provides the opportunity for students to further develop positive feelings toward science, to explore human emotions related to science, and to develop sensitivity and respect for the feelings of others (Donaldson, 2001). Robert Yager, in “A Vision for What Science Education Should Be Like for the First 25 Years of a New Millennium (2000),” expresses the need for science educators to expand curriculum to address more than facts and process skills. These often neglected domains include: imaging and creating, feeling and valuing, using and applying, and viewing science and its history as human endeavors. Many students decide early on that they do not like science because of its cold, factual, mathematical nature (Alber, 2001). However, science knowledge should be a part of everyone's education and enjoyment of the world's wonders. Poetry can provide a way of humanizing science and bringing creativity to the subject (Watts, 2001).

Several mineral poems that incorporate facts about physical properties, origins, and uses of minerals will be presented with visual images. The successful use of poetry in a high school earth science class in which students researched minerals and wrote poems of their own will be discussed. The activity had several outcomes: students appreciated that "learning doesn't have to be conventional and boring"; students were able to produce effective poems that correctly incorporated factual information; students felt a sense of accomplishment in writing a scientifically accurate poem; and a significant number of students reported their attitudes toward earth science had been positively affected as a result of the experience. Examples of student poetry and comments about the exercise will be given.

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MICROBIAL REDUCTION OF Fe(III) IN THE FITHIAN AND MULOORINA ILLITES: CONTRASTING EXTENTS AND RATES OF BIOREDUCTION

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This study was undertaken to investigate the rate and extent of reduction of Fe(III) in two different illite samples, Muloorina and Fithian, by facultative anaerobe, Shewanella putrefaciens CN32. The Fithian illite (API reference illite from Illinois) is relatively pure with only a trace amount of goethite. The starting material contained 4% of Fe, 19% of which is Fe(II) as determined by Mössbauer spectroscopy. Mössbauer spectroscopy also confirmed the presence of two different sites for Fe(III) in the illite structure. The surface area of the Fithian illite is 85.31 m²/g. The Muloorina illite, attained from Lake Eyre, S. Australia, has a surface area of 107.68 m²/g. The <0.2 µm size fraction was separated from a rock containing the Muloorina illite and used for bioreduction experiment. This size fraction is pure with no other Fe-containing minerals. The starting material contained 9.2% Fe, 93% of which is Fe(III) as determined by chemical and Mössbauer methods.

A subsurface iron-reducing bacterium, Shewenella putrefactions CN32, was used in the illite reduction experiments. For both bioreduction experiments, illite suspensions of 10 mg/mL were made in bicarbonate buffer and experimental tubes were inoculated with about 4.0 x 10⁻⁶-6.0 x 10⁻⁷ CN32 cells. In selected treatments, antraquinone-2,6-disulfonate (AQDS) was included as an electron shuttle to facilitate bioreduction while lactate was used as an electron donor. Controls were identical but no cells were added. Fe(II) production at various time points was determined by Ferrozine assay. Aqueous concentrations of major elements, Si, Al, Mg, and Fe were measured by direct current plasma emission spectroscopy. Lactate and its metabolic product acetate were measured by high performance liquid chromatography. Residual and biogenic solids were characterized by transmission electron microscopy, Mössbauer spectroscopy, and electron energy loss spectroscopy. The extent of reduction was much greater in the presence of AQDS for each illite sample, and the abiotic controls did not show any Fe(III) reduction. More importantly, the two illites exhibited contrasting extent and rate of bioreduction. Approximately 50-60% of Fe(III) in the Fithian illite (as measured by Ferrozine assay) was reduced within 4 days, whereas it took about two months to reduce 6-8% of Fe(III) in the Muloorina illite. In both cases, Fe(III) reduction was coupled with oxidation of lactate. The aqueous concentration of Fe increased over time and paralleled the trend of the biogenic Fe(II) production, but it accounted for only about 10% of total biogenic Fe(II), suggesting that most of bioproduced Fe(II) was either in biogenic solids or adsorbed onto solid surfaces.

Intensive characterizations of residual and biogenic solids are underway to delineate the reasons for the differences in the bioreduction behavior of the two illite samples. Surface area does not account for the differences. We speculate that these differences are caused by different structural sites of Fe(III): there exists two structural sites for Fe(III) in the Fithian illite as opposed to one site for Fe(III) in the Muloorina illite. One of the two sites is unique to the Fithian illite, and this site may be responsible for the extensive reduction for this illite sample. This site may be accessible to bacteria and thus may subject to more bioreduction.
The Turplu halloysite mines are economically important deposits situated between the low metamorphic Karakaya Complex (containing exotic giant limestone blocks) and volcanic rock contacts within the Sakarya Tectonic zone of NW Turkey. The deposits in this study are situated along the Kocadere River, which is a 2 km long strike-slip fault zone, about 20 km east of the town of Balya.

Petrographic studies of the calc-alkaline tuffs reveals they consist of devitrified glass and pumice fragments with small phenocrysts of quartz, feldspars, and biotite. The unaltered andesitic flows contain variable amounts of pyrite, quartz, plagioclase, orthopyroxene, amphibole, and biotite phenocrysts. X-ray diffraction, elemental analysis, scanning electron microscopy (SEM), thermal gravimetric analysis and infrared spectroscopy reveal a diverse assemblage of secondary clay-sized minerals. These include halloysite, hematite, goethite, psilomelane, gibbsite, alunite group, realgar and gypsum. Secondary minerals such as the halloysite, alunite, and realgar are likely a direct result of fossil hydrothermal alteration processes that took place at elevated temperatures along deep-seated structural features. Approximately 120 km west of the Balikesir region there is current hydrothermal activities in the Tuzla and Kestanbol hot springs. Post-hydrothermal alteration minerals related to weathering also impact the quality and distribution of the economically important halloysite. For example, Fe- and Mn-oxide and hydroxide distributions show evidence of mobilization, likely caused by siderophores produced in the resident regolith bacterial community.

These result represent a preliminary evaluation of the deposits. Geochemical and structural models needed to explain the mineralization pathways and spatial distribution of clays are currently being developed (see Ece and Schroeder, this volume). More detailed spatial mapping of the deposits and stable isotopic studies are planned to better define the genesis of these deposits.
Sodium poly(acrylic acid), Na-PAA, is a commonly used polyelectrolyte dispersant for processing of traditional ceramics such as porcelain. Traditional ceramics are typically comprised of clay, quartz and feldspar. Control of the suspension rheology is crucial to prevent segregation of the raw materials in suspension and for the forming of the ware prior to the high temperature firing process. Na-PAA has a low affinity for silica and silica-like surfaces and a high affinity for alumina-like surfaces so the adsorption behavior should correlate to the alumina-like surfaces on the kaolinite particle. To evaluate this concept the adsorption of Na-PAA on the surface of clay was investigated using a sub-micron alumina particle surface as a reference. The effect of polymer molecular weight on the adsorption of Na-PAA to alumina and industrial clay surfaces was investigated using a titration method. While the viscosity data confirmed the prediction for Na-PAA adsorption, there was a significant deviation in the measured adsorption levels compared to the predicted adsorption levels for the clay surface based upon the fraction of alumina-like surface area on the kaolinite particles. This deviation is demonstrated to be due to the presence of water-soluble organic species, specifically humic and fulvic acid, and other impurity clay minerals. These species were removed from the industrial clay by washing at pH 9.5 and sedimentation to remove the fine 2:1 layer silicates. After washing and beneficiating industrial clay samples the Na-PAA adsorption levels fall within the range predicted by the mineralogy of the kaolinite particle.
PROBING MICROBE/MINERAL AFFINITY IN HETEROGENEOUS GEOMATRICES USING LASER-BASED OPTICAL AND CHEMICAL IMAGER (LOCI)

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Many microbes are known to have affinities for specific minerals. It is difficult to determine microbe affinities in natural geomatrices that are heterogeneous on the micron scale. To investigate microbe affinity in complex, heterogeneous geomatrices, we have developed the Laser-based Optical and Chemical Imager (LOCI), a one-of-a-kind analytical instrument that combines a Fourier transform mass spectrometer (FTMS), unique laser-scanning system, custom optics for fluorescence detection, and software for automated data collection and analysis, along with an inference engine that produces maps of microbes and minerals on the sample surfaces.1 LOCI allows the interactions of microbes with geomatrices to be explored without disrupting the relationship of the microbes with the mineral surface. In a typical analysis, non-destructive surface fluorescence (for gfp-label microbes or fluorescing contaminant species) imaging of the sample surface is performed followed by destructive, high resolution, exact mass FTMS depth-profiling imaging. This allows the sorbates (microbes or contaminants) and the underlying mineral surface to be examined layer-by-layer, with a depth-resolution ranging from 1–10 µm between successive scans. At present, the system has spatial resolution capabilities down to 2 µm and can accept samples up to 3-inch diameters. Anaerobic samples can be easily handled by adapting a glove bag to the sample inlet purged with argon.

Data acquisition, analysis and interpretation are fully automated are invoked as separate steps that are initiated by the user.2 Depending on the user-defined laser desorption spot size and spacing between desorption sites, the data from a 1 mm² area may contain up to 10,000 files. The data interpretation software includes an inference engine that is pre-trained with a Fuzzy-logic lookup table of spectral characteristics that are indicative of specific minerals, contaminants, or microbes.3 The automation allows acquisition and interpretation of ~7200 spectra in an hour and a half. A user-friendly interface allows the accuracy of the inference engine to be easily verified. All of these features allow LOCI to offer the ability to correlate the spatial interactions between sorbates (microbes, contaminants, etc.) and the underlying mineral phase for large numbers of samples.

1Scott and Tremblay, Review of Scientific Instrumentation 2002, 73, 1108-1116.
PROVENANCE OF AN ARCHAEOLOGICAL CLAY DEPOSIT FROM AEGINA, GREECE

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Stylistic and petrographic analyses indicate that a distinctive group of ceramics was produced on the island of Aegina, Greece, during the Middle and Late Helladic periods of the Bronze Age (2000-1065 BC). Ceramic production encompassed a wide range of ceramic products including table, storage and cooking wares, known archaeologically as “Aeginetan Ware”. Present archaeological research places production at the large, fortified coastal settlement of Kolonna.

Electron microprobe analysis of constituent amphibole and biotite grains was conducted on various classes of “Aeginetan Ware” from Kolonna and Asine, a coastal village in the Argolid, Greece, and compared with a volcanic mineral composition databank for the South Aegean Volcanic Arc. The samples show a narrow range of amphibole compositions, which indicate that they were derived from a specific clay source on the island.

Recent geological fieldwork on Aegina identified an extensive clay source within an alluvial fan complex in the area of Skotini Gorge, south of prehistoric Kolonna. The clay deposit is located downstream from a Plio-Pleistocene biotite-hornblende dacite flow that has been hydrothermally altered in places. The clay fractions of both the altered dacitic flow and the alluvial clay contain abundant smectite-rich RO mixed layer illite-smectite. These results suggest that a significant component of the alluvial clay originated from the dacitic flow. Moreover, amphibole and biotite compositions in the Kolonna and Asine sample sets overlap with those of the altered dacite clay, suggesting that this clay could be the specific clay source for all local Aeginetan Ware.
CLAY MINERALS AS A SOURCE OF ELECTRON ACCEPTOR FOR MICROBIAL FE(III) RESPIRATION IN A PETROLEUM-CONTAMINATED AQUIFER

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Petroleum contamination within a sandy aquifer near Bemidji, MN (USA) has resulted in a sequence of anaerobic terminal electron accepting processes (TEAPs) downgradient from the source of contamination, including a large Fe(III)-reducing zone. Iron is generally the most abundant potential electron acceptor in many sedimentary environments and Fe(III) reduction is often observed to be a key process during the natural attenuation of contaminants. To better understand microbial Fe(III) reduction it is important to identify potential sources of bioavailable Fe(III) in sediments. The importance of Fe(III)-bearing minerals in the clay fraction of contaminated sediment for microbial Fe(III) respiration was investigated.

Comparison of sediments from a contaminated zone in which Fe(III) reduction was the predominant TEAP and from a nearby, uncontaminated background site revealed that the majority of changes associated with Fe(III) reduction occurred in the clay fraction. Although the clay fraction in background sediments accounted for only 0.4 - 0.6% by weight, it contained 30.4-57.4% of "bioavailable" (0.5 N HCl-extractable) Fe(III). Contaminated sediments collected from within the Fe(III)-reducing zone were depleted of clay fraction iron, indicating removal of reactive Fe(III) species during microbial Fe(III) reduction. Analytical transmission electron microscopy of clay fractions from both sites revealed the disappearance of thermodynamically unstable Fe(III) and Mn(IV) hydroxides (proto-ferrihydrite, lepidocrocite, and Fe vernadite) in the sediment from the Fe(III)-reducing zone. A decrease in smectitic clay minerals and goethite abundance was also observed.

Fe(II)- and Fe(III)-bearing minerals in the clay size fraction (mainly iron hydroxides and phyllosilicates) are difficult to separate or differentiate by physical methods. In order to find out which type of Fe(III) bearing mineral was potentially a preferred source of electron acceptor for Fe(III)-reducing microorganisms, model minerals were added to Bemidji sediment in which Fe(III) reduction was completed and methane production was the predominant TEAP. Addition of the model phyllosilicate mineral SWa-1 lowered steady state hydrogen concentrations to sustained levels associated with microbial Fe(III) reduction at a much greater rate than other tested minerals indicating this model phyllosilicate mineral as a preferable source of Fe(III) for indigenous Fe(III)-reducers in these sediments.
Zeolites are well known for their ion exchange, adsorption and acid catalysis properties. Different inorganic and organic pollutants have been removed from water at room temperature using various zeolites. Synthetic zeolite Faujasite Y has been used to remove inorganic pollutants including arsenic, cadmium and lead from water in continuous flow reactions below EPA’s maximum contamination limits. Successful removal of the gasoline additive MTBE has also been achieved using zeolite ZSM-5 below EPA’s advisory limit. Mixtures of these zeolites have been tested for complex matrix of the water pollutants. The zeolites showed a very good pollutant removal capacity with contact time less than 1 min. The pollutant removal capacity of the zeolites has been examined over a wide pH range. The apparent removal mechanisms for the various contaminants include cation and ligand exchange for the inorganic contaminants and acid-catalyzed hydrolysis for the organic contaminant.
MAMMALIAN-CELL TOXICITY OF PESTICIDES TREATED WITH REDOX-MODIFIED SMECTITE

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The fundamental concern about agricultural chemicals is their environmental fate and toxicologic risk to humans and other non-targeted animals. The application of pesticides to soil is typically direct or through post-emergence methods. Degradation of pesticides is typically considered to be a detoxification process and, therefore, a positive thing; but, evidence is insufficient to conclude that degradation always yields detoxification. While clay minerals are often regarded as catalysts for enhancing or decreasing the availability of pesticides to microorganismal degradation, recent studies have found that the iron (Fe) oxidation state in smectites directly affects the degradation of pesticides without microbial intervention. Yet, what does degradation mean when attempting to assess toxicologic risk? The objective of this study was to measure the influence of Fe oxidation state on the toxicity of pesticides to mammalian cells. Alachlor, oxamyl, dicamba, and 2,4-D were reacted with both oxidized and reduced ferruginous smectite (SWa-1). The supernatant from each pesticide/clay mixture was separated by centrifugation, filter sterilized, and used in multiple toxicity assays including those for cytotoxicity and genotoxicity. Results revealed that treatment with reduced smectite produced mixed effects on mammalian cell health, depending on the pesticide. Oxamyl and alachlor reacted with reduced SWa-1 showed a decrease in their overall cytotoxic potential. In addition, oxamyl showed a decrease in its overall genotoxic potential. Dicamba reacted with the reduced-clay treatment was more cytotoxic and genotoxic then the other treatments. Finally, no differences were observed between redox treatments for 2,4-D. The significance of these results is that oxidized smectites have virtually no influence on the toxicity of pesticides; whereas, reduced-Fe smectite plays a definite role in altering the cytotoxic and genotoxic potential of some agricultural pesticides. These results suggest Fe oxidation state of clay minerals should be taken into account in pesticide management programs.
ROLE OF HYDROXY–AI INTERLAYERED VERMICULITE AS STORAGE OF MOBILE Al$^{3+}$ IN THE FOREST SOILS DEVELOPED ON THE GRANITE BEDROCK IN KOREA

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Soil acidification is gradually accelerating due to increased deposition of acid rain in the Korea peninsula. Increased levels of mobile aluminium (Al$^{3+}$) toxic to roots of vegetation and aquatic biota, are detected in many places in the forest soils. The Al$^{3+}$ solubility is controlled by reactive Al(OH)$_3$ in many moderately acid soils (pH > 4.1), but by soil organic matters (SOM) in strongly acid soil (pH < 4.1). However, the Al$^{3+}$ dissolution process is not yet fully understood. In order to know the soil acidification process, we investigated the distribution and characterization of hydroxyl-Al interlayered vermiculite (HIV) from forest soils developed from the granite bedrock. Soil samples were taken from six forest areas with granite bedrock in Korea. Pine tree (Pinus densiflora) is the dominant vegetation at study area. But, spruce/fir tree also occur. The clay fractions from the six forest soils have similar compositions, consisting mainly of quartz, kaolinite and hydroxyl-Al interlayered vermiculite with minor amount of illite. Value of soil pH ranged from 3.66 to 5.14. BC/Al ratios of all forest soils were higher than 1. The concentration of extracted Al ranged from 2698 µgL$^{-1}$ to 8769 µgL$^{-1}$. The pH – pAl relationship for six forest soils, solution was undersaturated with respect to gibbsite (Al(OH)$_3$); log $K_{so}$ = 8.85 at 8°C at pH < 4.1. Under such condition, the Al solubility was controlled by hydroxy-Al vermiculite (HIV) better than complexation reaction with soil organic matter because the organic matter content was very low (<1.7%) in all study soils. Soil acidification generally leads to decreased (Ca+Mg+K)/Al molar ratios and increased concentration of mobile Al$^{3+}$ in the soil solution. Nevertheless, if vermiculite is included in forest soils, the mobile Al$^{3+}$ is tightly bound to its interlayer as positively charged polymers serving as storage of mobile Al$^{3+}$. The percentage of HIV influenced on mobile Al$^{3+}$ concentration and the ratios of base cations (BC) to Al in soil solution. Thus the aluminium toxicity can be mitigated by base cations in soil solution. Even though the pH value of the forest soils was low, the BC/Al ratios of most forest soils were high because the hydroxyl-Al interlayered vermiculite control the solubility of mobile Al$^{3+}$ in this forest soils.
BENTONITES AND TONSTEINS

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To most sedimentologists bentonites are clay-altered volcanic ash layers that are a result of explosive volcanism and as a consequence have a wide distribution. Bentonites are characteristically preserved as thin beds in low energy depositional environments, such as shales and coals, and have considerable stratigraphic value. Many bentonites in Mesozoic sediments consist of smectite. Some authors would restrict the term bentonite to smectite rich deposits irrespective of origin. As the diagenetic level increases the smectite is converted to illite via a mixed-layer clay. These are the K-bentonites. Another group were subjected to greater alteration forming kaolinite and these are the tonsteins.

The features by which bentonites are recognised as altered volcanic ashes will be reviewed. These include bed form, structures, textures, mineralogy and trace element geochemistry. The latter two also enable the original ash composition and the tectonic setting of the vulcanism to be determined. Although tonsteins result from the greatest level of alteration their classification and that of tuffs have many features in common, but some problems remain.
EFFECT OF SILICA FUME ON THE BEHAVIOR OF BURNT CLAY-LIME PASTES

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Silica fume has a significant effect on the hydration process of tricalcium silicate (C₃S) by lowering the concentration of Ca²⁺ and OH⁻ in liquid phase. The effect of partial substitution of burnt clay (mixed type) with silica fume in presence of lime (Ca(OH)₂) was studied in this investigation. Mixed type clay (Kafr Homid, Egypt) was activated by burning at 900°C then mixed with lime (constant weight ratio 30%) and silica fume (different weight ratios). The specimens after molding were hydrothermally treated at 10 atmosphere for periods 2, 12, 24 hours. The change occurring in the physico-chemical properties were investigated by compressive strength, chemically-combined water, bulk density and free lime contents measurements. Also the change in morphology and microstructure of some hardened pastes were investigated using SEM tests. The results of this study indicated that replacement of burnt mixed type clay by 5% silica fume in presence of lime improve the compressive strength at all ages, while replacement by 20% silica fume enhance compressive strength. This could be attributed to additional tobermorite gel (CSH phase) which formed due to the reaction of silica fume with Ca(OH)₂.
Buried soils which have both fragic and argilllic subsoil horizons have formed in the Holocene alluvial deposits of the North Branch of the Susquehanna River. Detrital and pedogenic mineral phases are reported for a “Btx” horizon sampled from a cutbank exposure at Wyoming, Pennsylvania. The whole soil mineralogy is described both from XRD results and textural relationships seen in thin section. The clay fraction (< 2 microns) consists of two discrete phases, neither of which is a “mixed-layer” clay. Detrital clay is inferred to consist predominantly of illite or “soil mica” (10 angstrom phase) while pedogenic clay is predominantly hydroxy-interlayered vermiculite (14 angstrom phase). The pedogenic origin of the 14 angstrom phase is inferred both from the thin section results and from a semi-quantitative analysis using the quartz (100) line as an internal standard. FTIR spectroscopy is also used to characterize the pedogenic HIV and compare it to clay from the source rocks for the alluvial sediment.
Remediation strategies employed for mitigation of low-pH, metal-sulfate drainage (i.e., acid rock drainage, ARD) may include passive treatment systems. While shown effective for neutralization of acid and removal of major ions (e.g., iron, aluminum, manganese), trace element removal during acid neutralization in passive systems is rarely investigated. Therefore, in this presentation, we will focus on the fate of trace metals in one common type of passive treatment system, the vertical flow wetland (VFW). Our experimental VFW contained a limestone buffered organic substrate (LBOS) and received low pH (<3), ferric iron-dominated ARD for two years. During this time, trace elements (As, Cd, Cr, Cu, U, Co, Ni, and Zn) were removed along a pH gradient controlled by a series of reaction zones that developed above a dynamic limestone dissolution front. Therefore, for the practical purpose of implementing LBOS to treat low pH, ferric iron-dominated ARD, high trace element removal efficiency can be expected as long as the limestone dissolution front does not pass completely through the substrate. With the exception of uranium, trace metal attenuation largely occurred above the limestone dissolution front in the transitional and oxide reaction zones. Trace metal removal was facilitated through sorption to primary organic matter and secondary hydrous iron and aluminum precipitates. The sorption selectivity within the LBOS follows the sequence:

As > Cu > Cr > Co = Ni = Zn = Cd > U.

Cadmium, copper, chromium, cobalt, nickel, zinc, and uranium were subject to remobilization as the pH decreased over time, although the degree of mobilization was trace element-dependent; arsenic was not remobilized. The following general order of trace element mobility can be applied to the LBOS:

U > Co = Zn ≥ Cd = Ni > Cu > Cr > As.
INTERLAYER CATION DIFFUSION IN VERMICULITE: A LABORATORY EXERCISE IN GEOCHEMICAL KINETICS

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This exercise reproduces for student laboratory use some classic experiments on interlayer cation diffusion in phyllosilicates. As hydrated ions enter vermiculite flakes from crystal edges, replacement of one interlayer cation with another modifies the interlayer region. Optical properties in the replaced zone change relative to unreplaced regions. Changes visible in transmitted light include differences in transparancy/opacity, and crenulation (“wrinkling”) due to volume change of the edge relative to the unreplaced interior portion.

Thin vermiculite flakes were trimmed into ~1x1 mm squares to create a smooth, uniform grain-boundary morphology. As-received or Mg-saturated vermiculite was the starting material, with cation-for-cation (usually cation-for-Mg) replacement accomplished by immersion in 1N cation-chloride solutions. Trials attempted so far included Li, Na, K, Mg, Ca, Sr, and Ba. Trials have been run at room-temperature (25°C) and at elevated temperatures (60-80°C). Specimens were transferred at measured time intervals to a thermal microscope stage for measurement of the replacement-zone thickness, then returned to the beaker for continued replacement.

Li, Na and Mg exchange gave potentially interpretable results at room temperature, but most such results were difficult to interpret because of the relatively slow kinetics at room temperature. Most trials to date have involved K-for-Mg exchange at elevated temperatures, for which interpretable results have been acquired with minimal difficulty. High-temperature trials involving most alkalis and alkaline earths appear to show promise for similar efforts.

The experimental diffusion coefficient for interlayer cation exchange was retrieved from replacement-zone thickness as a function of time. For comparison with literature, diffusion coefficients at elevated temperatures were adjusted to room temperature using the Arrhenius equation and published activation energies for the cation exchange process in appropriate clays. Room-temperature diffusion coefficients extrapolated from the experiments are several orders of magnitude higher than published values, but are sensitive to the assumed activation energy.

Aggregating several hundred published diffusion coefficients for cations through clays and other 2:1 phyllosilicates reveals that the diffusion coefficients decrease by about five orders of magnitude with increasing layer charge of the phyllosilicate. Published Arrhenius activation energies are lowest for monovalent cations diffusing through low-layer-charge phyllosilicates, higher for divalent cations diffusing through the same phyllosilicates and for diffusion of monovalent cations through mica, and highest for diffusion of divalent cations through mica. Among smectites and vermiculites, published data indicate that the Arrhenius activation energy for cation diffusion increases with increasing hydrated radius and with the increasing ionic potential of the diffusing interlayer cation. Samples from different stages of cation exchange can be examined by complementary techniques (e.g., X-ray diffraction [XRD], scanning electron microscopy [SEM]), to integrate geochemical kinetics with other aspects of mineralogy. The volumetric changes (crenulation and exfoliation) in the replaced edge region can be observed with conventional secondary SEM. XRD can be used to measure changes in d-spacings between replaced and unreplaced vermiculites, permitting introduction of several considerations involving cation hydration/dehydration, including the geometry and energetics of hydrated cations in solution and in the interlayer. This exercise allows students to use readily available equipment, and data they themselves generate, in quantitative homework exercises. Students can directly observe edge-weathering of micaceous materials in real time. The exercise illustrates several basic principles of chemical kinetics directly relevant to geology and mineralogy, including rate laws, diffusion, cation-exchange, and the temperature dependence and activation energy of reaction rates.
Weathering of biotite in saprolites developed on high-grade metamorphic parent rocks at the USDA Forest Service Coweeta Hydrologic Laboratory near Otto, NC, was examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). In XRD patterns of clay-size fractions of bulk soils and saprolites, the product of biotite weathering is detectable only by the presence of 1.2 nm (002) and 0.34 nm (007) peaks. Hand-picked pseudomorphs after biotite reveal 2.4 nm (001) and 0.82 nm (003) peaks, in addition to the 1.2 and 0.34 nm peaks. We interpret the XRD data to indicate the weathering of biotite to a regular 1:1 interstratification of 1.0 nm (biotite) and 1.4 nm (hydroxy-interlayered vermiculite) layers (hydrobiotite). The 1.2 nm peak is common in numerous other published XRD studies of weathered regoliths developed on micaceous parent materials, and is commonly interpreted as some form of a mixed-layer product of mica weathering. However, odd-order XRD peaks of a 2.4 nm structure are much less commonly reported, especially from weathered micas previously studied by TEM.

Lattice-fringe images of fresh Coweeta biotite and minimally weathered Coweeta material strongly resemble lattice-fringe images from other TEM studies in several ways. Lattice-fringe images of fresh Coweeta mica show thick packets of unaltered 1.0 nm mica. Most lattice fringe images of samples that showed 2.4 nm and higher-order peaks in XRD look identical to published TEM images of partly weathered micas from other studies that showed no XRD evidence of regular interstratification. Packets of three to ten 1.0 nm layers, separated by single 1.4 nm layers, are common in lattice-fringe images from Coweeta biotites, as in biotites from previously published biotite weathering studies. However, unlike previously published lattice-fringe images from naturally weathered biotites, some images from the least weathered (fresh) Coweeta biotite show indications of a two-layer periodicity. In more extensively weathered Coweeta materials, packets of up to three or four 2.0 nm packets (each consisting of two 2:1 layers) persist amidst less ordered material. Regular interstratification appears to favor the persistence of the hydrobiotite weathering product.

In order to determine more about the origin of two-layer periodicity in fresh (1.0 + 1.0 nm) and weathered (1.0 + 1.4 nm) biotite at Coweeta, preliminary structure images of fresh Coweeta mica have been acquired by HRTEM in several modes, including high-angle annular dark-field (HAADF). The two-layer periodicity is interpreted from structure images of fresh biotite as resulting from regular periodic alternation of two different layer orientations, differing from one another by rotation of ±60 degrees about z*; in other words, 2M₁ polytypism. At present, the results are consistent with the hypothesis (Banfield, personal communication) that parent-mica polytypism controls the interstratification of the weathering product. According to this hypothesis, 1M parent micas weather to randomly interstratified mica-vermiculite whereas 2M parent micas weather to regularly interstratified 1:1 mica-vermiculite. To date, combined XRD and TEM evidence of regular two-layer interstratification in parent biotite and its weathering products has been observed only in metamorphic biotites. Previous XRD/TEM studies lack any indication of two-layer periodicity and have all been on igneous biotites. Characterization of biotite weathering products influences both calculation of mineral weathering rates by geochemical mass-balance and comparisons between field and laboratory studies of mica weathering kinetics.
A planar waveguide is described for use with polymeric membranes containing a novel lead sensor and for use with clay membranes for use in determining redox state of the clay is described. The cell design is based loosely on the work of Heineman et al. The planar waveguide using an electroactive SnO$_2$ carries light from Xenon arc lamp to a Ocean optics array detector. It is tested using a nafion membrane with the colored Ru(bpy)$_3^{2+}$ compound.

The instrument will be used with a PVC membrane case on the SnO$_2$ electroactive substrate. Incorporated into the PVC membrane is a compound 18-crown6-umbelliferone with a 17 carbon tail. This compound is highly selective to lead and has at near neutral pH only a single competitive ion, Cu$^{2+}$. This ion can be discriminated against using the electroactive substrate. The instrument is also used on think clay films which contain oxidizable and reducible iron centers.

The paper will present details on the design of the sensor block and verification of its use in trial systems.
EFFECTS OF CATION EXCHANGE CAPACITY AND INTERLAMELLAR CATION IDENTITY OF SMECTITE CLAYS ON THE VISIBLE SPECTRA OF PORPHYRINS

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Porphyrins become protonated if a solution is sufficiently acidic. The pH at which protonation will occur depends on the pK_a of the specific porphyrin. If the hydration sphere of the interlamellar cation is acidic, the porphyrin will be protonated and a red shift in the Soret band is observed. The porphyrin under consideration has large substituent rings attached to the porphin core structure. These substituent rings can rotate with respect to the core. Any rotation will cause a change in the profile of the Q bands. The optimum orientation of the substituent to the porphin core as well as the porphyrin to the clay requires time. The orientation is studied by observing the Q bands with respect to time. Absorption spectra of the porphyrin-clay solution are taken periodically until the porphyrin resides in an equilibrium position.

Previous studies have examined the interaction of methylene blue with smectite clays. These results focused on the time it took methylene blue to reach optimum orientation in the interlamellar regions of the clay minerals. The research also considered the cation exchange capacity of smectites on the spectra of methylene blue (Bujdák et. al., 2001). This research will expand upon these results. The dyes used in previous studies were smaller and had a lower charge than the porphyrin used in this research. This study focuses on the effects of cation identity and clay CEC on porphyrin orientation in the interlamellar region with respect to time.

Spectroscopy (UV-Vis) is being used to study absorption. This approach allows changes in the porphyrin environment to be monitored over a period of time. The porphyrins will be exposed to a series of clays that have been purified and exchanged with Na^+, K^+, Mg^{2+}, Ca^{2+}, and Al^{3+} cations. The clays in this study have been obtained from the Source Clays Repository and include SHca-1, SWy-2, STx-1, SCa-3, and SAz-1. A short path length cell is being used to study the Soret bands and a longer path length cell is being used to study the Q bands.
MOLECULAR MODELING OF WATER CONFINED BETWEEN HYDROPHILIC SURFACES OF BRUCITE

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Detailed knowledge of the structure and dynamics of confined water is important for a wide range of topics, including molecular-level understanding of clay swelling, solvent structure and dynamics at mineral-water interfaces, and ion adsorption and exchange in aqueous geochemical systems. Molecular dynamics (MD) computational technique can provide invaluable insight about these processes and phenomena, in many ways complementing information obtainable from conventional spectroscopic and electrochemical measurements. The simulations presented here are for a simple model of liquid water held in 2-dimensional nano-confinement between two parallel electrostatically neutral, but hydrophilic surfaces of brucite, Mg(OH)2. These model results provide greatly increased, structurally detailed understanding of the surface related effects on the spatial variation in the water structure, local density, hydrogen bond organization, and cooperative low-frequency vibrational dynamics of H2O molecules at the surface.

Our NVT ensemble MD simulations were performed on a series of model systems consisting of 0.3 to 3.0 nm thick water layers (containing 35 to 360 H2O molecules) confined between two 1.9 nm thick brucite substrate layers. Periodic boundary conditions were applied in all three dimensions, and no constraints were imposed on the movements of substrate and water atoms in the simulation supercells. The results show that the water structure is significantly influenced by the brucite surface, with both H-bond donations to surface oxygens and H-bond acceptance from surface hydrogens in the first surface layer of H2O molecules playing a key role. The oxygen and hydrogen atomic density profiles show significant deviation from the bulk water structure to distances as large as 1.5 nm (3-5 molecular water layers) from the surface, with peaks in atomic density at 2.45, 5.05, 6.25, and 9.05Å from the surface. The local structural environment of water molecules varies significantly as the distance from surface increases. The first layer of water molecules has a 2-dimensional hexagonal arrangement, reflecting the brucite surface structure and has highly restricted translational and orientational degrees of freedom. There is a transitional structure at distances between the first and second peaks of the molecular density profile (between ca. 3 and 5 Å from the surface), where the orientations of H2O molecules are very restricted, but their translations are not. A partially ordered structure beyond the second peak of the oxygen density profile (from 0.5 to ~1.0nm) has very small restrictions on both translations and orientations and it is gradually changed to the structure of bulk water.
Clay minerals have been used in medicinal applications since Aboriginal times. Clay poultices are used to heal wounds; people eat clays to coat stomach linings and soothe indigestion; animals eat clay containing trace elements (i.e. As) that can kill worms. The reasons that various clay minerals are effective as medicines may be as variable as the ailment, but by studying the mechanisms by which clay minerals heal, we may gain insight to a variety of diseases and potential cures.

Buruli Ulcer is a flesh eating disease that is borne by *mycobacteria ulcerans*, a bacterium related to leprosy and tuberculosis. Line Brunet de Courssou, a French humanitarian, has been working in the Ivory Coast, Africa where this disease is becoming widespread. She has documented numerous case studies of healing the disease by applying a French green illite that she had used on wounds since her childhood (www.burulibusters.com). She appealed to the Clay Minerals Society scientists to study the particular illite that was successful in treatment of this disease. The question is, what makes this illite lethal to the mycobacteria when other clay minerals, even other illites, are not? What mechanism kills the bacteria?

Two French Green Illite samples were studied, one supplied by Argiletz, and another supplied by Agricur. The sample from Agricur was not successful in the treatment of Buruli, but was used as a poultice to stimulate skin granulation. The samples used in the field study were unpurified, but the dominant mineral is an Fe-rich (7 wt.%) illite. The crystals are hexagonal with texture similar to IMt-1 illite, but with a smaller particle diameter (avg. 200nm).

The two illite samples, along with clay mineral standards IMt-1, SWy-1 and KGa-1 were reacted with e-coli in an incubator at 37°C for 20 hrs. Results (right) show that the illite used to kill *mycobacteria ulcerans* actually promoted growth of e-coli over the standard growth rate without clay present. The second illite (Agricur) killed all of the e-coli in the culture. The “smoking-gun” or mechanism of bacterial death has yet to be identified for these killer clays. Possible mechanisms will be explored including adsorption and exchange properties, surface potential, pH, redox chemistry, and mineral morphology.
Lead transformation to pyromorphite, lead phosphates, through phosphate amendments may be a potential remedial strategy for immobilizing lead in contaminated soil and safeguarding human health and environment from the contamination. In most previous studies, the formation of pyromorphite in contaminated soil occurred through aqueous media. In situ transformation directly from lead minerals has not been investigated. This laboratory study aims at synthesizing pyromorphite from lead minerals under in situ field conditions. Lead minerals, including cerussite, lead oxide, plattnerite, anglesite, galena, as well as a soil sample amended with cerussite at a rate of 1 g Pb kg⁻¹, were directly mixed with phosphoric acid (w/w 85%) at a Pb:P molar ratio of 1:5. The reactions were incubated at room temperature under the conditions of simulated natural wet-dry cycles for one year. Formed pyromorphite was periodically analyzed by x-ray diffraction after the reaction, and the kinetics and efficacy of the transformation assessed. Results showed that the transformation of lead minerals to pyromorphite was mineral species-dependent, with the reaction kinetics: cerussite > lead oxide > plattnerite > anglesite > galena, and the efficacy of the transformation is limited. About 20-30% of cerussite and lead oxide were transformed to pyromorphites while the transformation of anglesite and galena was hardly detected during the reaction period. The incomplete transformation was attributed to reduced acidity and limited moisture conditions during the reaction. This study demonstrates that maintaining appropriate moisture, acidity, and soluble phosphate level in soils would enhance the immobilization of contaminated lead through pyromorphite formation.
POLYMER-SILICATE NANOCOMPOSITES: AN OVERVIEW

A. A. Zaman*, A. Nguyen1,3, S. Pregler1,2, A. Bhaskar2, and C. L. Beatty2

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Polymer/Silicate nanocomposites were prepared by melt compounding using a reactive twin-screw extruder. Nanocomposite polymeric materials offer unique property advantages induced not only by physical presence of the particles, but also by the dispersion state of the particles and the interaction of the filler with polymer molecules. In this work, different polymers and silicates have been used and effects of clay loading and shear rate (screw rotational speeds) on the properties of polymer nanocomposites have been investigated. The materials were characterized using tensile testing, DMTA, XRD, TEM and viscosity measurements. While generally incorporation of nano-particles results in samples of higher value modulus and also a higher value of stress to break, it was found that the mechanical properties strongly depend on the compatibilizer, additives, and the nature of interfaces governing the nanocomposites.

The concept of a critical shear rate for optimum dispersion of clay platelets has been proposed on the basis of the above study. Work supported by the U.S. Department of Energy, Office of Nuclear Energy, Science and Technology, under Contract W-31-109-Eng-38.
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