

# Summary of FY 2007 Geosciences Research

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# TABLE OF CONTENTS

<b>TABLE OF CONTENTS</b> .....	<b>2</b>
<b>FORWARD</b> .....	<b>9</b>
<b>THE GEOSCIENCES RESEARCH PROGRAM IN THE OFFICE OF BASIC ENERGY SCIENCES</b> .....	<b>10</b>
<b>ARGONNE NATIONAL LABORATORY</b> .....	<b>11</b>
Mineral-Fluid Interactions: Synchrotron Radiation Studies at the Advanced Photon Source.....	11
<b>IDAHO NATIONAL LABORATORY</b> .....	<b>13</b>
Pathways for Redox Transformation of Semiconducting Minerals: The Iron Oxides .....	13
<b>LAWRENCE BERKELEY NATIONAL LABORATORY</b> .....	<b>14</b>
Upgrade of the Computational Cluster at LBNL.....	14
Integrated Isotopic Studies of Geochemical Processes.....	14
Physicochemical Controls on Unsaturated Flow and Transport in Geological Media.....	16
Clay Mineral Surface Geochemistry.....	18
Rate Controls in Chemical Weathering: A Reactive Transport Approach.....	19
Nanoparticle Aggregation in Natural Aqueous Systems .....	20
Molecular-Level Studies of Mineral-Water Interface Structure and Chemistry .....	22
How Does Nanoparticle Structure Control Interfacial Phenomena? .....	23
Imaging Electronic and Atomic Redistribution during Redox Reactions at Surfaces.....	24
Development of Isotope Techniques for Reservoir and Aquifer Characterization.....	26
Kinetic Isotope Fractionation by Diffusion in Liquid.....	28
Seismic Signature of Permeable and Impermeable Fractures and Faults.....	29
Propagation of Elastic Waves in Complex Media .....	31
Joint Three-Dimensional Electromagnetic-Seismic Imaging: A Structurally Based Approach.....	32
Permeability Dependence of Seismic Amplitudes.....	33
Imaging Permeability and Fluid Mobility Using Time-Lapse Measurements .....	34
Air-Derived Noble Gases in Sediments: Sites and Mechanisms for Trapped Components.....	35
Seismic Wave Propagation in Earth Systems with Fluids and Fractures .....	36
Density-Driven Brine Convection: A Process for Accelerating CO <sub>2</sub> Dissolution and Enhancing Security of Geologic Storage .....	37
Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems.....	38
<b>LAWRENCE LIVERMORE NATIONAL LABORATORY</b> .....	<b>41</b>
Investigation of the Physical Basis for Biomineralization.....	41
Fluid Chemistry, Surface Chemistry and Fracture Mechanics: An Investigation of the Connection at the Nanoscale.....	42
Reactive Fluid Flow through Variable Aperture Fractures: Permeability Alterations Due to Dissolution .....	43
Why Does Aluminum Inhibit Silicate Dissolution Rates? An Experimental Study Combining Kinetics with HAFM and NMR to Determine the Reaction Mechanisms at the Silicate-Solution Interface.....	45

Kinetic Isotope Fractionation.....	46
Permeability and Electrical Resistivity in Partial Melts: An Integrated Study Combining Laboratory Measurements, X-ray Computed Tomography, and Computational Methods.....	47
Geochemical Imaging with the NanoSIMS.....	49
<b>LOS ALAMOS NATIONAL LABORATORY.....</b>	<b>51</b>
High Resolution/High Fidelity Seismic Imaging and Parameter Estimation for Geologic Structure and Material Characterization.....	51
Nonlinear Elasticity in Rocks.....	52
Elastic Wave Effects on Colloid Interactions and Their Influence on Porous Fluid Transport.....	53
Summer of Applied Geophysical Experience (SAGE).....	55
The Uranium Decay Series at a Finer Scale.....	56
Controls on Molecular-Scale Microbial Responses to Metals: Interactions of Bacteria, Metals and Environmental Nanoparticles.....	57
<b>OAK RIDGE NATIONAL LABORATORY.....</b>	<b>60</b>
Nanoscale Complexity at the Oxide/Water Interface.....	60
Fundamental Research in Isotope Geochemistry: Experimental, Molecular-Based Simulation, and Neutron-Scattering Studies of Fluids and Minerals.....	62
Rates and Mechanisms of Mineral-Fluid Interactions at the Nanoscale.....	63
Isotopic Fractionation of Carbonate Systems Relevant to Subsurface CO <sub>2</sub> -Sequestration.....	65
<b>PACIFIC NORTHWEST NATIONAL LABORATORY.....</b>	<b>67</b>
Reductive Mineralization of Nanometer-Sized Fe(III) Oxides in Grain Coatings and Micropores.....	67
Molecular Basis for Microbial Adhesion and Geochemical Surface Reactions: A Study Across Scales.....	69
Pathways for Redox Transformation of Semiconducting Minerals: The Iron Oxides.....	70
The Influence of Mineral Surfaces on Multi-electron Reduction Mechanisms for Polyvalent Metals.....	71
The Impact of Carbonate on Surface Protonation, Electron Transfer, and Crystallization Reactions in Iron Oxide Nanoparticles and Colloids.....	72
First Principles Simulation of the Temperature Composition and Pressure, Dependence of Natural Fluids.....	73
<b>SANDIA NATIONAL LABORATORY/ALBUQUERQUE.....</b>	<b>75</b>
The Nature of the Mineral-Water Interface: A Molecular Simulation and Spectroscopic Investigation.....	75
Metal-Anion Pairing at Oxide/Water Interfaces: Theoretical and Experimental Investigations from the Nanoscale to the Macroscale.....	76
Approaches to Some of the Outstanding Problems in the Heterogeneous Compactive Deformation of Geomaterials.....	77
Quantifying the Micromechanical Effects of Variable Cement in Granular Porous Media.....	79
The Importance of Flow-Enhanced Precipitation and Pulsatile Dispersion in Geochemical Systems.....	81
Investigation into the Relationship between Heterogeneity and Heavy-Tailed Solute Transport.....	84
<b>PART II: OFF-SITE.....</b>	<b>86</b>
<b>THE UNIVERSITY OF ALABAMA.....</b>	<b>86</b>
Molecular Basis for Microbial Adhesion and Geochemical Surface Reactions: A Study Across Scales.....	86
The Impact of Carbonate on Surface Protonation, Electron Transfer, and Crystallization Reactions in Iron Oxide Nanoparticles and Colloids.....	88

<b>ARIZONA STATE UNIVERSITY .....</b>	<b>90</b>
A SIMS Study of the Chemical Dynamics of Organic/Inorganic Interactions in Sedimentary Basins.....	90
<b>BOSTON UNIVERSITY.....</b>	<b>92</b>
Collaborative Research: Understanding Multi-Scale Space-Time Patterns in Crustal Deformation Processes: Towards Ensemble Forecasting in Complex Tectonic Systems .....	92
<b>CALIFORNIA INSTITUTE OF TECHNOLOGY .....</b>	<b>94</b>
Experimental Petrology and Geochemistry of Volatile-Bearing Silicate Melts.....	94
Isotope Tracer Studies of Diffusion in Silicates and of Geological Transport Processes Using Actinide Elements.....	96
<b>UNIVERSITY OF CALIFORNIA, BERKELEY.....</b>	<b>97</b>
How Do Interfacial Phenomena Control Nanoparticle Structure? .....	97
Microbial Metabolism and the Nature of Metal Sulfide Biomineralization Products .....	99
Diffusion/Dispersion Transport of Chemically Reacting Species.....	101
Extracting Geological Stresses and Anisotropy from Rocks by Means of Neutron Diffraction .....	103
<b>UNIVERSITY OF CALIFORNIA, DAVIS.....</b>	<b>105</b>
Thermodynamics of Minerals Stable Near the Earth’s Surface.....	105
The Impact of Carbonate on Surface Protonation, Electron Transfer, and Crystallization Reactions in Iron Oxide Nanoparticles and Colloids.....	107
How Do Interfacial Phenomena Control Nanoparticle Structure? .....	108
Proton Exchange Rates and Other Elementary Reactions in Large Aqueous Molecules: A Combined Experimental and Simulation Project .....	109
Collaborative Research: Understanding Multi-Scale Space-Time Patterns in Crustal Deformation Processes: Towards Ensemble Forecasting in Complex Tectonic Systems .....	111
<b>UNIVERSITY OF CALIFORNIA, SANTA BARBARA.....</b>	<b>113</b>
Physiochemical Evidence of Faulting Processes and Modeling of Fluid Flow in Evolving Fault Systems in Southern California.....	113
<b>UNIVERSITY OF CALIFORNIA, SANTA CRUZ .....</b>	<b>115</b>
High Resolution/High Fidelity Seismic Imaging and Parameter Estimation for Geological Structure and Material Characterization.....	115
<b>UNIVERSITY OF CALIFORNIA, SAN DIEGO.....</b>	<b>117</b>
First Principles Simulation of the Temperature Composition and Pressure, Dependence of Natural Fluids	117
<b>UNIVERSITY OF CHICAGO .....</b>	<b>119</b>
GeoSoilEnviroCARS: A National Resource for Earth, Planetary, Soil and Environmental Science Research at the Advanced Photon Source .....	119
Synchrotron X-ray Microprobe and Microspectroscopy Research in Low Temperature Geochemistry .....	120
Kinetic Isotope Fractionation by Diffusion in Liquids.....	121
<b>CLARK UNIVERSITY.....</b>	<b>123</b>
Physics of Channelization: Theory, Experiment, and Observation .....	123

<b>CLAY MINERALS SOCIETY</b> .....	<b>125</b>
Enchanted Clays: 44 <sup>th</sup> Annual Meeting of the Clay Minerals Society .....	125
<b>COLORADO SCHOOL OF MINES</b> .....	<b>127</b>
Prestack Amplitude Analysis of Wide-Azimuth Seismic Data for High-Resolution Reservoir Characterization .....	127
Monitoring the Subsurface with Multiple Scattered Waves and Quasi-Static Deformation .....	129
Investigation into the Relationship between Heterogeneity and Heavy-Tailed Solute Transport.....	131
<b>UNIVERSITY OF COLORADO</b> .....	<b>133</b>
Monitoring the Subsurface with Multiple Scattered Waves and Quasi-static Deformation.....	133
<b>UNIVERSITY OF CONNECTICUT</b> .....	<b>135</b>
Air-Derived Noble Gases in Sediments: Sites and Mechanisms for Trapped Components.....	135
<b>UNIVERSITY OF FLORIDA</b> .....	<b>136</b>
Pore-Scale Simulations of Dissolution Breakthrough in Rough Fractures.....	136
<b>GEORGE WASHINGTON UNIVERSITY</b> .....	<b>138</b>
Crystal Defects, Etch Pits, and Rough Surfaces: A More Complete Picture of Mineral-Water Interactions during Dissolution and Growth.....	138
<b>GEORGIA INSTITUTE OF TECHNOLOGY</b> .....	<b>140</b>
Barite Growth and Dissolution at the Molecular Scale .....	140
<b>HARVARD UNIVERSITY</b> .....	<b>142</b>
Growth and Dissolution of Iron and Manganese Oxide Films .....	142
<b>UNIVERSITY OF HOUSTON</b> .....	<b>144</b>
Seismic Imaging Beneath an Unknown Overburden: Method Development and Evaluation on Synthetic and Real Data .....	144
<b>IDAHO STATE UNIVERSITY</b> .....	<b>146</b>
Redox Interaction of Cytochromes and Bacteria with Oxide Surfaces: Probing Redox-Linked Conformation Change .....	146
<b>UNIVERSITY OF ILLINOIS</b> .....	<b>148</b>
Computational and Spectroscopic Investigations of the Molecular Scale Structure and Dynamics of Geologically Important Fluids and Mineral-Fluid Interfaces .....	148
Field-Constrained Quantitative Model of the Origin of Microbial and Geochemical Zoning in a Confined Fresh-Water Aquifer .....	150
<b>UNIVERSITY OF ILLINOIS AT CHICAGO</b> .....	<b>152</b>
Mineral-Fluid Interactions: Synchrotron Radiation Studies at the Advanced Photon Source.....	152
Nanoscale Reactivity of Clays, Clay Analogues (Micas), and Clay Minerals .....	153
<b>INDIANA UNIVERSITY</b> .....	<b>155</b>
Significance of Isotopically Labile Organic Hydrogen in the Thermal Maturation of Source Rocks .....	155

<b>JOHNS HOPKINS UNIVERSITY</b> .....	<b>157</b>
Physiochemical Evidence of Faulting Processes and Modeling of Fluid Flow in Evolving Fault Systems in Southern California.....	157
Crystal Chemistry of Toxic Metal Sequestration.....	159
Predictive Single-Site Protonation and Cation Adsorption Modeling.....	161
Development of New Biomarkers for Surficial Earth Processes.....	162
<b>UNIVERSITY OF MARYLAND</b> .....	<b>163</b>
Theoretical Studies on Heavy Metal Species in Solution.....	163
<b>MASSACHUSETTS INSTITUTE OF TECHNOLOGY</b> .....	<b>165</b>
Collaborative Research: Evolution of Pore Structure and Permeability of Rocks under Hydrothermal Conditions.....	165
Physics of Channelization: Theory, Experiment, and Observation.....	167
Rheological Properties of Earth’s Lithosphere: Experimental Constraints on Low-Temperature Plasticity of Olivine-Rich Rocks at High Pressures.....	169
<b>UNIVERSITY OF MASSACHUSETTS, AMHERST</b> .....	<b>171</b>
Quantifying the Micromechanical Effects of Variable Cement in Granular Porous Media.....	171
<b>MINERALOGICAL SOCIETY OF AMERICA</b> .....	<b>173</b>
Support of MSA and GS Short Courses and the Companion Reviews Volumes.....	173
<b>UNIVERSITY OF MINNESOTA</b> .....	<b>175</b>
Rheological Properties of Earth’s Lithosphere: Experimental Constraints on Low-Temperature Plasticity of Olivine-Rich Rocks at High Pressures.....	175
<b>NATIONAL ACADEMY OF SCIENCES</b> .....	<b>177</b>
Board on Earth Sciences and Resources and Its Activities.....	177
Grand Research Questions in Solid-Earth Sciences.....	179
<b>UNIVERSITY OF NEW MEXICO</b> .....	<b>181</b>
Investigation into the Relationship between Heterogeneity and Heavy-Tailed Solute Transport.....	181
<b>THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK</b> .....	<b>183</b>
Complex Fluids in Self-Affine Fractures.....	183
Study of Damping Granular Materials.....	185
<b>STATE UNIVERSITY OF NEW YORK, STONY BROOK</b> .....	<b>187</b>
Complexities Affecting the Rate and Mechanism of Pyrite Oxidation: An Interdisciplinary Approach.....	187
Microscale Processes and Macroscopic Behavior of Porous Geomaterials.....	189
Up-Scaling Geochemical Reaction Rates for CO <sub>2</sub> in Deep Saline Aquifers.....	191
<b>UNIVERSITY OF NORTH TEXAS</b> .....	<b>193</b>
The Influence of Mineral Surfaces on Multi-electron Reduction Mechanisms for Polyvalent Metals.....	193
<b>NORTHWESTERN UNIVERSITY</b> .....	<b>195</b>

Approaches to Some of the Outstanding Problems in the Heterogeneous Compactive Deformation of Geomaterials .....	195
Surface Charge Densities and Acidities of Biogeochemically Important Organic Adlayers at Mineral/Water Interfaces Studied by Nonlinear Optics.....	197
<b>THE OHIO STATE UNIVERSITY .....</b>	<b>199</b>
Metal-Anion Pairing at Oxide/Water Interfaces: Theoretical and Experimental Investigations from the Nanoscale to the Macroscale .....	199
<b>OREGON STATE UNIVERSITY .....</b>	<b>201</b>
Efficient Inversion of Multi-Frequency and Multi-Source Electromagnetic Data .....	201
<b>PENNSYLVANIA STATE UNIVERSITY .....</b>	<b>203</b>
Rate and Mechanism of Transformation of Bedrock into Saprolite During Spheroidal Weathering .....	203
<b>PRINCETON UNIVERSITY .....</b>	<b>205</b>
Up-Scaling Geochemical Reaction Rates for CO <sub>2</sub> in Deep Saline Aquifers .....	205
<b>PURDUE UNIVERSITY .....</b>	<b>207</b>
Self-Assembling Sub-Porosity: The Effect on Fluid Flow and Seismic Wave Propagation .....	207
<b>RENSELAER POLYTECHNIC INSTITUTE .....</b>	<b>209</b>
Properties of Interfaces in Fluid-Bearing and Fluid-Absent Rocks .....	209
<b>UNIVERSITY OF SOUTH CAROLINA .....</b>	<b>211</b>
Understanding Long-Term Solute Transport in Sedimentary Basins: Simulating Brine Migration in the Alberta Basin, Canada .....	211
<b>STANFORD UNIVERSITY .....</b>	<b>212</b>
Framework for Constitutive Branching in Porous Rocks Undergoing Brittle Faulting and Cataclastic Flow .....	212
Geochemical Controls on Nuclear Magnetic Resonance Measurements .....	213
Porous Rock with Fluid: Impact of Heterogeneity on Reservoir Transport and Elastic Properties and Application to Unconventional Pore-Filling Materials.....	214
Structural Heterogeneities and Paleo-Fluid Flow in an Analog Sandstone Reservoir .....	216
<b>TEMPLE UNIVERSITY.....</b>	<b>219</b>
Complexities Affecting the Rate and Mechanism of Pyrite Oxidation: An Interdisciplinary Approach .....	219
<b>TEXAS A&amp;M UNIVERSITY .....</b>	<b>221</b>
Kinetics and Mechanisms of Calcite Reactions with Saline Water .....	221
Time-Lapse Seismic Monitoring and Performance Assessment of CO <sub>2</sub> Sequestration in Hydrocarbon Reservoirs .....	223
<b>UNIVERSITY OF TEXAS.....</b>	<b>225</b>

Metal-Anion Pairing at Oxide/Water Interfaces: Theoretical and Experimental Investigations from the Nanoscale to the Macroscale .....	225
Predicting Fracture Porosity Evolution in Sandstone .....	227
<b>VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY.....</b>	<b>229</b>
Investigation of the Physical Basis for Biomineralization.....	229
Frontiers In Biogeochemistry And Nanomineralogy: Studies In Quorum Sensing And Nanosulfide Dissolution Rates .....	231
<b>UNIVERSITY OF WISCONSIN.....</b>	<b>233</b>
Mapping of Temporal and Spatial Phase Transitions of CaCO <sub>3</sub> in Echinoderm Skeletons: Key Insights into Basic Mechanisms in Biomineralization .....	233
Quantifying the Micromechanical Effects of Variable Cement in Granular Porous Media.....	234
High Precision Ion Microprobe Analysis of Low Temperature Quartz Cements .....	236
<b>WOODS HOLE OCEANOGRAPHIC INSTITUTION .....</b>	<b>238</b>
Collaborative Research: Evolution of Pore Structure and Permeability of Rocks Under Hydrothermal Conditions.....	238
Laboratory Constraints on the Stability of Petroleum at Elevated Temperatures: Implications for the Origin of Natural Gas.....	240
Using Comprehensive Two-Dimensional Gas Chromatography to the Explore the Geochemistry of the Santa Barbara Oil Seeps.....	242
<b>WRIGHT STATE UNIVERSITY .....</b>	<b>244</b>
Fluid Chemistry, Surface Chemistry and Fracture Mechanics: An Investigation of the Connection at the Nanoscale.....	244
<b>UNIVERSITY OF WYOMING.....</b>	<b>247</b>
Waveguide Scanning Photocurrent Microscopy (WaSPM): A New Molecular Imaging and Characterization Tool.....	247
Redox Interaction of Cytochromes and Bacteria with Oxide Surfaces: Probing Redox-Linked Conformation Change.....	249
<b>YALE UNIVERSITY .....</b>	<b>251</b>
Freezing in Porous Media: Phase Behavior, Dynamics and Transport Phenomena.....	251
Plants, Weathering, and the Evolution of Atmospheric Carbon Dioxide and Oxygen.....	253
Code and Documentation Release for Fluid-Rock Interaction Models .....	254
<b>DOE/OBES GEOSCIENCES RESEARCH: HISTORICAL BUDGET SUMMARY .....</b>	<b>255</b>

## FORWARD

The Department of Energy's research provides a foundation of fundamental knowledge in areas relevant to the Department's missions, and this is particularly true in the area of Geosciences, which has applied programs in multiple offices. The research support also maintains our stewardship for geosciences research capabilities at the DOE National Laboratories. Excellent fundamental science that can improve and support DOE's mission needs also provides basic understanding applicable to many other areas of Earth science beyond DOE's borders. The Geosciences Research Program resides within the Division of Chemical Sciences, Geosciences and Biosciences, part of the Office of Basic Energy Sciences of the Office of Science. The participants in this program include researchers at Department of Energy laboratories and academic institutions. These activities are formalized by a contract or grant between the Department of Energy and the organization performing the work, providing funds for salaries, equipment, research materials, and overhead. Collaborative work among these institutions is encouraged. The summaries in this document, prepared by the investigators, describe the scope of the individual projects. The Geosciences Research Program includes research in the two broad areas of geophysics and geochemistry. Particular focus areas of interest include rock physics, flow and transport of geologic fluids through porous and fractured media, analytical geochemistry and experimental and theoretical geochemistry. The research is foundational to progress in the Department of Energy's long-range technological needs. Because of the variety of the research needs in the different applied DOE programs, fundamental approaches with multiple potential applications are favored. The Office of Basic Energy Sciences has recently completed a series of Basic Research Needs workshops including one entitled Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems. All of the workshop reports can be downloaded from the BES website. Further information on the Geosciences Research Program, including recent program activities and highlights, may be found on the Geosciences Programs home page at: <http://www.sc.doe.gov/production/bes/geo/geohome.html>.

## THE GEOSCIENCES RESEARCH PROGRAM IN THE OFFICE OF BASIC ENERGY SCIENCES

The Geosciences Research Program is directed by the Department of Energy's (DOE's) Office of Science (SC) through its Office of Basic Energy Sciences (OBES). The Geosciences Research Program emphasizes research leading to fundamental understanding of Earth's natural processes and properties that will advance the forefront of scientific knowledge, as well as help solve geosciences-related problems in multiple DOE mission areas. Activities in the Geosciences Research Program are directed toward building the long-term fundamental knowledge base necessary to provide for energy technologies of the future. Future energy technologies and their individual roles in satisfying the nation's energy needs cannot be easily predicted. It is clear, however, that these future energy technologies will involve consumption of energy and mineral resources and generation of technological wastes. The Earth is a source for energy and mineral resources, and is also the host for wastes generated by technological enterprise. Viable energy technologies for the future must contribute to a national energy enterprise that is efficient, economical, and environmentally sound.

The Geosciences Research Program is divided into two broad categories, *Geophysics* and *Geochemistry*.

***Geophysics***: This sub-area focuses on innovative and improved approaches to interrogating the physical properties of Earth's crust through better collection and analysis of rock physics, seismic, and electromagnetic data and improving understanding of geophysical signatures of fluids and fluid-bearing reservoirs.

***Geochemistry***: This sub-area focuses on innovative and improved ways to interrogate the chemical properties of the Earth's crust through investigations of mineral-fluid interactions and studies of rates and mechanisms of reactions at the atomistic/molecular scale; studying coupled flow and reactivity in porous and fractured rocks; and tracking of mineral-mineral and mineral-fluid processes using isotopes.

The Geosciences Research Program evolves with time and progress in these and related fields. Individual research projects supported by this program at DOE national laboratories, academic institutions, research centers, and other federal agencies typically have components in more than one of the categories or subcategories listed. In addition, it is common for research activities to involve a high level of collaboration between investigators and different institutions. Cross-cutting issues include: improving understanding of basic properties of rocks, minerals, and fluids; determining physical, chemical, and mechanical properties of multi-phase, heterogeneous, anisotropic systems; improving analysis of rock deformation, flow, fracture, and failure, and characterization of fluid transport properties of large-scale geologic structures. Research progress, in addition, will be based on developing advanced analytical instrumentation and computational methods, including: higher-resolution geophysical imaging and inversion tools, angstrom-scale resolution analysis of heterogeneous minerals with x-ray and neutron methods, and advancing computational modeling and algorithm development.

## PART I: ON-SITE

### ARGONNE NATIONAL LABORATORY

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### Mineral-Fluid Interactions: Synchrotron Radiation Studies at the Advanced Photon Source

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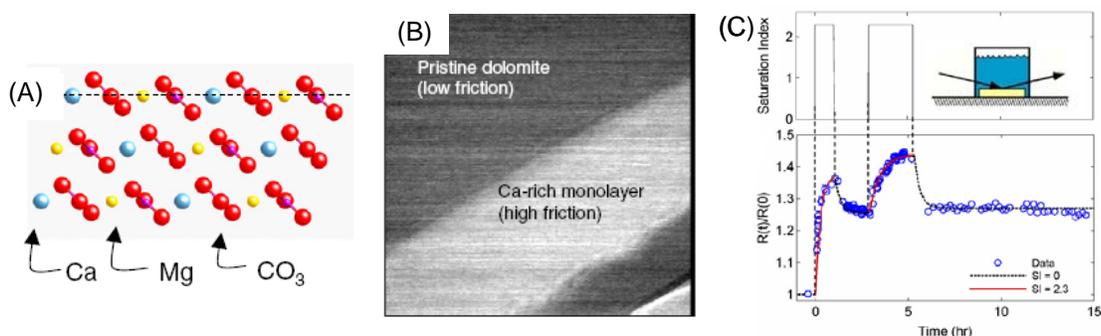
**Objectives:** The objective of this program is to advance the basic understanding of rock-fluid and soil-fluid interactions through experimental studies on atomic-scale processes at mineral-fluid interfaces. This is crucial to establishing the relation between atomic-scale processes and macroscopic geochemical transport in natural systems.

**Project Description:** The principle approach is to observe single-crystal mineral surfaces *in situ* during chemically controlled reactions with fluids using high brilliance synchrotron radiation. Experimental techniques include high resolution X-ray scattering (X-ray reflectivity, x-ray standing waves, resonant anomalous X-ray reflectivity) as well as X-ray absorption spectroscopy. Phenomena of interest include mineral-water interface structure, adsorption/desorption of ions and organic molecules, dissolution, precipitation and growth. Experiments are performed on common rock- and soil-forming minerals under conditions representative of geochemical environments near Earth's surface. A fundamental understanding of the molecular-scale processes is obtained through direct observations of interfaces before, during and after reaction.

**Results:** Recent research focused on two general areas of mineral-water interface reactivity: (1) advances in observing mineral-water interface reactivity with  $\sim\text{\AA}$ -resolution, including growth, ion adsorption and interfacial hydration, and (2) advances in analysis of X-ray based interfacial techniques. Observations of dolomite surfaces in contact with saturated and supersaturated solutions led to new insights into the "dolomite problem" (i.e., the apparent inability of dolomite to precipitate). The results showed that dolomite readily reacted with supersaturated solutions, but that the reaction was self-limiting and partially irreversible. The surface was terminated by a two-layer thick compositionally altered layer,  $\text{Ca}_x\text{Mg}_{1-x}(\text{CO}_3)_2$  film with  $x\sim 3/4$  when in contact with a super-saturated solution. The surface exposed to a saturated solution was found to have a distinct termination depending on whether it was freshly cleaved or previously exposed to the supersaturated solution illustrating that the reactions are partially irreversible.

Measurements of hematite (012)-water interfaces revealed a distinct interfacial hydration structure suggesting that the hydration structure is laterally-ordered. This structure was also similar to that observed previously for the alumina (012)-water interface. The technique of X-ray standing waves was used to image the adsorption site distribution of arsenate on hematite (012). These results confirmed previous studies concluding that  $\text{AsO}_4$  adsorbs primarily in a bridging bidentate adsorption geometry to singly coordinated surface oxygen sites. The results also revealed two coexisting but inequivalent terminations of the hematite (012) surface, each with equivalent adsorption affinity for  $\text{AsO}_4$  adsorption and with an equivalent local adsorption geometry.

We also demonstrated a formalism that images interfacial ion distributions without the need to fit data to specific structural models. This “model-independent” imaging approach makes use of the inherent phase sensitivity of resonant anomalous X-ray reflectivity (RAXR). Each RAXR spectra (i.e., reflectivity vs. photon energy) is used to obtain an amplitude,  $A(Q)$ , and phase,  $P(Q)$ , of the element-specific partial density profile at a particular momentum transfer,  $Q$ . The elemental profile is then recovered by simple Fourier transformation:  $\rho(z) = Z/(2\pi A_{\text{uc}}) \sum A(Q) \cos[2\pi P(Q) - Qz] \Delta Q$ , where  $Z$  is the atomic number of the resonant atom,  $A_{\text{uc}}$  is the surface unit cell area,  $z$  is the distance with respect to the surface plane, and  $\Delta Q$  is the spacing between RAXR spectra.



**Figure:** (A) Schematic side view of the dolomite (104) surface. (B) Lateral-force microscopy image of a dolomite surface with pristine and reacted regions, imaged during reaction. The reaction effectively stops when the surface is coated by the reaction product. (C) Real-time X-ray reflectivity data of dolomite in saturated and supersaturated solutions, showing the reaction kinetics, the self-limiting reaction and the irreversibility with respect to the pristine surface,  $R(t)/R(0) = 1$ .

## IDAHO NATIONAL LABORATORY

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### **Pathways for Redox Transformation of Semiconducting Minerals: The Iron Oxides**

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**Objectives:** This project aims to: 1) Determine chemical mechanisms for dissolution of specific surfaces of common electrically semiconducting minerals such as the iron oxides, 2) Establish linkages to overall macroscopic dissolution behavior, in particular for chemically and morphologically complex surfaces commensurate with those found in nature, and 3) Develop and apply analytical methods for quantifying complex surface morphologies in microscopic image data, and computational molecular methods for simulating dissolution dynamics of complex mineral surfaces.

**Project Description:** This project is a closely-coupled experimental and computer modeling study that focuses on characterizing the chemical pathways involved in the dissolution of iron oxide minerals. In particular, this project emphasizes understanding the dynamics from initial well-defined surfaces to advanced stages of dissolution, and in linking this understanding to macroscopic behavior. This project fills gaps in knowledge of the dissolution rates and mechanisms for specific crystallographic surfaces where such information is typically only assumed. Mechanisms of iron oxide dissolution in particular entail a possible role for solid-state charge migration affecting the rate of growth and the resulting morphology of dissolution and growth features. This project relies primarily on surface-specific scanning probe microscopic observations and surface spectroscopic characterization in conjunction with molecular dynamics simulations, electronic structure calculations, and kinetic Monte Carlo simulations to help identify key mechanistic processes.

**Results:** Kinetic Monte Carlo models initially developed during the first cycle of funding for this project under the title of “Multi-resolution structure and reactivity of kinetically roughened oxide surfaces: Nanometric scaling behavior and molecular scale controls.” continued to be adapted for application to the dissolution and solid-state transformation of iron oxide minerals. The Monte Carlo algorithm is based on the classification of discrete events according to their rates. A relatively small number of classes (typically 20-30) allow events that have a very wide distribution of rates to be selected with the correct probability and with a high acceptance probability. As a result, the kinetic Monte Carlo algorithm is much faster than earlier algorithms that were used to simulate similar process if the system size is large and the range of rate constants is large. Kinetic Monte Carlo simulations of the dissolution and solid-state transformation of iron oxides will be based on the mechanisms and rates determined experimentally and by *ab initio* (density functional theory) calculations and molecular dynamics simulations by the PI (Kevin Rosso) and his collaborators at the Pacific Northwest National Laboratory. A manuscript describing the kinetic Monte Carlo algorithm and some of its applications is nearing completion.

## LAWRENCE BERKELEY NATIONAL LABORATORY

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### Upgrade of the Computational Cluster at LBNL

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**Objectives:** Provide advanced computational capability in geophysics and geochemistry to address needs in subsurface imaging using seismic and electromagnetic wavefields and complex geochemical modeling. Address critical needs within the DOE mission, including waste legacy issues and energy and environmental security, which are difficult to address with existing computational facilities.

**Project Description:** Establish a state-of-the-art cluster technology at LBNL that uses advanced message transfer in a parallel fashion between the multi-processor nodes that optimizes load balance between processor speed, memory allocation and data transfer.

**Results:** A 256 processor DELL cluster has been expanded to 512 processors at Lawrence Berkeley National Laboratory (LBNL) Earth Sciences Division. The original cluster was assembled through a joint collaborative effort between LBNL's Scientific Cluster Support (SCS) Division, Dell and the National Center for Supercomputing Applications (NCSA) University of Illinois Urbana. The expansion allows researchers at LBNL in Geochemistry to address fundamental computational problems in a variety of geochemical applications. Sustained performance of the new cluster on large-scale geophysical inverse modeling codes, and geochemical analysis using all 512 processors, is commensurate with other similar cluster platforms within the DOE complex, such as Pacific Northwest Laboratory (PNL) Molecular Science Computing Facility - MPP2. Its 3.7 Tflop performance places this computer well within the "top 500 list" in the world. Scaling tests on the new cluster also show excellent scaling, as time to solution decreases in direct proportion to the number of processors employed for a given problem. The scientific benefit of the new cluster will be employed in the advancement of subsurface science using new geophysical imaging technologies. With dedicated and sufficient computing power these imaging technologies will now offer a great benefit to understanding 3-D complex subsurface processes at an unparalleled level of resolution and accuracy and directly impact BES Geosciences missions in Energy and Environment, including its programs in BER, fossil, geothermal energy, nuclear waste disposal and environmental site characterization and clean up.

### Integrated Isotopic Studies of Geochemical Processes

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**Objectives:** Combine high-precision measurements of isotopic ratios in natural materials with mathematical models and laboratory experiments to understand the nature and time scales of geochemical transport processes.

**Project Description:** Geochemical processes are studied using measurements of isotope ratios and trace element concentrations in natural materials and laboratory experiment products. Funding also supports laboratory operations for the Center for Isotope Geochemistry, which includes mass spectrometry labs for the measurement of isotopic ratios of solid radiogenic elements (Sr, Nd, Pb, Ca, U, etc.), light stable isotopes (O, C, H, Li, N, S, Ca, Fe, etc.), and noble gases (He, Ne, Ar, Kr, Xe). Measurements of isotope ratios in natural systems are used to measure the influence of competing chemical and physical processes, and to determine their rates and evolution with time. This information is critical for understanding the workings of geological systems ranging in size from microorganisms, plants, and soils, to groundwater reservoirs, volcanoes, the oceans, and the atmosphere. Our aim is to advance the state of the art of the isotopic approaches, and to use these advances to investigate fundamental issues in geochemistry. Mathematical models are developed to help extend the application of isotopic measurements. Modeling and systematic measurements of simple natural systems are supplemented by efforts to improve sampling methodologies and measurement techniques.

**Results:** (1) *U-Th-He:* We have demonstrated that U–Th/<sup>4</sup>He ages can be obtained from relatively U-poor olivine phenocrysts from late Quaternary basalts. The approach employs abrasion to remove the outer rinds of olivine crystals, which addresses problems with <sup>4</sup>He implantation from U-rich groundmass, and a specially designed extraction system that allows U, Th and He concentrations and isotopic compositions to be measured on the same olivine grains. The success of this method indicates that we have a good understanding of the nuclear processes and transport properties in olivine crystals, and suggests that we have a substantial new tool for understanding the rates of geological processes. New measurements of ca. 100 ka basalts have been directly compared with Ar-Ar ages and show that U-Th-He may provide more reliable ages for basalts of this age.

(2) *Ca isotope fractionation probe of mineral precipitation processes:* The mechanisms by which dissolved ions are attached to mineral surfaces to allow solid crystals to grow from aqueous solution are poorly characterized even for familiar minerals. We study the processes at mineral surfaces using isotopes, an approach based on chemical differences between isotopic species - their mobility in solution, rates of attachment and detachment from mineral surfaces, and thermodynamic affinity in different chemical bonding environments. We have shown that at equilibrium there is no Ca isotopic fractionation during precipitation of calcite. Because the equilibrium fractionation is near zero for Ca, the finite isotopic fractionations observed are entirely dependent on processes at the mineral-water interface. Recent results indicate that Ca isotope fractionation can be modeled assuming that isotope-dependent attachment kinetics are the primary cause. Measurements of natural soils and saline lake sediments also show that kinetic isotope fractionation occurs during dessication events with durations of days to weeks.

(3) *Retardation of calcite dissolution by clay and organic material:* We have investigated the Sr and Ca isotopic composition of pore fluids in sediments that consist of mixtures of biogenic calcite, clay and 1 to 5% organic carbon. In these sediments, even though the biogenic calcite is generally unstable, the isotopic composition of the pore fluids indicates that there is virtually no calcite dissolution over millions of years. This contrasts with sediments that are nearly pure biogenic calcite, in which calcite dissolves and re-precipitates at rates of  $10^{-5}$  to  $10^{-8}$  yr<sup>-1</sup> depending on age. The cause of this nearly

complete suppression of calcite dissolution is not known, but the strong association of clay + organic material suggests that the surfaces of the calcite crystals are modified. The effects may have implications for geologic carbon sequestration and for reconstruction of past climate changes from sedimentary records.

(4) *U-series alpha-recoil as a nanoscale probe of natural systems*: Our studies of ( $^{234}\text{U}/^{238}\text{U}$ ) of fine-grained marine sediments show systematic effects suggesting that  $\alpha$ -recoil associated with the decay of  $^{238}\text{U}$  is primarily responsible for  $^{234}\text{U}$  depletions in minerals. Because the rate of  $^{234}\text{U}$  loss reflects the scale of recoil, which is 30-50 nm, and the shape and surface properties of mineral grains, the U-series characteristics of minerals constitutes a nanoscale probe of mineral surfaces. The rate of this process in natural systems also affects the interpretation of most U-series data from fluids. Models for quantifying the  $\alpha$ -recoil loss fraction based on theoretical estimates of recoil range, mineral grain geometry, surface area constraints, and chemical methods have been developed. We continue to build a data set for size –separated granitic sediment grains in the range of a few microns to ca. 50  $\mu\text{m}$ . The U series effects complement other measurements of grain surface area and give additional information on surface roughness and dissolution rates.

(5) *Collaborative studies*: We also work with other BES investigators on isotopic fractionation due to diffusion in aqueous fluids and silicate liquids, and in modeling isotopic effects using numerical reactive transport codes. The diffusion studies have the dual objective of characterizing the isotopic effects for application to natural geochemical processes, and using them to understand the chemical structure of the fluids and melts. The modeling studies relate isotopic effects to models of mineral reaction kinetics, in order to allow isotopic measurements to be used as monitors of chemical reactions in nature.

## Physicochemical Controls on Unsaturated Flow and Transport in Geological Media

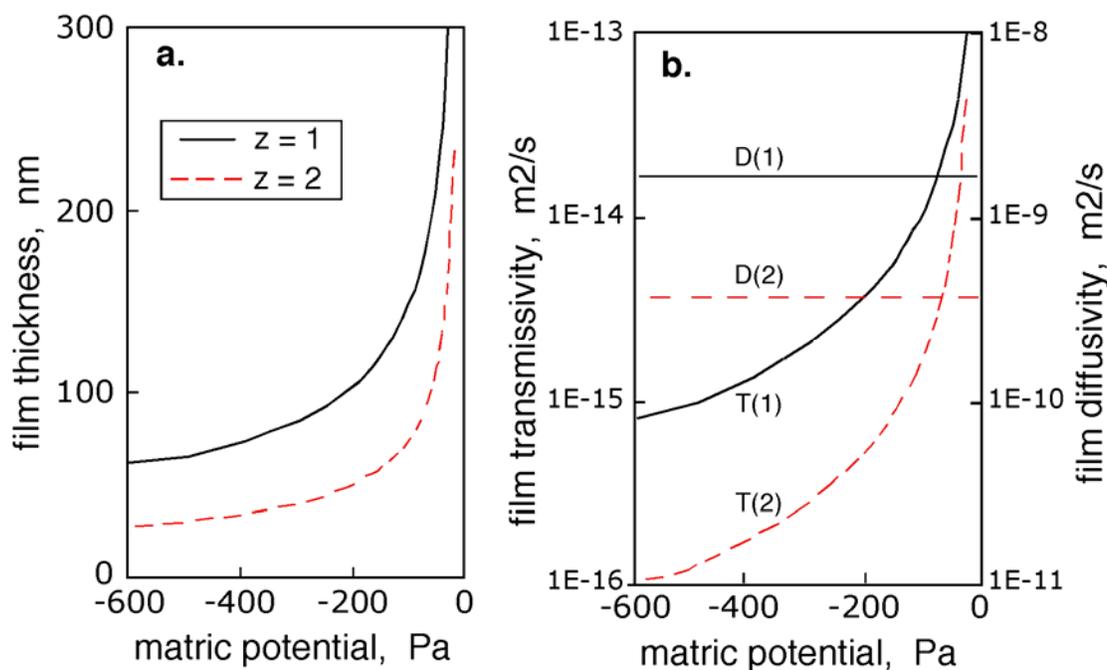
Tetsu K. Tokunaga, 510/486-7176, [tktokunaga@lbl.gov](mailto:tktokunaga@lbl.gov)

**Objectives**: The flow of water and transport of chemicals through soils and deeper partially saturated geologic formations is strongly dependent on the water content (saturation), with flow and transport rates at low saturation levels controlled by properties of water films. However, some basic properties of water films in unsaturated media remain poorly understood. Two environmentally important characteristics being investigated in this study are the film thicknesses dependence on capillary (matric) potential, and possible dependence on major ion chemistry.

**Project Description**: Matric (capillary) potentials of water films coating mineral surfaces are being controlled in a small suction plate chamber by equilibration with aqueous solutions under regulated sub-atmospheric pressures. The Kapton-windowed chamber is placed in front of an X-ray beam (National Synchrotron Light Source X26A, and Advanced Photon Source 13-ID-C) used to determine film thicknesses through X-ray fluorescence of monovalent ( $\text{Rb}^+$  and  $\text{Br}^-$ ) and divalent ( $\text{Mg}^{2+}$  and  $\text{SeO}_4^{2-}$ ) ion tracers in the water films. These hard X-ray synchrotron sources are necessary for efficient X-ray fluorescence monitoring of ionic tracers in water films within sealed environmental control chambers. The measurements on flat mineral surfaces are providing information on limiting conditions for unsaturated flow and transport, and also test various equilibrium models for adsorbed water film thickness. The experiments on microscopically rough surfaces, including natural fracture surfaces, are testing capillary film flow models.

**Results:** Using aqueous solutions of RbBr and MgSeO<sub>4</sub> (300 mM in each case), film thickness standards were prepared by evaporating these salts on filter paper and tested at NSLS X26A and GSECARS 13-ID-C. A linear X-ray fluorescence response was measured on calibration samples (Rb<sup>+</sup>, Br<sup>-</sup>, and SeO<sub>4</sub><sup>2-</sup>), with an equivalent film thickness detection limit of about 5 nm. Our redesigned version of the film cell is constructed from an aluminum block in order to eliminate background Br fluorescence from plastic parts, and can be used to equilibrate and obtain measurements on two different samples in tandem. The most recent experiments have focused on aqueous film measurements on flat quartz glass surfaces and roughened (10 μm root mean-square roughness) glass, at very near-zero matric potentials. The ionic strength and ion valence dependence of film thicknesses is being determined through comparisons of systems containing RbBr versus MgSeO<sub>4</sub> solutions. These measurements indicate that saline (I = 0.3 to 1.2 M) water films at near-zero matric potential have thicknesses in the range of only 10 to 100 nm. Such thin saline films are predicted to have extremely low transmissivities (volumetric flux per wetted width, at unit hydraulic gradient), on the order of 10<sup>-15</sup> m<sup>2</sup> s<sup>-1</sup> and less. In the opposite limit of films of very dilute aqueous solutions (the Langmuir limit), we have shown that their thicknesses and transmissivities at near-zero matric potentials are much greater, and capable of supporting significant advective transport. Finally, we have recently shown that Langmuir water films have the unusual characteristic of a constant hydraulic diffusivity, independent of film thickness (Figure 1).

Water films in the range of tens to hundreds of nm thickness are common in unsaturated soils and rocks, yet have previously been inaccessible to direct measurements, even by synchrotron X-ray microtomography. This new approach is allowing direct quantification of unsaturated transport properties within water films under environmentally relevant conditions, including physicochemical influences on unsaturated hydraulic properties. It is particularly useful for measurements of area-averaged (nominally 1 mm<sup>2</sup>) film hydraulic properties on natural, rough surfaces.



**Figure 1.** Water film characteristics at low ionic strength (Langmuir-limit), at near-zero matric potentials. (a.) Water film thicknesses for dilute 1:1 ( $z = 1$ ), and 2:2 ( $z = 2$ ) solutions. (b.) Water film transmissivities and hydraulic diffusivities.

## Clay Mineral Surface Geochemistry

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**Objectives:** The overall objective of this project is to investigate the properties of clay mineral nanoparticles at molecular scales using computer simulation methods. Current research focused on *ab initio* quantum mechanical calculations of the photochemical properties of layer type MnO<sub>2</sub> nanoparticles, which are of great importance both to the development of new materials for technological applications and to the understanding of Mn biogeochemical cycling.

**Project Description:** Manganese(IV) oxides are known to impact a broad range of biogeochemical processes, mainly through their high capacity for metal cation sorption and their facile oxidation of organic and inorganic compounds. An important structural characteristic of these oxides is the presence of Mn(IV) cation vacancies whose charge deficit is typically compensated by metal cations or protons. These vacancies have long been identified as strong adsorption sites for metals, but they may also play an important role in Mn redox biogeochemistry, particularly photo-induced redox reactions. Because detailed electronic band structure is the key to understanding photo-induced redox reactions, Mn(IV) oxides were investigated using *ab initio* quantum mechanics as realized in the code, CASTEP, which is implemented on the massively-parallel supercomputing platforms of the National Energy Research Scientific Computing Center.

**Results:** We investigated MnO<sub>2</sub> both vacancy-free and containing cation vacancies compensated by protons. Our band structure calculations showed that a Mn(IV) vacancy reduces the band gap energy (Figure 1a) and separates photo-excited electrons and holes (Figure 1b). A reduction in band-gap energy generates more pairs of electrons and holes upon illumination, and the distinct separation of charge carriers enhances their transfer before loss by recombination. Therefore, Mn(IV) vacancies enhance effectively the photoconductivity of layer type MnO<sub>2</sub>, facilitating photo-redox reactions between the mineral and inorganic or organic compounds.

Layer type Mn(IV) oxide nanoparticles found in weathering environments and natural waters are produced mainly by bacteria. The structures of these nanoparticles, which contain up to 16 % cation vacancies, are the topic of active experimental and theoretical research to determine if they can serve as design templates for new materials in energy technology. In fact, recent studies in materials science indicate that synthetic layer type Mn(IV) oxide nanoparticles with cation vacancies like those found in the biogenic MnO<sub>2</sub> minerals are semiconductors that produce photocurrent under visible light stimulation, thus making them very attractive for applications in energy storage, solar cell fabrication, and catalysis. Our prediction of substantial band gap energy reduction by cation vacancies indicates that photocurrent production by layer type MnO<sub>2</sub> nanoparticles can be optimized by control of vacancy concentrations during laboratory synthesis.

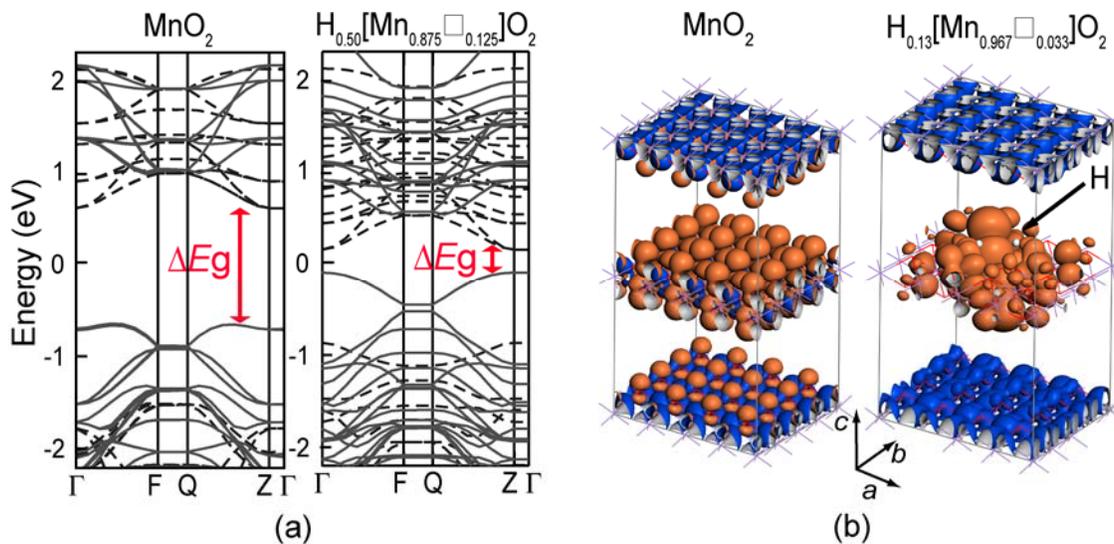


Figure 1. Calculated electronic properties of vacancy-free  $\text{MnO}_2$  (left) and  $\text{MnO}_2$  containing either 12.5 or 3.3 % Mn(IV) vacancies charge-compensated by protons (right). (a) Band structures, showing reduction of the band gap energy ( $\Delta E_g$ , denoted by a red double arrow) from 1.3 to 0.3 eV. (Solid lines denote bands for spin-up electrons while dashed lines denote bands for spin-down electrons.) (b) Charge distributions for valence-band maximum hole states (orange) and conduction-band minimum electron states (blue), showing that a cation vacancy compensated by protons (H) effectively separates photo-induced charge carriers against recombination.

## Rate Controls in Chemical Weathering: A Reactive Transport Approach

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**Objectives:** The objective of this project is to increase our understanding of the controls on reaction rates in natural porous media and to quantify the rates of precipitation and nucleation of important secondary mineral phases in soils and aquifers, a critical deficiency in current hydrogeochemical models. The present lack of understanding limits our ability to develop effective bioremediation schemes for contamination cleanup, to develop predictive models for  $\text{CO}_2$  sequestration in deep aquifers, and even to determine the fundamental controls on the rates of chemical weathering, an important long-term regulator of atmospheric  $\text{CO}_2$  levels.

**Project Description:** The project consists of two principal parts: 1) an experimental study of kaolinite dissolution and precipitation rates at  $22^\circ\text{C}$  conducted in well-mixed flow-through reactors, and 2) a study of porosity and permeability change in basaltic rocks due to chemical weathering and its effect on the rate and mechanism of weathering rind growth.

**Results:** Dissolution and precipitation rates of low defect Georgia kaolinite (KGa-1b) as a function of Gibbs free energy of reaction (or reaction affinity) were measured at  $22^\circ\text{C}$  and pH 4 in continuously stirred flow-through reactors. Steady state dissolution experiments showed slightly incongruent dissolution, with a Si/Al ratio of about 1.12 that is attributed to the re-adsorption of Al on to the kaolinite surface. No inhibition of the kaolinite dissolution rate was apparent when dissolved aluminum

was varied from 0 and 60  $\mu\text{M}$ . The relationship between dissolution rates and the reaction affinity can be described well by a Transition State Theory (TST) rate formulation with a Temkin coefficient of 2

$$R_{diss} \left( \frac{\text{mol}}{\text{m}^2\text{s}} \right) = 1.15 \times 10^{-13} \left[ 1 - \exp \left( \frac{-\Delta G}{2RT} \right) \right]$$

Stopping of flow in a close to equilibrium dissolution experiment yielded a solubility constant for kaolinite at 22°C of  $10^{7.57}$ .

Experiments on the precipitation kinetics of kaolinite showed a more complex behavior. One conducted using kaolinite seed that had previously undergone extensive dissolution under far from equilibrium conditions for 5 months showed a quasi-steady state precipitation rate for 105 hours that was compatible with the TST expression above. After this initial period, however, precipitation rates decreased by an order of magnitude, and like other precipitation experiments conducted at higher supersaturation and without kaolinite seed subjected to extensive prior dissolution, could not be described with the TST law. The initial quasi-steady state rate is interpreted as growth on activated sites created by the dissolution process, but this reversible growth mechanism could not be maintained once these sites were filled. Long-term precipitation rates showed a linear dependence on solution saturation state that is generally consistent with a two dimensional nucleation growth mechanism following the equation

$$R_{ppt} \left( \frac{\text{mol}}{\text{m}^2\text{s}} \right) = 3.38 \times 10^{-14} \exp \left[ -\frac{181776}{T^2 \ln \Omega} \right]$$

Further analysis using Synchrotron Scanning Transmission X-ray Microscopy (STXM) in Total Electron Yield (TEY) mode of the material from the precipitation experiments showed spectra for newly precipitated material compatible with kaolinite.

A combination of X-ray micro-computed tomography (CT), tracer diffusion experiments, and 3D diffusion modeling were used to examine changes in total and effective porosity and effective diffusion coefficients across a weathering interface in a weathered basalt clast from Costa Rica. A critical porosity of ~12%, below which changes in total porosity do not translate to changes in effective porosity, suggests that effective porosity is a more appropriate predictor than total porosity of transport parameters in low porosity systems. We propose a modification of Archie's Law to incorporate the effects of a critical or threshold porosity. To test the modified Archie's Law, diffusion experiments were performed on unweathered and weathered basalt. Additionally, 3D pore-networks were defined using the CT data by assigning tortuosity values to each grid cell based on the CT number and 3D numerical diffusion experiments were run for CT data ranging from 3% to 33% total porosity. The modified Archie's Law predicts effective diffusion coefficients from both numerical and physical diffusion experiments better than Archie's Law using total porosity and demonstrates the importance of evolving pore connectivity as a result of chemical weathering.

The similar computational approach was used with 3D reactive transport simulations to determine an effective or "upscaled" reactive surface area that incorporates the detailed geometry of the pore structure created as a result of weathering. These upscaled geometric reactive surface areas are about one order of magnitude lower than the physical (e.g., BET) surface areas.

## Nanoparticle Aggregation in Natural Aqueous Systems

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**Objectives:** Nanoscale oxide and oxyhydroxide minerals are commonly found in the natural environment, and play important roles in adsorbing and sequestering aqueous ions including nutrients such as phosphates and contaminants such as heavy metals. These materials are typically subjected to natural flocculation events upon formation that reduce the nanoparticle surface area that is accessible by aqueous ions. However, no quantitative studies have been performed addressing the impact of different aggregation processes on effective surface area. Our goal is to determine the nanoscale morphology of nanoparticle aggregates of iron oxyhydroxide nanoparticles, and assess the effects of different kinds of aggregation processes on metal uptake to the mineral surfaces.

**Project Description:** We synthesized a suspension of ~6 nm iron oxyhydroxide nanoparticles and subjected portions of this suspension to analogues of natural aggregation processes. These included: pH variation around the point of zero surface charge (simulating the neutralization of acid mine drainage); ionic strength elevation (simulating mixing of aquifer and brackish water); drying; and freezing. Following aggregation, three days of dialysis returned each sample to the initial control conditions (pH 5, 0.001 M ionic strength), without significant change in aggregation state. The effect of aggregation on metal ion uptake was then studied by exposing batches of aggregated and control samples to 0.5 mM  $\text{Cu}(\text{NO}_3)_2$  at pH 6.0 for 24 hours. These conditions were shown in previous pH-dependent uptake studies on non-aggregated nanoparticles to facilitate almost complete metal adsorption. Copper uptake results are given in Figure 1. The nanoscale morphologies of the (re)hydrated aggregates were studied with small-angle x-ray scattering (SAXS), shown in Figure 2.

**Results:** While all aggregation processes caused visual flocculation and settling, there were large quantitative differences in the impact on Cu uptake. Aggregation via pH or ionic strength variation caused a modest drop in uptake relative to non-aggregated nanoparticles, while freezing and drying processes resulted in significant reductions in uptake (Fig. 1). The SAXS data provide insight into aggregate morphology and permit the batch uptake experiments to be interpreted. Under aqueous conditions, the nanoparticles form open fractal-like networks, characterized by relatively low values of geometric fractal dimension (~ 1.4). By contrast, drying or freezing force the nanoparticles into densely packed clumps of porous material. We are using simulation techniques to generate representative morphologies of the aggregates, with examples shown in the insets to Figure 2.

These findings illustrate the diverse nanoporous structures that can be generated by natural nanoparticle aggregation processes. In particular, they highlight the important role of water in preserving hydrated channels among aggregated nanoparticles that are permeable to aqueous ions.

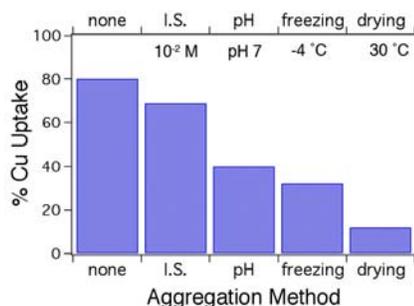


Figure 1. The proportion of  $\text{Cu}^{2+}(\text{aq.})$  adsorbed from solution onto  $\text{FeOOH}$  nanoparticles that were either fully suspended or aggregated via different mechanisms. I.S. = “ionic strength”.

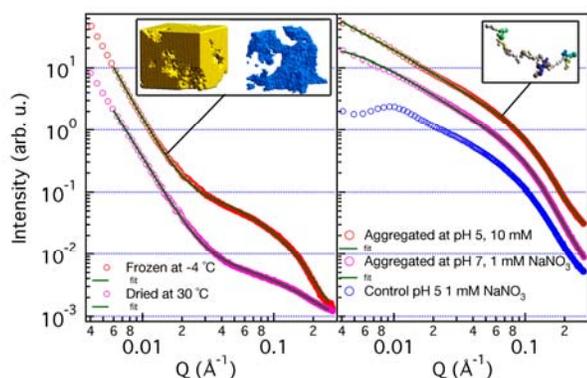


Figure 2. *In situ* small-angle x-ray scattering (SAXS) analysis of FeOOH nanoparticle aggregates in suspension (control), or aggregated. Fits to the experimental SAXS patterns permit representative aggregate morphologies to be generated (inset). Left inset: Pore structure of a compact nanoparticle aggregate generated by freezing. Brown = particle structure, blue = pore structure. Right inset: Structure of a fractal aggregate generated by increasing ionic strength.

## Molecular-Level Studies of Mineral-Water Interface Structure and Chemistry

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**Objectives:** We wish to define the specific molecular geometries of mineral surfaces equilibrated with aqueous solutions, including the nature of surface relaxations or reorganizations, the attachment sites and type of binding of sorbates, and the structure of interfacial water. This type of information is important for the testing of molecular reaction models and simulation techniques that model the sorption/desorption and incorporation of migrant species in natural fluids, and hence determine the fate and transport of both toxic and nutrient species in the environment.

**Project Description:** Our studies are done using a combination of molecular probes, largely synchrotron-based, with relatively simplified model systems. The chief synchrotron methods are: surface diffraction by which we can refine the position and occupation of surface atoms at an interface; surface x-ray spectroscopy by which we can obtain specific structural information about the local molecular environment of a sorbed molecule at an interface; and nonlinear optical spectroscopy whereby we can probe the infrared vibrational spectrum of water molecules only at the solid-aqueous solution interface. Variations on these techniques also yield specific information such as the redox state of surface atoms, or the lifetimes of particular surface species.

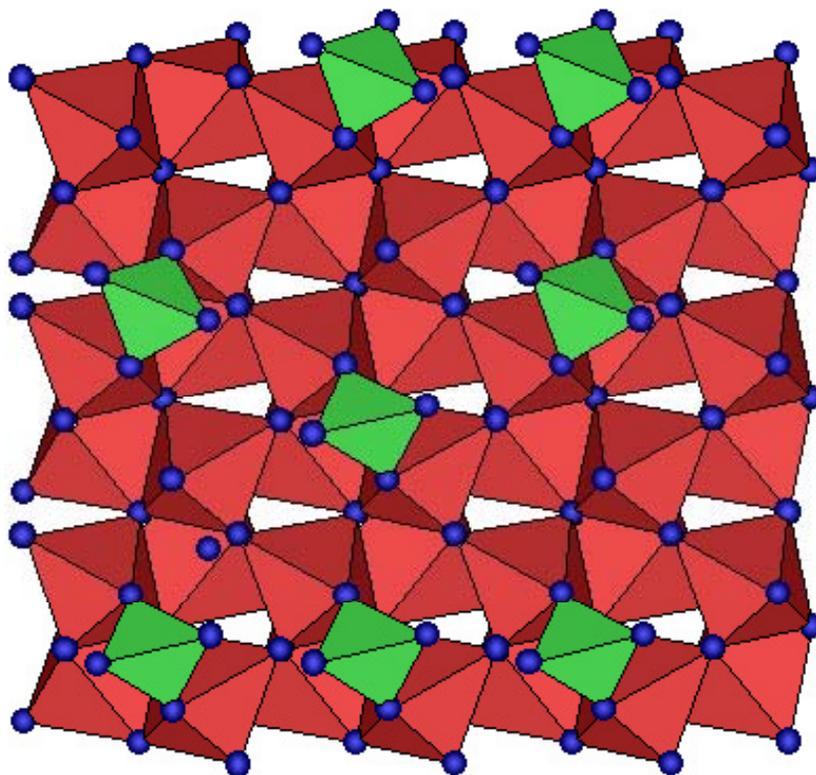


Figure 1. Geometry of sorbed silicate (green tetrahedral) on the R-plane (1-102) surface of hematite at 40% occupancy. At higher occupancy vertical silicate polymer chains are expected to form.

**Results:** Our most recent work focuses on the hematite, goethite, diaspore and corundum surfaces. For hematite we are interested in the surface variations produced by acids or bases, as well as the geometry of sorbed species like arsenate or silicate. Results have shown that the geometry of monomeric silicate sorption is as a bidentate complex with strong surface attachment. Molecular dynamic simulations and *ab initio* calculations are in progress to determine the relative stability of the experimentally deduced topology. For the goethite surface we found that the surface is relaxed from the bulk, but also has two distinct layers of ordered water at the termination. Analogous surface refinements are in progress for the aluminum-analog of goethite—diaspore. Our surface SFG water studies show that the pH point of zero charge (PZC) for clean corundum (0001) faces is ca. 6.3, rather than the ca. 9.0 measured for corundum powders. Continuing work suggests the differential is due to the types of Al hydroxyl sites exposed in powders. The silicate/hematite work is vital to an understanding of how the reactivity of natural Fe oxide surfaces changes in varied environments, and whether effective remediation approaches for particular pollutants are efficacious. The goethite and diaspore work are crucial to the application of surface complexation modeling with accurate molecular parametrization. For example, current models assume bulk-goethite like structure for the interface, which we show is not accurate. Further work will compare the interface structures and interface water of goethite and diaspore.

### How Does Nanoparticle Structure Control Interfacial Phenomena?

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Jillian F. Banfield (UC Berkeley)

**Objectives:** Our past work has shown that nanoparticles differ in structure and strain depending on their precise chemical environment. It is also anticipated that structure, strain and reactivity may change as a function of size. Our investigations aim to characterize possible differences in sorption mechanisms as a function of Fe oxyhydroxide (goethite and ferrihydrite) nanoparticle size, growth rate, and degree of aggregation.

**Project Description:** Our studies are done using a combination of molecular probes, bulk measurements, and thermodynamic measurements. Some of the analysis is done in concert with molecular dynamic simulations. For nanoparticle size and shape we employ small angle x-ray scattering (SAXS) and dynamic light scattering (DLS), while the specific molecular nature of surface species is determined with extended x-ray absorption fine structure spectroscopy (EXAFS). Other aspects of nanoparticle structure are determined via determination of pair correlation functions with high energy wide angle x-ray scattering (WAXS). The x-ray measurements are done at the APS (Advanced Photon Source) and SSRL (Stanford Synchrotron Radiation Laboratory) synchrotron sources.

**Results:** Most recent work has focused in two areas. 1) The nucleation and initial growth of nanoparticles on quartz and other single crystal surfaces have been studied as models for how natural surfaces become either activated or passivated by such nanoparticle development. We developed a grazing-incidence SAXS technique which allows examination *in situ* of the initial phases of nanoparticle growth under bulk water solution, the first time this has been accomplished. The technique has been used to study heterogeneously-nucleated iron oxyhydroxide nanoparticle formation on quartz as a function of solution ionic strength, iron concentration and temperature. We find very strong dependence of the early nanoparticle size and shape on ionic strength, and a changeover in growth mode as size increases. Surface features such as steps and terraces have an effect on nucleation at the earliest stages, with nucleation tending to occur on terraces near steps. After initial nucleation, secondary nucleation events occur on already nucleated particles, leading to a different growth topology. 2) The effect of different ligands on the structure of ZnS nanoparticles show well-defined regimes of behavior depending on the strength of the ligand-zinc bond. Strongly bound ligands like water have a dramatic effect on the surface, reducing strain throughout the nanoparticles, while weakly bound ligands like methanol allow considerable strain to persist post formation, creating a well-defined core-shell structure. Intermediate strength bound ligands show a weaker core-shell topology. These effects have now been studied by combined experimental measurements and MD simulations, with excellent agreement.

### **Imaging Electronic and Atomic Redistribution during Redox Reactions at Surfaces**

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**Objectives:** A number of important geochemical reactions are activated by electron transfer at mineral surfaces. Processes include reductive and oxidative dissolution, coupled redox-sorption of complexes, respiration of surface-associated biota, photoactivated reactions, and electrochemical cell reactions. Our research focuses on electron-transfer initiated dissolution reactions, which are important drivers for acid mine drainage development and pollutant transfer in the environment. The actual electron transfer is faster than can be studied by currently available means, but the series of succeeding relaxation steps can be probed to elucidate much of the reaction mechanism.

**Project Description:** In reductive dissolution electrons are transferred from solution species via shared surface ligands to surface metal ions, like Fe(III), producing surface Fe(II) species. The Fe(II)-O bonds at the surface must lengthen from this reaction, introducing surface vibrations and a general expansion of the surface. This localized strain may act to limit the numbers of Fe(II) that can be produced at the surface, depending on the rate of electron transfer within the mineral. We wish to measure the rate of Fe(II) buildup on Fe oxide surfaces and the ultimate concentration limit, as well as surface and bulk conduction rates. These processes are slower than electron transfer, but for investigation microsecond to picosecond time-resolution is necessary. We are conducting such experiments at the APS (and soon also at the ALS) starting with observations of Fe(II) creation from a photostimulated ligand attached to Fe oxide nanoparticles and single crystal surfaces. A femtosecond laser system activates electron transfer from the ligand, and the synchrotron x-rays detect the result at variable delay times after the excitation. This is a “pump-probe” experiment. Part of the project includes development of fast surface diffraction methods using new 2D pixel detectors, and custom designed software.

**Results:** Our first static experiments at the APS beamline 13ID showed proof of concept with respect to electron injection from the organic ligand alizarin red into the (1-102) hematite surface. A significant amount of surface Fe(II) (Figure 1) is produced within minutes of exposure to the dye. We observe the Fe(II) by collecting surface diffraction data via the (10L) crystal truncation rod. Collection of complete data sets will enable refinement of the electronic configuration of the excited hematite surface, and this process can be done as a function of time-delay to detect the time-progress of charge migration and relaxation. Our first time-resolved experiments at the APS beamline 11-ID showed measurable Fe(II) creation in 2 nm maghemite particles with eosin Y surface ligands with a time delay of 154 nanoseconds, but no similar effect using alizarin red. In these experiments the nanoparticles were studied in a continuously refreshed slurry, and the near Fe K-edge x-ray absorption spectra was collected.

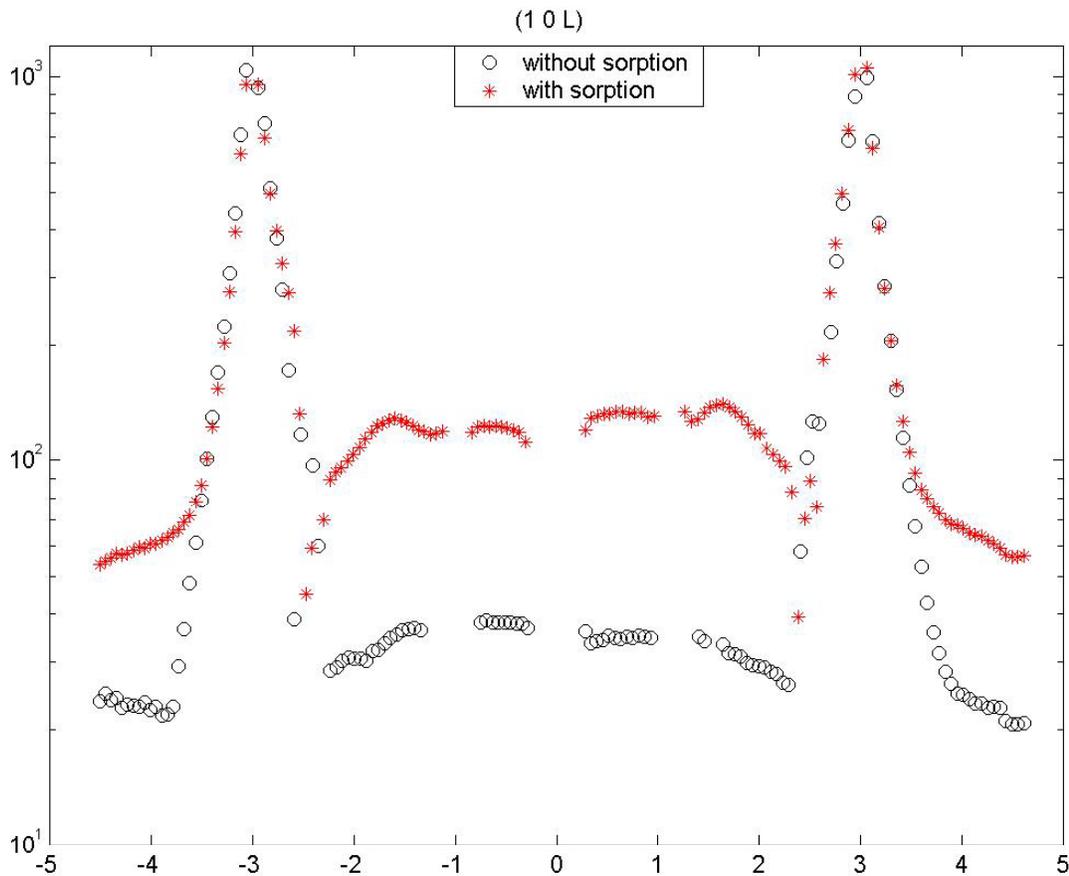


Figure 1. (10L) crystal truncation rod measured for the bare hematite (1-102) surface without alizarin red sorption (circles), and after 10 minute exposure to alizarin red solution in ambient light (red asterisks). The features at  $L=-1.6, 1.6$  are due to surface Fe(II). Collected at GSECARS sector 13 APS using 2D Pilatus pixel detector system.

The static results with large single crystal hematite surfaces suggest that significant concentrations of Fe(II) are stable for long time periods, but that control of the injection process may be difficult. The time-resolved nanoparticle results show that varied ligands can have much different injection probability, and that beam damage (either from laser or x-rays) may have a significant effect on nanoparticle structure or chemistry. Both issues are being investigated in the next series of experiments.

## Development of Isotope Techniques for Reservoir and Aquifer Characterization

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**Objectives:** This project develops geochemical and isotope techniques for reservoir and aquifer characterization in support of CO<sub>2</sub> geologic sequestration studies and measurement of groundwater ages. Two projects constitute the main focus of our research: (1) the development of isotope tracers to study and quantify water-CO<sub>2</sub> interaction along a flow path as part of planned CO<sub>2</sub> pilot injection tests and (2)

assisting in the evaluation, verification, and application of new isotopic techniques for placing time constraints on groundwater flow.

**Project Description:** *Phase-Partitioning Tracers and CO<sub>2</sub>-Injection:*

The primary sites being considered for underground sequestration of anthropogenic CO<sub>2</sub> are active or depleted oil and gas reservoirs, deep aquifers, and underground coal beds. An important issue for gas transport in water-saturated zones is the amount of interstitial pore water, the extent of gas-water interaction and the chemical impact on the reservoir due to CO<sub>2</sub> injection. Modeling predicts that precisely measured details of a chromatographic separation profile for a suite of gases with different solubility would provide important information regarding the extent of gas-water interaction and provide an integrated gas/H<sub>2</sub>O volume ratio. Noble gases are well suited for chromatographic separation studies because they exhibit a smooth increase in solubility by a factor of ~10-15 from Ne to Xe and are chemically inert with very low concentrations in most rocks and minerals, minimizing the effects of potential water-rock interaction. During and after CO<sub>2</sub> injection, temporal and spatial changes in the isotopic compositions of various solutes (e.g. Ca, Sr, Pb, C, O) are expected to trace the occurrence and rates of mineral dissolution and precipitation driven by changes in the chemical attributes of the water-rock system as a result of CO<sub>2</sub> injection.

**Results:** *Isotope Tracers and CO<sub>2</sub>-Injection:*

Our initial work has focused on gas-water interaction using noble gases as phase-partitioning tracers. For proof of concept, a noble gas monitoring project was conducted as part of a CO<sub>2</sub> sequestration experiment in the Frio Formation in the Gulf Coast South Liberty Field, Texas in which noble gases along with other tracers were injected along with the CO<sub>2</sub> stream and monitored downstream. Although experimental difficulties in measuring Ne and Xe prevented us from taking full advantage of the wide disparity in solubility, significant differences in peak arrival times for Kr and SF<sub>6</sub> were observed, despite the close proximity of the monitoring and injection wells, which would act to minimize the anticipated chromatographic effect. From the difference in Kr and SF<sub>6</sub> peak arrival times and solubility, an inferred integrated aqueous phase saturations of ~32-45% was calculated. Preliminary results were presented at the Fourth Annual Conference on Carbon Capture and Sequestration. The pilot test demonstrated the utility of phase-partitioning tracers, such as noble gases, in defining reservoir environments and processes relevant to geologic sequestration of CO<sub>2</sub>. Currently we are formulating field projects in support of the SECARB and WESTCARB demonstration projects.

**Project Description:** *Groundwater Ages:*

Placing time constraints on recharge and flow of groundwater is an extremely important and difficult problem that affects a wide variety of geologic processes that are relevant to environmental issues, such as water resource management, CO<sub>2</sub> sequestration, waste management, and paleoclimate studies and subsurface water-rock reaction and transport rates. To address these and similar issues, reliable techniques for determining aquifer recharge rates and water residence ages are required.

**Results:** *Groundwater ages:*

In collaboration with Neil Sturchio, University of Illinois, Chicago and Dr. Zheng-Tian Lu, Physics Division, Argonne National Laboratory, radio-chlorine (<sup>36</sup>Cl) and radiogenic noble gases (<sup>4</sup>He and <sup>40</sup>Ar) were measured to assess the residence time of old groundwater in the Nubian Aquifer of the Western Desert of Egypt. A systematic increase in the amount of radiogenic <sup>4</sup>He that accumulated in the groundwater along the inferred flow path confirmed the age progression indicated by the <sup>36</sup>Cl/Cl ratios,

but a flux of external radiogenic  $^4\text{He}$  equivalent to  $\sim 3.5$  times the *in situ* production rate of the aquifer is required to reconcile the  $^4\text{He}$  accumulation ages with those determined from  $^{36}\text{Cl}$ . Furthermore, a divergence of the oldest sample ( $\sim 650$  kyr) from a linear trend between the  $^{36}\text{Cl}$  age and the amount of accumulated  $^4\text{He}$  suggests the external  $^4\text{He}$  flux is not constant along the entire flow path. We are expanding this line of research to include other radio-chronometers, such as  $^{81}\text{Kr}$ , by investigating old groundwater from aquifers of the mid-continental United States. An initial suite of samples collected from springs and wells predominately across Kansas and Missouri have analyzed and a second suite has been collected.

### **Kinetic Isotope Fractionation by Diffusion in Liquid**

*John N. Christensen, 510-486-6735, [jnchristensen@lbl.gov](mailto:jnchristensen@lbl.gov); Frank M. Richter (Univ. of Chicago), Ian D. Hutcheon and Ross W. Williams (LLNL)*

**Objectives:** Our research seeks to document and quantify kinetic isotope fractionation during chemical diffusion, and most recently thermal diffusion, in a variety of liquids ranging from silicate melts to water.

**Project Description:** Our experiments regarding diffusion of dissolved salts in water and other liquids (e.g. methanol) involve a simple diffusive system that acts as a Rayleigh fractionator. The system consists of a small spherical container that communicates via a small tube with a much larger volume in which it is immersed. We fill the spherical container with a solution of the dissolved salt of the element to be measured for kinetic effects, and allow diffusion to the larger volume of initially pure water. Different diffusive pairs are run for different length of times, after which the run products are measured for their isotopic composition by multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) (or other methods as appropriate). The resultant data from the experiments provides determinations of the relative diffusivities of elements or isotopes.

**Results:** In our previous research, we found no measurable diffusive isotopic fractionation of magnesium, but small but well-resolved isotopic fractionation of both Li and Cl. Molecular dynamics calculations by Ian Bourg and Garrison Sposito have reproduced our results. They suggest that the small isotopic fractionation we observed for diffusion in water compared to that in silicate melt, is related both to the number of water molecules in hydration spheres around the dissolved ions as well as the residence time of water in the inner hydration shell.

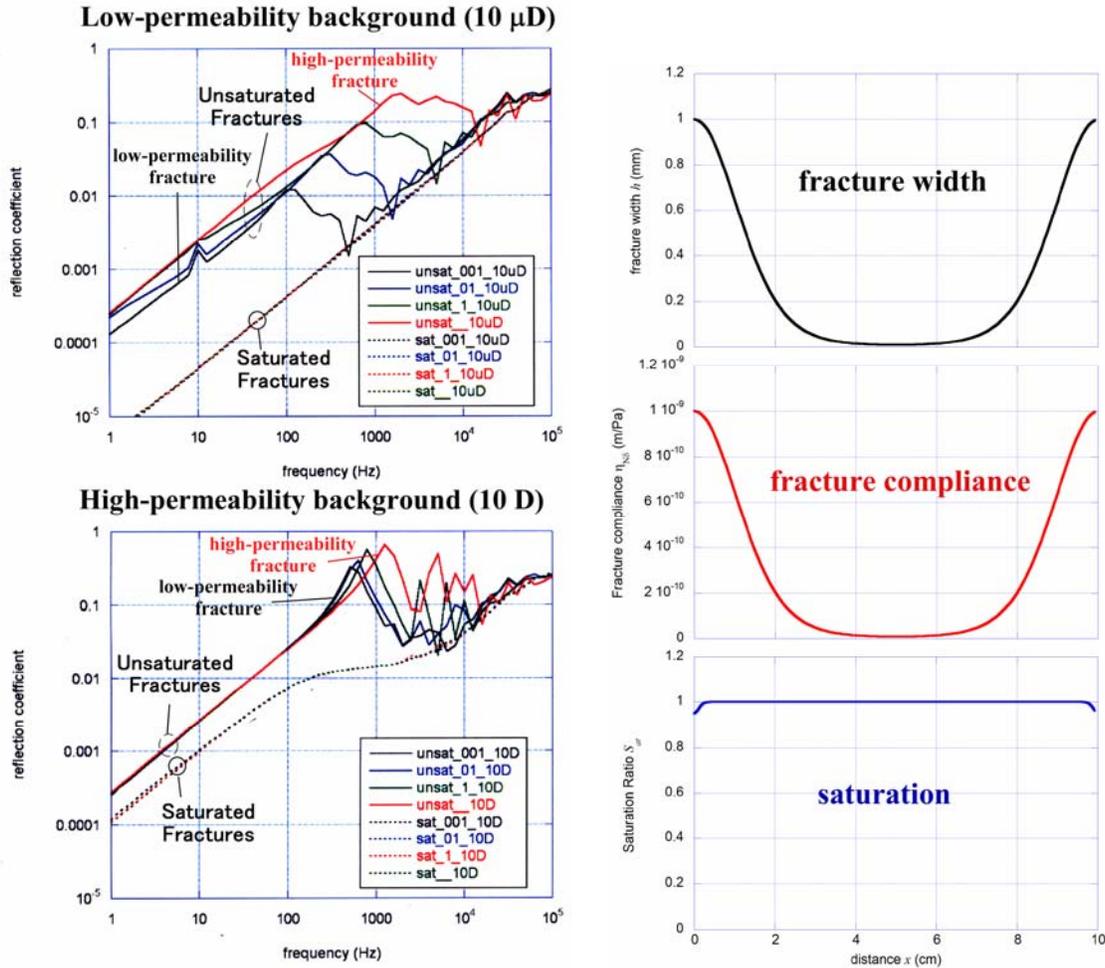
We have developed and refined a new technique using MC-ICPMS to measure the isotopic composition of K (i.e. the  $^{41}\text{K}/^{39}\text{K}$  ratio) to a precision of better than  $\pm 0.3$  ‰ ( $2\sigma$ ). Our measurements of experiments involving diffusion of K in water have demonstrated fractionation of the  $^{41}\text{K}/^{39}\text{K}$  ratio of up to  $\sim 8$  ‰ relative to the starting solution (Fig. 1). The data indicate a fractionation factor of  $0.99804 \pm 0.00055$ , representing the ratio ( $D^{41}\text{K}/D^{39}\text{K}$ ) of the relative diffusivities of  $^{41}\text{K}$  and  $^{39}\text{K}$  ions in water. This value is within error for our previously determined value for  $D^7\text{Li}/D^6\text{Li}$  ( $=0.99772 \pm 0.00026$ ), despite a smaller mass fraction difference for K, suggesting a greater fractionation effect for K compared to Li. This would be consistent with a lower charge density for the larger  $\text{K}^{1+}$  ion, and implies a shorter residence time for  $\text{H}_2\text{O}$  in the hydration sphere of  $\text{K}^{1+}$ . In diffusion experiments using methanol (a less polar solvent than water), we have found that Li diffuses faster than K, the opposite of what is observed for their relative diffusivities in water. Comparing K diffusion in water to diffusion in methanol we have



upon a fracture model for non-poroelastic media, by envisioning a fracture as a thin layer of poroelastic medium. This approach provides a set of boundary conditions relating the velocity and stress across a fracture as a function of mechanical and hydraulic properties. This model is further extended to examine how heterogeneous distributions of fracture and fluid properties along a fracture affect seismic wave scattering.

**Results:** During this reporting period, we first extended previously developed poroelastic seismic boundary conditions for a homogeneous fracture and derived conditions for a heterogeneous fracture. These new seismic boundary conditions were combined with a previously developed technique for computing seismic wave scattering by a heterogeneous, elastic fracture. The resulting new model allows us to compute seismic wave scattering by a heterogeneous, poroelastic fracture. Numerical models were developed for both one dimensional and two dimensional fractures with arbitrary distributions of fracture compliance, fracture opening, fluid properties (including saturation), and fracture permeability (although the model needs to be periodic at some length scale).

Using this model, we conducted a parametric study for the reflection amplitude of incident fast P-waves (in the Biot's sense), for a range of assumed but realistic fracture and fluid parameters (Figure 1). The results showed that 100%-water-saturated fractures do not exhibit significant dependence on the fracture permeability—the same result as a homogeneous fracture. However, including a very small amount of gas within a fracture dramatically increased the permeability-dependence of the scattering response as well as its frequency dependence. Further, we observed that the permeability of the background medium relative to the fracture also plays an important role in determining the permeability-dependent scattering of seismic waves.



**Figure 1.** Reflection coefficients (amplitudes) of normally incident fast P waves on an infinite, periodic 1D model fracture. Fracture width and compliance used in the computation are also shown for one cycle. The saturation profile applies only to the unsaturated cases. The dynamic permeability of the fracture was computed assuming a flat parallel channel, with a reduction factor varying from 1/1000 to 1.

## Propagation of Elastic Waves in Complex Media

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**Objectives:** The general objective is to perform fundamental research on elastic wave propagation in media with various types of heterogeneity and various scales of heterogeneity. The challenge is to develop computational methods that consistently account for the various types and scales of heterogeneity while retaining fidelity to the basic physics of the problem.

**Project Description:** At the smallest scale where the media is typically described in a statistical sense a dynamic composite medium approach will be used to model both the velocity and attenuation in a self-consistent manner for all frequencies. In order to treat the effects of large-aspect inclusions such as elongated pores or flattened cracks it will be necessary to derive the solution to the boundary value

problem for scattering of elastic waves by a spheroid. The Maslov integral approach will be used to treat wave propagation at the scales where the media can be described in a deterministic manner with a general three-dimensional model that includes both smoothly varying properties and discontinuities. Having developed and integrated these basic approaches, a number of extensions will be considered, guided by testing through application to realistic data sets.

**Results:** The effort during FY07 was concentrated on solving the boundary value problem for scattering of elastic waves by a spheroidal inclusion, which is an essential first step in the extension of the dynamic composite medium theory. The development of the theoretical solution in spheroidal coordinates was completed for both prolate and oblate spheroids and most of the computer coding of this solution was also completed. Exclusion rules that half the number of simultaneous equations to be solved were developed for the mode coupling problem that arises in all non-spherical scattering problems. These equations were treated with both LU and SVD decompositions and satisfactory numerical results were obtained with both approaches, although the LU method appears to be more efficient. The computer coding and numerical testing of the algorithms required to calculate the spheroidal eigenvalues and eigenfunctions were also nearly completed. The spheroidal solution was compared with the known spherical solution and the agreement was excellent, confirming the basic structure of the spheroidal solution and the convergence of the modal series. This first part of the research project was almost completed by the end of the year, with a few remaining tasks related to numerical testing of some special cases such as large aspect ratio and fluid inclusions.

### **Joint Three-Dimensional Electromagnetic-Seismic Imaging: A Structurally Based Approach**

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**Objectives:** Provide an enabling technology in subsurface imaging using seismic and electromagnetic wavefields, addressing critical needs within the DOE mission, including waste legacy issues and energy and environmental security, which are difficult to address with existing 3D geophysical imaging technologies.

**Project Description:** Establishing the precise relationship between electrical conductivity and seismic wave velocities and their interrelationships to fluid properties in 3D heterogeneous media (saturation, porosity and permeability) is of fundamental interest in subsurface science. Knowledge of such relationships could lead to a much better understanding of subsurface fluid, flow and transport, with critical implications for environmental site characterization and remediation, exploration for oil and gas and reservoir monitoring for safe sequestration of CO<sub>2</sub>. Correlations between electrical and seismic properties are increasingly observed at different scales in collocated experiments. For example, relevant data from multidimensional dc resistivity and seismic refraction investigations of the near surface have conventionally been inverted separately leading sometimes to unequivocal models. Joint inversion of such data is a better approach and allows for an objective testing of the resistivity-velocity and fluid property interrelationships on experimental data. The types of electromagnetic and seismic data to be considered include, controlled and natural source electromagnetic measurements and amplitude and travel time seismic data sets.

**Results:** This is a new project that has begun in October 2006. Nevertheless we have made some initial

progress. Because the grids used to simulate electromagnetic (EM) and seismic data are different, due to the methods differing resolving power, it makes sense to impose an independent grid for the joint imaging of the two types of data sets. While the underlying grids used to simulate the EM and seismic data will be distinct, grid-transfer operators need first to be developed to transfer predicted and observed data, cost functional and its gradients, from the forward modeling grids to the common inversion grid. We have now demonstrated this concept in the context of 3D controlled electromagnetic inversion and provides the framework to make joint 3D imaging practical. Without grid separation the meshing required for EM field simulation would need to exactly match the fine level of meshing dictated by the seismic data and geology, thereby producing enormous and impractical meshes for 3D EM field simulation.

## Permeability Dependence of Seismic Amplitudes

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**Objectives:** The goal of this research is to develop a quantitative understanding of what seismic attenuation is due to. Many attenuation mechanisms have been proposed over the years, but only a few recent models have both begun to predict attenuation levels consistent with field measurements in the seismic band (10 Hz to a few kHz) and been based on a realistic physical description of rocks. These models assume that rock contains “mesoscopic-scale” heterogeneity, which is defined as heterogeneity over scales larger than the grains, but smaller than the seismic wavelengths. When rocks containing mesoscopic structure are stressed, the more compliant parts of the rock respond with a larger fluid pressure change than the stiffer parts, which results in fluid flow and wave attenuation.

**Project Description:** The approach taken in this study to better understand the mechanism of seismic attenuation in the presence of mesoscopic heterogeneity is largely one of numerical simulation. Computer-generated synthetic rock samples are created that have spatially variable poroelastic moduli and porous-continuum properties (e.g., porosity and permeability) distributed over the pixels. The numerical experiments consist of applying a time-varying stress to the sample surface, and measuring the resultant sample strain (defined as the average local strain throughout a sample). The Fourier transform of the stress and strain determine the sample’s complex frequency-dependent moduli, while the ratios of the imaginary and real parts of these moduli define the inverse quality factor  $1/Q$  for the compressional and shear modes. The local response within such synthetic samples is obtained using finite-difference approximations of Biot’s poroelasticity equations. A range of experiments on diverse synthetic materials are performed in order to learn how seismic attenuation is quantitatively related to the presence of mesoscopic-scale heterogeneity.

**Results:** In FY2007 we began investigating the effect on seismic properties caused by immiscible fluid distributions within samples of computer-modeled rocks. We used the pore-scale invasion percolation algorithm on grids much finer than our finite-difference poroelastic grid to create random distribution of two immiscible fluids within a computer rock sample. Invasion percolation has been proven to do a good job in creating the same type of self-affine fractal fluid distributions that are observed in laboratory studies when flow is occurring at very low capillary number (i.e., when capillary forces dominate viscous forces). We observed the same type of power law behavior in seismic attenuation (as measured by  $1/Q$ ) as a function of frequency  $Q(f) = f^b$  that we observed in 2006 when there is self-affine structure

in the compressibility of the framework of grains. The main difference is that the exponent  $b$  changed from one random realization of the invasion percolation algorithm to the next and changed depending on which fluid was taken to be less compressible. It also changed depending on how the fluid bulk modulus in our poroelastic finite-difference voxels was related to the underlying fluid structure of the invasion percolation algorithm (i.e., a majority rule for deciding which fluid to use, or a Reuss average of the underlying bulk moduli present). The observed attenuation power law exponent  $b$  was not simply related to the known Hurst exponent of the invasion percolation model. Work is ongoing in trying to sort out these myriad of observations so that a clear story can be told of how seismic properties are related to the fluid distributions.

In addition, the finite-difference code was extended to include the physics of viscous-boundary layer development at high enough frequencies. This non-trivial exercise allows us to now apply our finite-difference algorithm to unconsolidated sands. Unconsolidated sands have a high permeability so that the onset of viscous boundary layers occurs at relatively low frequencies (say 10 kHz). Last, laboratory experiments were begun that aim to quantify the amount of meso-scale heterogeneity inside of real rocks. These measurements are ongoing.

### **Imaging Permeability and Fluid Mobility Using Time-Lapse Measurements**

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**Objectives:** I am investigating the fundamental relationships between changes in time-lapse geophysical attributes and sub-surface flow properties. A key feature of this work is the development of new ways to relate changes in geophysical observations directly to flow properties. The ultimate goal is to further our understanding of multi-phase flow in the sub-surface and to develop methods for estimating flow properties. Time-lapse geophysical observations are a relatively new source of information, used to infer saturation and pressure change induced by the movement of fluids. It is possible to infer flow properties within the Earth, such as porosity and permeability, using time-lapse measurements. Doing so requires new approaches for relating saturation and pressure change to flow properties.

**Project Description:** In this project I explore new ways to relate time-lapse measurements and flow properties in the subsurface. One set of methods utilizes trajectory-based modeling of fluid flow and transport in order to map time-lapse observables, primarily time-lapse seismic amplitude changes, into images of subsurface permeability. Another set of methods follows directly from the equation governing pressure evolution in a multiphase environment. In this approach time-lapse geophysical data are used to infer pressure changes in the subsurface. These estimates of pressure change are mapped into subsurface permeability via the multiphase pressure equation. The mapping is linear and allows for an examination of model parameter resolution. The methods have been applied to time-lapse seismic data and to measurements of deformation.

**Results:** During the past year I explored two topics: (1) How well time-lapse seismic data can resolve water influx in a reservoir and infer permeability within the reservoir (2) How to use time-lapse deformation data to image permeability variations within a reservoir.

#### *Seismic Resolution of Water Influx-*

Methods for geophysical model assessment, in particular the computation of model parameter resolution, indicate the value and the limitations of time-lapse data in estimating reservoir flow

properties. A trajectory-based method for computing sensitivities provides an effective means to compute model parameter resolution. I examined the common situation in which water encroaches into a reservoir from below, as due to the upward movement of an oil-water contact. Though the techniques are not limited to this case, I considered the situation in which the time-lapse response is primarily due to changes in saturation. Using straight-forward techniques I found that, by including reflections off the top and bottom of a reservoir tens of meters thick, I could infer reservoir permeability based upon time-lapse data. I found that, for the case of water influx from below, using multiple time-lapse 'snapshots' does not necessarily improve the resolution of reservoir permeability. An application to time-lapse data from the Norne field in the North Sea illustrated that I could resolve the permeability near a producing well using reflections from three interfaces associated with the reservoir.

#### *Using Time-Lapse Deformation Data to Infer Permeability-*

Transient pressure variations within a reservoir can be treated as a propagating front and analyzed using an asymptotic formulation. From this perspective one can define a pressure 'arrival time' and formulate solutions along trajectories, in the manner of ray theory. I combined this methodology and a technique for mapping overburden deformation into reservoir volume change as a means to estimate reservoir flow properties, such as permeability. Given the entire 'travel time' or phase field, obtained from the deformation data, I constructed the trajectories directly, thereby linearizing the inverse problem. A numerical study indicated that, using this approach, one may infer large-scale variations in flow properties. In an application to Interferometric Synthetic Aperture (InSAR) observations (Figure 1, left panel) associated with a CO<sub>2</sub> injection at the Krechba field, Algeria, I imaged pressure propagation to the northwest. An inversion for flow properties indicated a linear trend of high permeability (Figure 1, right panel). The high permeability correlated with a northwest trending fault on the flank of the anticline defining the field.

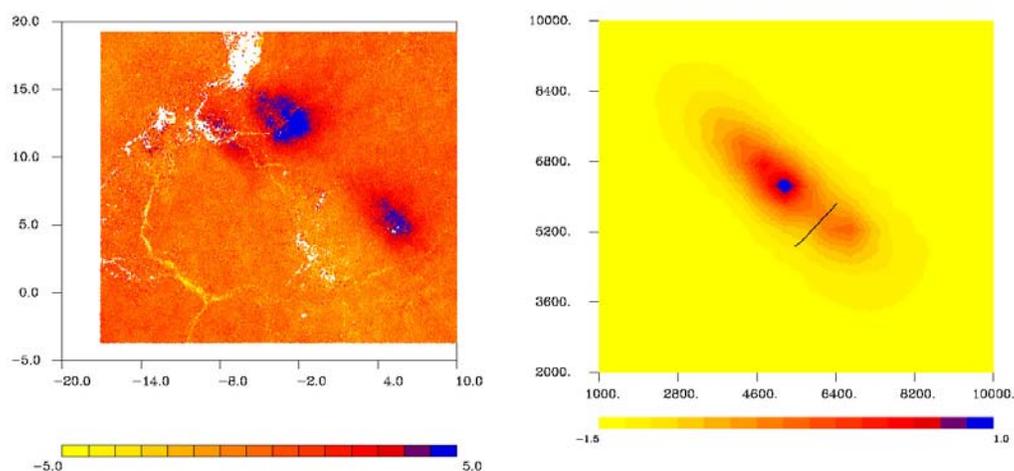


Figure 1

### **Air-Derived Noble Gases in Sediments: Sites and Mechanisms for Trapped Components**

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**Objectives:** This project seeks to isolate and identify enriched noble gas components in sediments and address the fundamental processes that lead to noble gas acquisition and retention, thereby improving the application of noble gas isotope studies to multiphase fluid processes in the Earth's crust.

**Project Description:** Sedimentary rocks and oil field gases typically are enriched in heavy noble gases: Xe/Ar ratios of ~10-10,000 times the ratio in air have been observed. Although abundance patterns suggest an adsorption hypothesis, three observations argue against adsorption as the only mechanism: (1) The difference between Xe and Ar adsorption coefficients (Xe ~30× Ar) is too small to account for the observed large relative Xe enrichments; (2) heating experiments suggests the enriched component is tightly bound, counterintuitive to a simple adsorption history; (3) many sedimentary rocks (~half) and some oil field gases contain excess Ne in conjunction with excess Xe.

**Results:** We have found large Xe enrichments in the organic silica of diatomites and sponge needles extracted from live sponges (*Calyxnicæensis*) that can not be accounted for by the entrapment of water saturated with air at one atmosphere. Step-wise degassing releases He, Ne, and Ar from these samples at low temperatures (T~400 °C), whereas Kr and Xe are retained up to temperatures in excess of ~1400 °C. We have yet to find excess noble gases in inorganic silica phases, such as diagenetic euhedral quartz and petrified wood. We are in the process of analyzing diatoms (*Thalassionira weissflorii*) grown in the laboratory under controlled conditions to determine if the excess heavy noble gas enrichment reflects biotic processes or a post-mortem/depositional effect. Possible post-depositional effects are being investigated in sediment samples from sapropels of the Black Sea and the Mediterranean as well as oceanic sediments from the Peru Trench (organic rich) and the Antarctic (Si-rich). We have also initiated a study of lab aggregated nanoparticles. In preliminary analyses, we found that aggregated  $\alpha$ FeOOH (goethite) to be enriched in He and Ne up to 1000 and 40 times that expected for an equal mass of air-saturated water, respectively. Step-wise degassing suggests that processes other than adsorption or diffusive acquisition of air-derived He and Ne are responsible for the excesses. These observations are being verified with re-analyses of  $\alpha$ FeOOH samples agglomerated in solutions of different pH.

### **Seismic Wave Propagation in Earth Systems with Fluids and Fractures**

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**Objectives:** The main objective of this continuing project has been to understand the physics of seismic wave propagation in earth systems. Specific systems of interest are normally those containing fluids (oil, gas, water, CO<sub>2</sub>) in rock pores. Seismic waves are used to image the earth, and thereby locate potential deposits of resources or contaminants, depending on the focus of the investigation. In addition, the waves can also be used in special cases to characterize the nature and state of the pore fluids. One example is Amplitude Versus Offset (AVO) analysis (or bright spots) which can be used to distinguish liquids from gases. But other methods with similar objectives have been developed in this project over the last several years.

**Project Description:** Prior work of the PI has focused on isotropic systems or finely layered systems, but recent work concentrates instead on systems that might be intrinsically anisotropic or that become anisotropic due to the presence of oriented fractures (either dry or containing fluids). Anisotropy has been analyzed using both approximate and rigorous analytical methods, as well as computational

methods when appropriate. Inclusions that are very flat fluid-filled or only partially saturated cracks, and/or dry cracks can all have a very strong effect on the seismic wave propagation speed and also on losses via wave attenuation. Results are particularly important therefore in reservoirs containing arrays of vertical fractures containing fluids, and have implications for estimating fluid permeability as well as the seismic properties. The PI has recently been working with researchers in industry who have done extensive numerical simulations of fractured reservoirs, and one of our recent successes has been to show how to analyze large amounts of such data and reduce the information contained therein to a few pertinent constants that can then be used to analyze and/or study other characteristics of fractured reservoirs. In all cases the PI takes special care to incorporate as much rigorous information (such as rigorous mathematical bounds and results from the best effective medium theories) and known-to-be-correct physical theories such as Gassmann's theory for mechanics of systems having fluids in pores into the overall analyses.

**Results:** The work in the last year has stressed seismic waves in anisotropic systems where the anisotropy is mainly due to the presence of oriented fractures such as HTI (horizontally transversely isotropic) systems. Fractures may be either gas- or liquid-filled. Some of this work has now been published in *Geophysical Journal International* and related work was also published in *Geophysics*. Results are expected to help explain various discrepancies that have been noted in well-logging, laboratory, and field data by many workers. Other recent related work has been able to show how to make use of various types of effective medium theories, including certain rigorous bounding methods, for both dry and saturated cracked/fractured systems. The Sayers and Kachanov (1991) approach of parametrizing the mechanical behavior of fractured systems has been generalized to permit rigorous analysis of fluid effects on these systems, and in particular the rigorous results differ significantly from the usual *ad hoc* approach taken by most authors. It has also been shown in several different contexts how fluids influence both compressional wave and shear wave behavior in anisotropic systems.

### **Density-Driven Brine Convection: A Process for Accelerating CO<sub>2</sub> Dissolution and Enhancing Security of Geologic Storage**

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**Objectives:** The purpose of this project is to investigate the process of dissolution-diffusion-convection (DDC) as a mechanism for transferring CO<sub>2</sub> stored in a saline aquifer to the aqueous phase.

**Project Description:** For purposes of geologic storage, CO<sub>2</sub> would be injected into saline formations at supercritical temperature and pressure conditions, and would form a separate phase that is immiscible with the aqueous phase (brine). Supercritical CO<sub>2</sub> (scCO<sub>2</sub>) has lower density than the aqueous phase and would experience an upward buoyancy force. Accordingly, the CO<sub>2</sub> is expected to rise to the top of the permeable formation, and spread out laterally beneath a low-permeability caprock. Free CO<sub>2</sub> is highly mobile due to its low, gas-like viscosity, and could escape from the storage formation wherever (sub-) vertical pathways are available, such as fractures or faults through the caprock, or improperly abandoned wells. Over time, an increasing fraction of CO<sub>2</sub> may dissolve in the aqueous phase, and eventually some of the aqueous CO<sub>2</sub> may react with rock minerals to form poorly soluble carbonates. Dissolution into the aqueous phase and eventual sequestration as carbonates are highly desirable processes as they would increase permanence and security of storage. Dissolution of CO<sub>2</sub> will establish phase equilibrium locally

between the overlying CO<sub>2</sub> plume and the aqueous phase beneath. If the aqueous phase were immobile, CO<sub>2</sub> dissolution would be limited by the rate at which aqueous CO<sub>2</sub> is removed from the interface between CO<sub>2</sub>-rich and aqueous phases by molecular diffusion in the aqueous phase. This is a very slow process. However, dissolution of CO<sub>2</sub> is accompanied by a small increase in the density of the aqueous phase, creating a negative buoyancy force that could give rise to downward convection of CO<sub>2</sub>-rich brine, while inducing upward movement of brine with low CO<sub>2</sub> concentration. Such density-driven convection could greatly accelerate the rate at which dissolved CO<sub>2</sub> migrates away from the interface between CO<sub>2</sub>-rich and aqueous phases, and thereby could greatly accelerate the dissolution of the free CO<sub>2</sub>.

The buoyant convection process induced by denser aqueous phase overlying less dense fluid is intrinsically multi-scale in nature, i.e., at early time the process occurs on the scale of a few pores and over time grows by many orders of magnitude to eventually encompass field-scale convection and mixing. At the present time no methods are available to represent such processes within the context of a field-scale numerical model. In a space-discretized representation, CO<sub>2</sub> dissolution, aqueous diffusion of CO<sub>2</sub>, and buoyant convection in the aqueous phase will at early times proceed on a sub-grid level, will then grow to grid block size, and eventually will encompass many grid blocks, at which time they can be explicitly resolved. Finer space discretization will reduce the characteristic times involved in this progression, but will not change the fact that only the late-time process is amenable to explicit representation in field-scale numerical models.

The activities planned for this research include the following.

- laboratory flow experiments for visualizing the DDC process and providing quantitative data for model testing and calibration;
- development of high-resolution numerical models to gain quantitative insight into DDC and its controlling parameters;
- development of approximate numerical techniques for representing DDC in coarsely-gridded field scale problems.

**Results:** This project has just started and no reportable results are available yet.

### **Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems**

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**Objectives:** This report is based on a BES Workshop on Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems, February 21–23, 2007, to identify research areas in geosciences, such as behavior of multiphase fluid-solid systems on a variety of scales, chemical migration processes in geologic media, characterization of geologic systems, and modeling and simulation of geologic systems, needed for improved energy systems. In addition to providing a Co-Chair for the effort (Dr. Don Depaolo) LBNL also provided logistical support to edit, assemble and produce the final report.

**Project Description:** Serious challenges must be faced in this century as the world seeks to meet global energy needs and at the same time reduce emissions of greenhouse gases to the atmosphere. Even with a

growing energy supply from alternative sources, fossil carbon resources will remain in heavy use and will generate large volumes of carbon dioxide (CO<sub>2</sub>). To reduce the atmospheric impact of this fossil energy use, it is necessary to capture and sequester a substantial fraction of the produced CO<sub>2</sub>. Subsurface geologic formations offer a potential location for long-term storage of the requisite large volumes of CO<sub>2</sub>. Nuclear energy resources could also reduce use of carbon-based fuels and CO<sub>2</sub> generation, especially if nuclear energy capacity is greatly increased. Nuclear power generation results in spent nuclear fuel and other radioactive materials that also must be sequestered underground. Hence, regardless of technology choices, there will be major increases in the demand to store materials underground in large quantities, for long times, and with increasing efficiency and safety margins.

This report describes the scientific challenges associated with geologic sequestration of large volumes of carbon dioxide for hundreds of years, and also addresses the geoscientific aspects of safely storing nuclear waste materials for thousands to hundreds of thousands of years. The fundamental crosscutting challenge is to understand the properties and processes associated with complex and heterogeneous subsurface mineral assemblages comprising porous rock formations, and the equally complex fluids that may reside within and flow through those formations. The relevant physical and chemical interactions occur on spatial scales that range from those of atoms, molecules, and mineral surfaces, up to tens of kilometers, and time scales that range from picoseconds to millennia and longer. To predict with confidence the transport and fate of either CO<sub>2</sub> or the various components of stored nuclear materials, we need to learn to better describe fundamental atomic, molecular, and biological processes, and to translate those microscale descriptions into macroscopic properties of materials and fluids. We also need fundamental advances in the ability to simulate multiscale systems as they are perturbed during sequestration activities and for very long times afterward, and to monitor those systems in real time with increasing spatial and temporal resolution. The ultimate objective is to predict accurately the performance of the subsurface fluid-rock storage systems, and to verify enough of the predicted performance with direct observations to build confidence that the systems will meet their design targets as well as environmental protection goals.

**Results:** The report summarizes the results and conclusions of a Workshop on Basic Research Needs for Geosciences held in February 2007. Five panels met, resulting in four Panel Reports, three Grand Challenges, six Priority Research Directions, and three Crosscutting Research Issues. The Grand Challenges differ from the Priority Research Directions in that the former describe broader, long-term objectives while the latter are more focused.

The grand challenges identified are: *Computational thermodynamics of complex fluids and solids*, *Integrated characterization, modeling, and monitoring of geologic systems* and *Simulation of multiscale geologic systems for ultra-long times*.

The priority research directions identified are *Mineral-water interface complexity and dynamics*, *Nanoparticulate and colloid chemistry and physics*, *Dynamic imaging of flow and transport*, *Transport properties and in situ characterization of fluid trapping, isolation, and immobilization*, *Fluid-induced rock deformation*, and *Biogeochemistry in extreme subsurface environments*.

Last but not least the crosscutting research issues identified were: *The microscopic basis of macroscopic complexity*, *Highly reactive subsurface materials and environments* and *Thermodynamics of the solute-to-solid continuum*.

The Grand Challenges, Priority Research Directions, and Crosscutting Issues described in the report define a science-based approach to understanding the long-term behavior of subsurface geologic systems in which anthropogenic CO<sub>2</sub> and nuclear materials could be stored. The proposed research is based on development of a new level of understanding—physical, chemical, biological, mathematical, and computational—of processes that happen at the microscopic scale of atoms, molecules and mineral surfaces, and how those processes translate to material behavior over large length scales and on ultra-long time scales. The results of the research will have a wide range of implications from physics and chemistry, to material science, biology and earth science.

## LAWRENCE LIVERMORE NATIONAL LABORATORY

Energy and Environment Directorate  
Chemistry, Materials, and Life Sciences Directorate  
Livermore, CA 94550

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### Investigation of the Physical Basis for Biomineralization

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**Objectives:** The objectives of this project are to: 1) determine the impact of acidic polypeptides and proteins on Mg and Sr signatures in calcite; 2) map the pathways and kinetics of template-directed nucleation and growth of calcite on Asp-rich polypeptide and protein derivitized SAMs; 3) develop comprehensive models of kink-limited growth and mineral dissolution over the range of reasonable materials; 4) develop a model for silica dissolution that is rooted in a mechanistic understanding and quantified through a formalism based on the thermodynamics of surfaces and the kinetics of solute attachment and detachment.

**Project Description:** The purpose of this project is to investigate biomolecular controls on crystal growth and dissolution. To achieve this purpose we are utilizing *in situ* force microscopy to investigate nucleation and growth of calcite surfaces under controlled conditions of temperature and supersaturation in the presence of acidic peptides, proteins, Sr and Mg. Concomitantly, we are performing molecular modeling to elucidate the stereochemical relationships between additives and crystal surfaces leading to growth modification, as well as ion-beam spectroscopy to determine distributions of incorporated additives. For all modifiers, our results to date have provided significant advances in our quantitative understanding of controls on calcite growth morphology, kinetics, and habit. Our methodology for investigating nucleation has also utilized *in situ* atomic force microscopy, but has focused on quantifying nucleation kinetics and phase transformations at self-assembled monolayers (SAMs). Concomitantly, we have used X-ray absorption spectroscopy to follow the structural evolution of the SAMs and Raman spectroscopy and *in situ* electron microscopy to follow the evolution of the mineral structure and phase during template-directed nucleation.

**Results:** In FY07, we had a breakthrough in our imaging capability that now allows us to image single atomic kink sites on step edges. We have applied this to calcite to collect the first kink statistics for any inorganic crystal, and used those statistics to calculate the kink energy. We combined this result with kinetic Monte Carlo models of impurity poisoning of growth in the regime where kinks are rare and showed that the predicted dependence of step speed on impurity concentration is similar to what is observed for calcite with  $\text{Sr}^{2+}$ . Based on these results we have submitted a manuscript that calls for a revision of the accepted picture of growth in which steps are described thermodynamically using the Gibbs-Thomson effect with one based on kink-site kinetics. We also submitted a manuscript showing that dissolution of amorphous  $\text{SiO}_2$  follows an exponential dependence on driving force as expected for crystalline solids where the opening of a dissolution pit is a nucleated process. Through a combination

of experimental analyses and theoretical considerations, we argued that differences in coordination number create the equivalent of terrace sites and step edge sites, thus leading to a nucleated dissolution process. In essence, a glasses need to be viewed as a “rumpled” lattice where the loss of long range order merely limits the length-scale over which dissolution pits can extend. Finally, we successfully fabricated and filled our TEM fluid cells and are preparing to perform our first imaging experiments.

### **Fluid Chemistry, Surface Chemistry and Fracture Mechanics: An Investigation of the Connection at the Nanoscale**

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**Objectives:** The project objective at LLNL/LBL (see separate Wright State University input) is to study the coupling of chemistry and mechanics at the molecular scale. This objective requires development of new capabilities for the Hydrothermal Atomic Force Microscope (HAFM).

**Project Description:** We are studying the coupling among fluid chemistry, surface chemistry, and applied stress and the resulting impacts on subcritical crack growth (SCG) and mineral growth/dissolution using *in situ* scanning probe microscopy (SPM). In order to achieve this objective, the project will develop a mini-bending jig for the HAFM and make extensive modifications (see Results below) to accommodate the jig and to greatly increase the scan range. We are also working with a grad student at WSU by modeling her Plug Flow Reactor experimental results.

**Results:** During this second year of the project we continued our extensive modifications of the HAFM to permit studies of the connection between mechanics and chemistry. Last year we developed a mini-bending jig for the HAFM. The bending jig that we designed and constructed permits us to achieve stress intensity factors ranging from  $2.5 \times 10^{-2}$  to  $7.2 \times 10^{-1}$  MPa  $\cdot$  m<sup>1/2</sup>. This covers the stress range pertinent to most materials of geologic significance. It is constructed entirely of non-reactive materials and fits within the flow cell of the modified HAFM. We redesigned the HAFM to use a longer piezo tube that extends the x-y scan range from 30 to 120  $\mu$ m and the z-range from 1.2 to 2.3  $\mu$ m. We extended the HAFM body to accommodate the new, longer piezo tube. We devised a new Kalrez<sup>®</sup> membrane shape and used a new composition material for the membrane that has a higher T limit, lower durometer (it's softer), and yet has a lower gas permeability. The new shape uses a pre-formed dimple that lowers stiffness and drag on the piezo. This new membrane is shown in Fig. 1, along with the mini-bending jig attached to the Ti sample holder positioned on the end of the piezo tube.

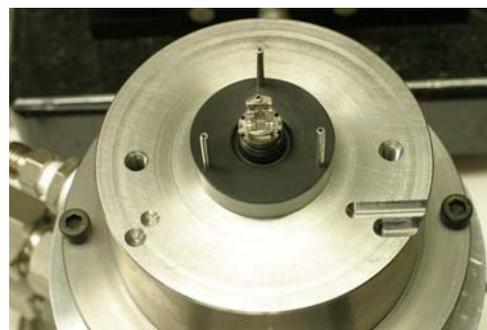


Fig. 1 Pre-shaped Kalrez membrane and mini-bending jig

After calibrating the new HAFM, we made our first real SCG measurements and realtime movies of the process in the HAFM under controlled T, P, and fluid chemistry conditions, including switching fluid composition during an experiment. In this experiment we initiated a small (20 $\mu$ m) crack using a Vickers indenter, stressed the sample and then imaged the crack in a pH 5.5 (equilibrated with the atmosphere) aqueous fluid for several hours. We then switched the incoming fluid to a pH 9 dilute buffer solution and watched the crack grow to over 120  $\mu$ m length.

We noted that limiting the x-y range to that provided by the piezo motion alone would prevent us from “stacking” experiments, where conditions are changed multiple times with one setup. One can only track crack motion (or anything else) for 120  $\mu\text{m}$ .

This year we redesigned the HAFM to use the new style TopView© optical head, that provides the ability to make lateral force measurements (frictional force microscopy) and also allows realtime movie making using the optical CCD camera. The base plate for the optical head was redesigned to use a kinematic mount consisting of 80-pitch screws, allowing fine positioning/focusing of the laser on the tip and to permit flow of cooling water through it. We designed and had manufactured an etched foil heater for the larger flow cell. We then tested the heater to assure that we could achieve cell temperatures up to the design limits without overheating the optical head body.

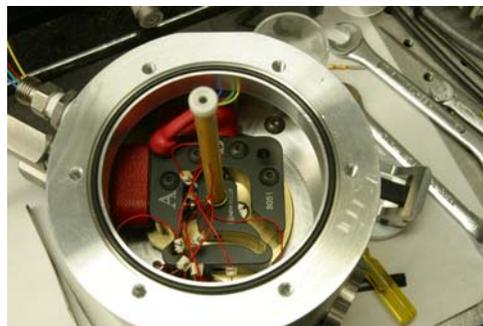


Fig. 2 Piezo mounted on Picostage

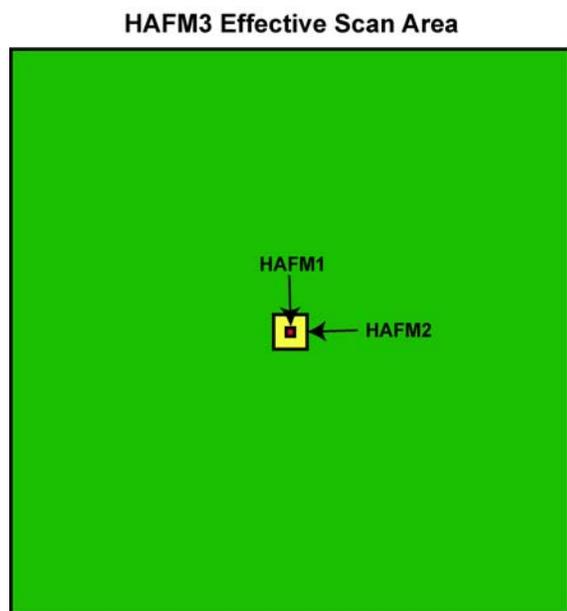


Fig. 3 Relative scan

Finally, we redesigned the HAFM to include a Picostage positioner for translating the piezo+sample over a  $\pm 1$  mm range, increasing the effective scan range by 1000x. In Fig. 2 we show the piezo tube mounted in the Picostage positioner. This piezo/stage assembly is located within the pressurized microscope base, which is separated from the overlying flow cell by the Kalrez® membrane. Because the Picostage translator itself uses a piezo/friction approach to achieve motion, step size can be as small as 30 nanometers. In Fig. 3 we show the relative size of the scan areas available through the three designs for the HAFM to date. The dramatic improvement in range now provides the HAFM with nearly the same range in sample positioning as the mechanical stage used by the Digital Instruments MultiMode AFM.

### Reactive Fluid Flow through Variable Aperture Fractures: Permeability Alterations Due to Dissolution

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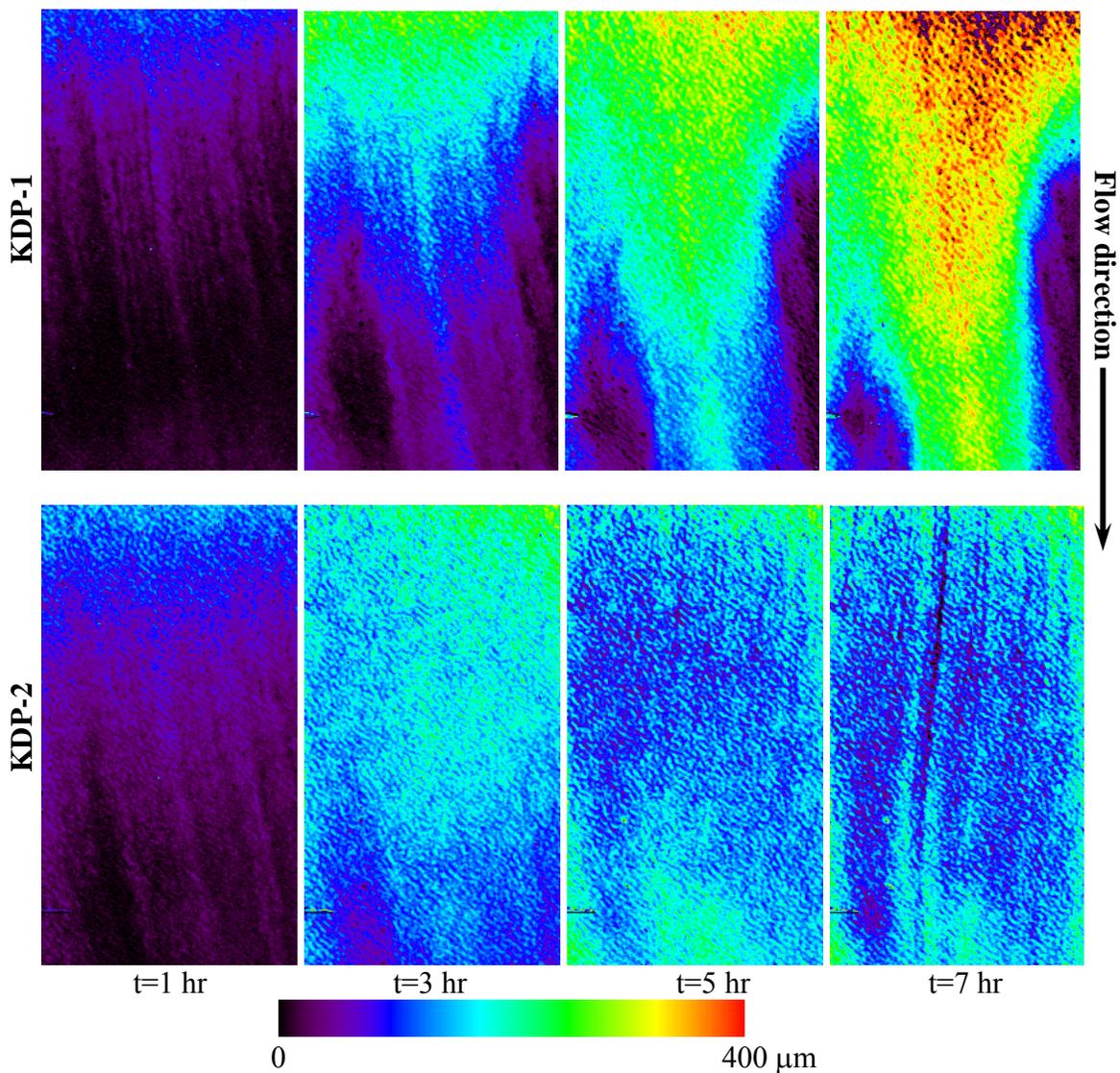
**Objectives:** The objective of this project is to explore the local mechanisms that lead to transmissivity alterations in variable-aperture fractures under conditions that cause coupled chemical alteration and mechanical deformation of fracture surfaces.

**Project Description:** Transparent, variable-aperture fractures fabricated by mating a 9.4- x 14.5-cm rough glass surface with a smooth reactive surface ( $\text{KH}_2\text{PO}_4$  crystal) allow reproducible experiments in fractures with well-characterized surface mineralogy. Previously developed light transmission methods yield high-resolution ( $83 \times 83 \mu\text{m}$  pixels at  $\pm 4 \mu\text{m}$  measurement resolution) measurements of fracture apertures over the entire fracture repeatedly during experiments. As part of this project, we have developed an experimental system that applies a steady confining stress to the fracture surfaces without obscuring the transparency of the experimental system. This new approach allows direct, non-invasive measurements of the changing distribution of fracture apertures during experiments involving coupled chemical alteration and mechanical deformation. In addition to providing valuable insights into the relative importance of competing mechanisms, these experiments provide detailed quantitative data sets that are ideal for evaluating new pore-scale computational models that explicitly represent these mechanisms.

**Results:** Dissolution experiments conducted under constant normal stress demonstrate different behavior depending on the initial flow rate. As we observed during previous zero-strain experiments, higher flow rates lead to more uniform concentrations of the dissolving minerals and preferential dissolution in smaller aperture regions. When a confining stress is applied to the fractures, experiments show an initial increase in transmissivity due to dissolution of the surfaces and an increase in fracture aperture. However, after this initial period of transmissivity increases, dissolution-induced strains begin to compete with the increasing fracture aperture. The relative magnitudes of aperture increases due to dissolution and decreases dissolution and damage of contacts depends strongly on the relative magnitude of surface reaction rates and advective transport of dissolved minerals, which is controlled by the initial flow rate in our experiments.

**Figure 1** shows images of measurements of aperture change during two experiments at different initial flow rates (KDP-1:  $0.02 \text{ cm}^3/\text{s}$ ; KDP-2:  $0.04 \text{ cm}^3/\text{s}$ ) and the same confining stress (0.21 MPa). The initial 9.4- x 14.5-cm fracture aperture fields were spatially correlated over small distances ( $< 1 \text{ mm}$ ) but relatively homogeneous at larger scales with a mean fracture aperture  $95.3 \mu\text{m}$ . At the slow flow rate (KDP-1) the development of a distinct dissolution channel leaves regions with relatively little change in fracture aperture. These regions support the fracture surfaces and minimize the amount of strain associated with dissolution. At the high flow rate (KDP-2), the absence of distinct dissolution channels leads to relatively uniform dissolution rates throughout the fracture that are inversely correlated with fracture aperture. Thus, areas surrounding contacting asperities dissolve relatively quickly. This results in gradually decreasing contact areas and increasing stress until the remaining contacting asperities break leading to relatively large sudden reductions in fracture aperture. These results are somewhat surprising in that larger flow rates, which remove more mass from the fracture surface, lead to smaller increases in fracture transmissivity than slower flow rates. These results emphasize the importance of understanding the relative magnitudes of surface reaction rates and advective/diffusive transport in predicting possible transmissivity alterations resulting from coupled reactive fluid flow, particularly in the presence of significant stresses.

Figure 1



**Why Does Aluminum Inhibit Silicate Dissolution Rates? An Experimental Study Combining Kinetics with HAFM and NMR to Determine the Reaction Mechanisms at the Silicate-Solution Interface**

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**Objectives:** This project investigates aluminum geochemistry in the presence of silicate phases combining water chemistry with NMR to determine the reaction mechanism responsible for the observed effect of dissolved aluminum on silicate reaction rates.

**Project Description:** Characterizing the structural form of Al(III) associated with silicate solids has been the subject of interest for a number of years because dissolved Al(III) is known to inhibit dissolution rates and correspondingly enhance precipitation rates for silicate minerals. In order to determine the reaction mechanisms responsible for this behavior, we use both bulk and surface-selective solid-state NMR techniques to identify the coordination geometry and chemical environment of Al(III). We investigate a variety of aluminosilicate precipitates and mineral surfaces such as amorphous silica, quartz, and kaolinite that have reacted with dissolved aluminum from pH 4 to 8.

**Results:** We studied uptake mechanisms for dissolved Al on amorphous silica by combining bulk-solution chemistry experiments with solid-state NMR techniques ( $^{27}\text{Al}$  MAS NMR,  $^{27}\text{Al}\{^1\text{H}\}$  cross-polarization (CP) MAS NMR and  $^{29}\text{Si}\{^1\text{H}\}$  CP-MAS NMR). We find that reaction of Al (1mM) with amorphous silica consists of at least three reaction pathways; (1) adsorption of Al to surface silanol sites, (2) surface-enhanced precipitation of an aluminium hydroxide, and (3) bulk precipitation of an aluminosilicate phase. From the NMR speciation and water chemistry data, we calculate that  $0.2 (\pm 0.04)$  tetrahedral Al atoms  $\text{nm}^{-2}$  sorb to the silica surface and that this amount is nearly constant from pH 4.3-8.2. Once the surface has sorbed roughly half of the total dissolved Al ( $\sim 8\%$  site coverage), aluminium hydroxides and aluminosilicates precipitate from solution. These precipitation reactions are dependent upon solution pH. We find that the Si:Al stoichiometry of the aluminosilicate precipitate is roughly 1:1 and suggest a chemical formula of  $\text{NaAlSiO}_4$  in which  $\text{Na}^+$  acts as the charge compensating cation. For the adsorption of Al, we propose a surface-controlled reaction mechanism where Al sorbs as an inner-sphere coordination complex at the silica surface. Analogous to the hydrolysis of  $\text{Al}(\text{OH}_2)_6^{3+}$ , we suggest that rapid deprotonation by surface hydroxyls followed by dehydration of ligated waters results in four-coordinate  $(>\text{SiOH})_2\text{Al}(\text{OH})_2$  sites at the surface of amorphous silica.

### **Kinetic Isotope Fractionation**

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**Objectives:** The primary objective of the proposed research is to explore and quantify major element isotopic fractionations (i.e., “isotopic fingerprints”) associated with mass transport processes within and between phases, one of which is in most cases a liquid – either water or a silicate melt.

**Project Description:** The Lawrence Livermore National Laboratory part of this project involves measuring the isotope fractionation of chemically diffusing species using the GV IsoProbe multi-collector ICPMS and Cameca NanoSIMS at LLNL and the Nu Instruments MC-ICPMS at UC Davis. In FY07 we proposed to evaluate potential “isotopic fingerprints” of mass transport by determining whether or not there is an isotopic effect associated with the partial loss of an element by dissolution (e.g., the loss of magnesium relative to calcium during calcite dissolution), potentially analogous to the isotopic fractionations associated with preferential loss of Mg by evaporation. Ocean acidification and associated carbonate and aragonite dissolution has become a major environmental issue, as more and more anthropogenic  $\text{CO}_2$  dissolves in the ocean. Developing isotopic monitors of carbonate dissolution could provide a new quantitative measure of ocean acidification rates.

**Results:** The Mg isotopic compositions of two species of separated forams from DSDP Sites 590B and 575 were measured at Lawrence Livermore National Laboratory; the foram separates were prepared by

Linda Anderson, UC Santa Cruz. Relative to the DSM3 standard, we found a suggestion of small differences in magnesium isotopic composition between two species. Four analyses of *Pu. Obliquatulata* yielded a mean  $\delta^{25}\text{Mg}$  of  $-3.0\pm 0.65\%$ , while three analyses of *G. tumida* yielded a mean  $\delta^{25}\text{Mg}$  of  $-1.3\pm 0.57\%$ . These initial results will be reexamined in FY08 after additional chemical purifications of the Mg fractions to remove trace amounts of residual Ca. Activities in FY08 will focus on measuring the Mg isotopic composition of forams to see if it correlates with commonly used dissolution proxies (e.g., Mg/Ca). We are looking for is an isotopic fingerprint of the preferential loss of Mg relative to Ca during dissolution, We also performed initial studies of trace element distributions in calcium carbonates using the LLNL NanoSIMS. NanoSIMS chemical mapping, carried out at  $\sim 250$  nm resolution, revealed significant heterogeneities in Mn, Sr and Ba in carbonates exhibiting little to no contrast in backscattered electron images. Both Mn and Ba exhibit sub-micron size “hot spots” in which the concentration is enhanced more than ten-fold. These NanoSIMS studies will be a major activity in FY08. The goal being to reexamine the extent of recrystallization of carbonate sediments as a function of age to determine if different parts of the materials making up carbonate sediments have significantly different reactivity.

### **Permeability and Electrical Resistivity in Partial Melts: An Integrated Study Combining Laboratory Measurements, X-ray Computed Tomography, and Computational Methods**

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**Objectives:** The objectives of this project are to address the questions of percolation threshold, melt interconnectivity, and permeability in partial-melts by synthesizing materials and performing electrical conductivity measurements at high pressure and temperature followed by characterization using x-ray microtomography (XRCT) and lattice-Boltzmann simulations of permeability and to test the hypothesis that non-wetting melt compositions can be extracted on timescales constrained by geochemistry to form metallic cores in planetesimals.

**Project Description:** We propose to synthesize FeS/FeNiS olivine partial-melts with a variety of compositions and melt fractions and determine melt percolation threshold and interconnectness through the use of in situ electrical measurements and XRCT on run products. Lattice-Boltzmann simulations will be used to estimate permeability in these systems and determine the appropriate scaling laws.

The components of this study include:

1. Synthesis and characterization of compositionally relevant silicate-sulfide partial-melts.
2. Perform x-ray microtomography on recovered samples and relate the 3D melt structure to transport properties.
3. Perform electrical conductivity measurements on the partial-melts at controlled conditions.
4. Use the results to constrain models of melt segregation and core formation.

Results and developed techniques apply to many physical problems including evaluating mechanisms of planetary core formation. The results will be used to test the hypothesis that non-wetting melt compositions can be extracted on timescales constrained by geochemistry to form metallic cores in planetesimals.

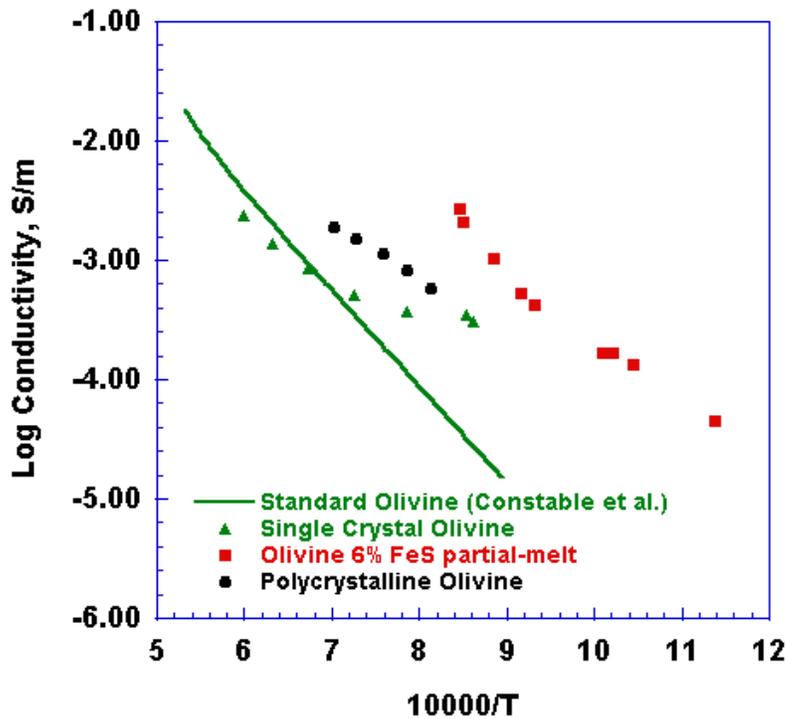


Figure 2. Electrical conductivity measured in the piston cylinder at 1 GPa compared to the model for dry olivine (green curve). Single crystal San Carlos olivine (unoriented, green triangles), polycrystalline San Carlos olivine (black circles), olivine FeS partial-melt (6%, red squares). The single crystal conductivity agrees well with the standard model except at lower temperatures, consistent with the results of Du Frane et al. (2005). As expected the partial-melt is more conductive than the dry samples.

**Results:** In FY07 all milestones and several significant results were achieved, including publication of a paper in Geophysical Research Letters. A key experimental achievement was the successful development of a reliable electrical conductivity assembly for the piston cylinder. The cell and measurement techniques have a high success rate and provide repeatable electrical measurements for single crystals, polycrystalline samples, and partially-molten samples (see figure). Design elements of the piston cylinder assembly will be implemented in the multi-anvil assembly in FY08.

Electrical conductivity measured in the piston cylinder at 1 GPa compared to the model for dry olivine (green curve). Single crystal San Carlos olivine (unoriented, green triangles), polycrystalline San Carlos olivine (black circles), olivine FeS partial-melt (6%, red squares). The single crystal conductivity agrees well with the standard model except at lower temperatures, consistent with the results of Du Frane et al. (2005). As expected the partial-melt is more conductive than the dry samples.

X-ray microtomography was performed at the Advanced Light Source beamline 8.3.2. Further development of the beamline has resulted in an improvement in imaging capability to a pixel size of 880 nm. Further improvements in spatial resolution are pending. We have also improved our data volume analysis capability by writing routines to analyze cluster sizes, wall thicknesses and interrelation of specific pore size distributions. Several collaborations were supported that use the imaging and computational techniques developed for partial-melts. These collaborations expand the scope of geological and physical problems that can be addressed and as a result of these efforts the PI has been asked to lead an Approved Beamline Program at the Advanced Light Source.

## Geochemical Imaging with the NanoSIMS

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**Objectives:** The objective of the project is to develop the operating procedures and fundamental parameters required for the routine application of the NanoSIMS, the latest development in elemental and isotopic microanalysis, to geochemical problems, by addressing problems that cannot be solved without this capability. We will determine the relative sensitivity factors required for quantification, investigate the use of energy filtering and quantify parameters such as the  $M^+/MO^+$  relative ion yields for a variety of geochemically important trace elements and matrices. We will couple the chemical imaging capabilities of the NanoSIMS with the synthesis capabilities of the laser-heated diamond anvil cell to determine the partitioning of trace elements among phases characterizing the earth's lower mantle. We are also investigating the partitioning of trace elements between zircon and melt to support studies of zircon provenance. Finally we will develop the combined use of conventional SIMS and NanoSIMS profiling to obtain average lattice and grain boundary diffusion coefficients and to sample diffusive anisotropy at the individual grain level.

**Project Description:** The NanoSIMS is a recently developed secondary ion mass spectrometer (SIMS) with lateral spatial resolution as good as 50 nm. Coupled with its high transmission, the instrument has the potential to address a number of geochemical problems that were heretofore intractable, essentially taking trace element and isotopic analysis to a spatial scale approaching that of transmission electron microscopy (TEM). The performance and applicability must, however, be verified and developed for geochemical applications. This project will contribute to the development of geochemical imaging in three applications to natural and experimentally produced materials that are related by the need for high-resolution imaging. The applications include: (1) experimental determination of trace element partitioning between zircon and melt, and chemical imaging of natural zircons to assess chemical changes induced by radiation damage, (2) an experimental investigation of the partitioning of transition metals in lower mantle phases, applying the NanoSIMS to materials synthesized in the diamond anvil cell (DAC) and determining the effects of pressure induced spin-state transitions on mineral composition, and (3) the development of methods to determine diffusion profiles in single micron-size grains in a polycrystalline matrix, enabling the investigation of the effects of composition on diffusive transport in minerals.

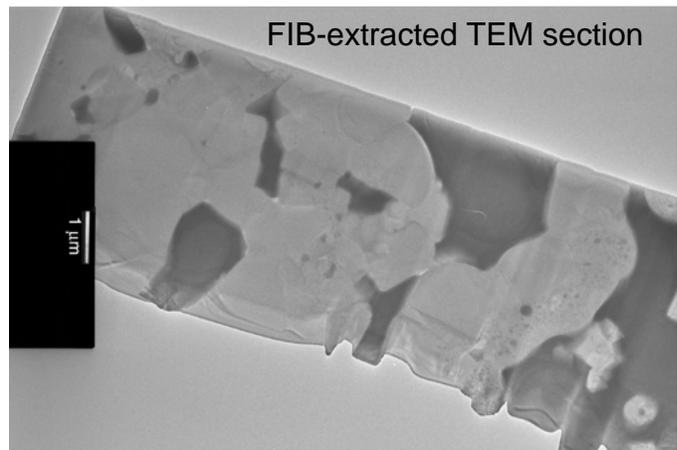


Figure 3. FIB-extracted TEM section of transformed MORB.

**Results:** A combination of nanometer-resolution secondary ion mass spectrometry (a Cameca NanoSIMS 50) and analytical transmission electron microscopy was used to image the major and trace chemistry of a mid-ocean ridge basalt transformed to a lower mantle phase assemblage in a laser-heated diamond anvil cell (LH-DAC) at 55 GPa and 2100°C. The sample was extracted from the DAC using a “focused ion beam” device (FIB, Figure 1) and a phase assemblage of Mg-perovskite, Ca-perovskite, stishovite and a calcium ferrite-structure phase was observed. For the first time, quantitative analysis spanning the entire range of concentrations, from major elements such as silicon (49.5 wt% SiO<sub>2</sub>) to trace elements such as strontium (118 ppm), scandium, and yttrium (both at 40 ppm) was obtained for a lower mantle assemblage and trace element partitioning

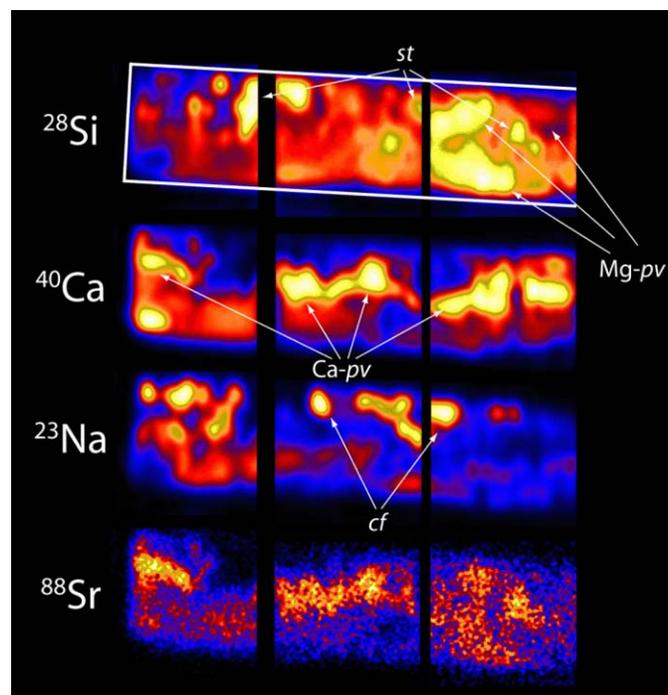


Figure 2. <sup>28</sup>Si, <sup>40</sup>Ca, <sup>23</sup>Na, and <sup>88</sup>Sr secondary ion images of transformed MORB FIB section in Figure 1. Ca-Pv = Ca perovskite, Mg-Pv = Mg perovskite, st = stishovite, cf = Ca ferrite

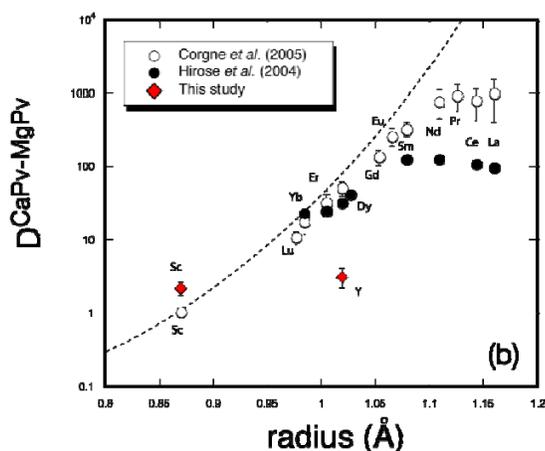


Figure 3. Comparison of CaPv-MgPv partition coefficients obtained at 55 GPa (this study) with results obtained at 25 GPa as a function of ionic radius. The decreasing fractionation with pressure is due to a combination of pressure and increasing Al concentration in MgPv.

patterns constrained (Figure 2). The results indicate that higher pressures and increasing Al content decrease inter-element fractionation (Figure 3) with important implications for the chemical evolution of the early Earth. This type of measurement demonstrates that even the most complex mineral assemblages can be probed using this combination of techniques and opens new pathways towards the characterization and quantification of geochemical interactions and processes occurring in the deep Earth. Current work is focussed on the partitioning of Mg-Fe and transition metals between Mg-perovskite and ferropericlase as a function of pressure extending to the core-mantle boundary.

## LOS ALAMOS NATIONAL LABORATORY

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### High Resolution/High Fidelity Seismic Imaging and Parameter Estimation for Geologic Structure and Material Characterization

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**Objectives:** The objectives of this project are to use wave equation migration to improve the quality of information that can be obtained from seismic images. We also seek to exploit the natural advantage of our methods for providing reflection amplitude vs. angle information that can be used to infer *in situ* parameters like rock properties and fluid type and content.

**Project Description:** High-resolution/high fidelity seismic imaging is critically important for both exploration and production management of energy resources and monitoring of geological CO<sub>2</sub> sequestration. New oil/gas reservoirs are mostly located in complicated geological areas, sophisticated imaging methods for complex structures are needed to pinpoint the targets. We are enhancing our multi-domain seismic imaging techniques for high-resolution/high fidelity imaging. We exploit the natural advantages of our method for providing reflection amplitude vs. angle information that can be used to infer *in situ* parameters like rock properties and fluid type and content. We also are developing imaging methods using multi-component elastic data. High-resolution/high fidelity seismic imaging will help in characterizing the crack distribution, fluid and gas content and changes of reservoir parameters during operation of reservoirs for production or during environmental protection efforts such as those involving nuclear waste disposal, CO<sub>2</sub> sequestration, and groundwater contamination monitoring and remediation.

**Results:** (1) We developed a novel numerical modeling method to simulate wave propagation in strongly heterogeneous media using a mimetic finite-difference scheme on an unstructured grid. This is the first to introduce the mimetic finite-difference scheme to solve the wave equation. The new method enables us to define arbitrary shapes of geological interfaces including the free surface without any approximation. (2) We developed a new vector-imaging condition for elastic-wave reverse-time migration. Our new vector-imaging condition properly handles polarizations of P- and S-waves, and our numerical migration examples using pure elastic-wave reverse-time migration demonstrate that our new imaging condition significantly improves image resolution compared with conventional imaging conditions. (3) We developed a finite-difference method for sensitivity analysis of elastic-waves with respect to changes in reservoir properties such as P- and S-wave speeds. Conventional seismic-wave illumination analysis is used for survey designs for oil/gas exploration, but cannot be used for designs for reservoir monitoring. Our new sensitivity method can be used for optimized designs of source/receiver distribution for monitoring of production reservoirs and geological carbon sequestration. (4) A Special Issue on "Computational Geophysics" edited by Lianjie Huang and Michael Fehler was published on-line in September 2007 and in hard copy in January 2008.

## Nonlinear Elasticity in Rocks

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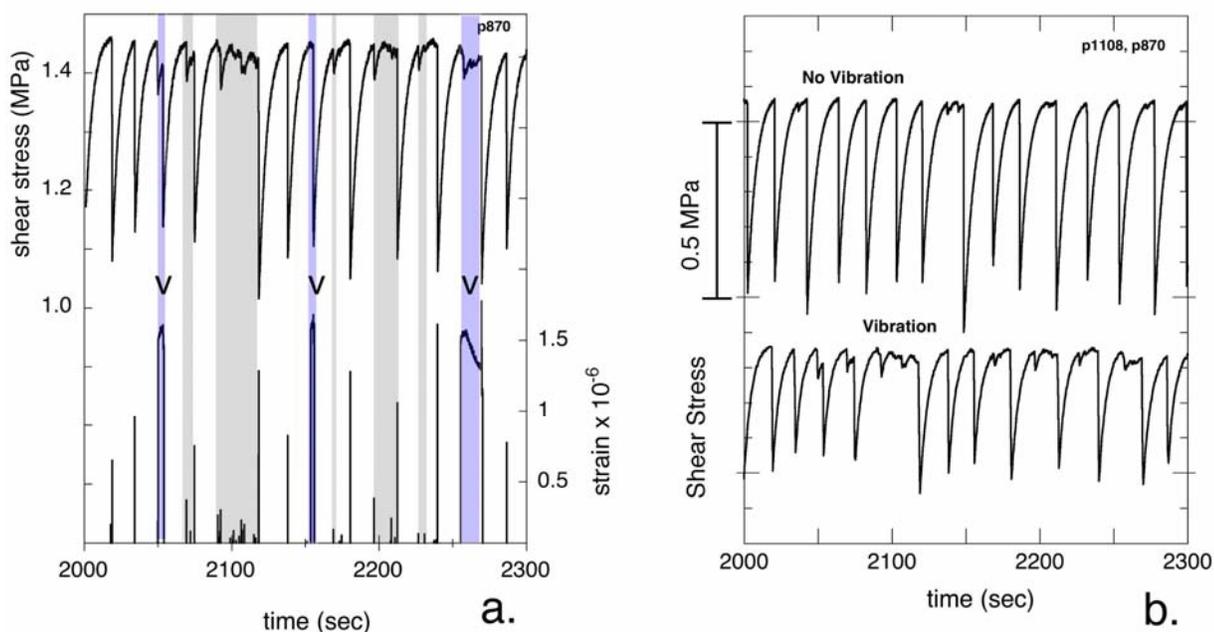
**Website:** <http://www.lanl.gov/orgs/ees/ees11/geophysics/nonlinear/nonlinear.shtml>

**Objectives:** We are studying the Nonlinear Nonequilibrium Dynamical (NND) properties of Earth materials with the goal of understanding the physics of nonlinear response in these materials and their application to a variety of earth processes. The topics of interest include the interaction of elastic waves with a fault in the Earth and in the laboratory. In particular, we are studying the phenomenon of dynamic earthquake triggering by elastic waves.

**Project Description:** In our work conducted over the last year we were attempting to understand the role of NND in dynamic earthquake processes, primarily the role in the phenomenon of dynamic earthquake triggering, by conducting laboratory studies of stick-slip. Dynamic earthquake triggering is the process whereby one earthquake causes others to take place, both nearby, in the form of aftershocks, but also at distance far from the originating earthquake. Remarkably, triggering has been interpreted to be delayed by minutes, days or weeks after the wave disturbance. The physical origin of dynamic triggering of earthquakes remains one of the least understood aspects of earthquake processes. We hypothesize that the dynamic, elastic-nonlinear behavior of fault gouge under disturbance by a seismic wave may be responsible for triggering. We base our hypothesis on observations of characteristics of the triggering process in natural systems, and laboratory dynamic-experiments of stick-slip conducted using granular media, a surrogate for fault gouge.

**Results:** To better understand the physics of dynamic triggering and the influence of dynamic stressing on earthquake recurrence, we conducted laboratory studies of stick—slip in granular media with and without applied acoustic vibrations. Glass beads were used to simulate granular fault zone wear material, sheared in a double-direct configuration under constant normal stress, while subject to transient or continuous perturbation by acoustic waves. We found that small magnitude failure events, corresponding to triggered aftershocks, occur when applied sound-wave amplitudes exceed several microstrain (see figure). These events frequently occur as part of a cascade of small events (delayed triggering). Vibrations also cause large slip events to be delayed significantly relative to those without wave perturbation. The effects are observed for many major-event cycles after vibrations cease, indicating a strain memory in the granular material. Vibration-induced disruption of periodic stick slip is linked to failure of granular force chains. Dynamic stressing of tectonic faults may play a similar role in determining the complexity of earthquake recurrence.

In summary, our results show that granular-friction processes are consistent with two of the most common observations in earthquake seismology: 1) small amplitude waves can trigger failure both immediately and delayed relative to the strain transient, and 2) earthquake recurrence patterns are complex. Understanding the role of vibration-induced disruption of earthquake recurrence could have significant implications for seismic hazard assessment and reliable interpretation and even forecasting of earthquakes.



**Figure:** (a) (top) Shear stress versus experimental time; (bottom) measured, rectified strain amplitudes of the detected acoustic waves for vibration experiments. Blue overlays show times and durations of vibrations (also denoted by “v”). Vibration has a marked influence on the stick—slip behavior. For instance the applied vibration at ~2050 sec produces an immediate, small-magnitude stick—slip. Two more major stick—slips follow where no vibration is applied, but they exhibit longer recurrence times as well as multiple small-amplitude failures in between—these are triggered events. Regions of triggered events are denoted in light grey. Similarly, irregular cycles occur following the applied vibration at 2155 sec. Vibration applied at ~2255 sec produces immediate stick—slip of a small magnitude event and an increased major—event recurrence interval. (b) Comparison of non-vibration versus vibration experiment showing increased recurrence and irregular behavior due to acoustic waves. P1170 & p870 refer to experiment numbers.

### Elastic Wave Effects on Colloid Interactions and Their Influence on Porous Fluid Transport

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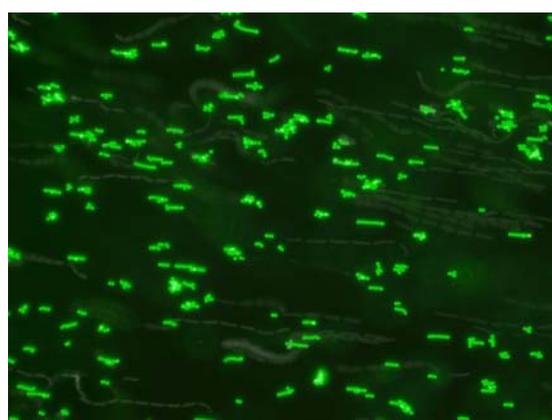
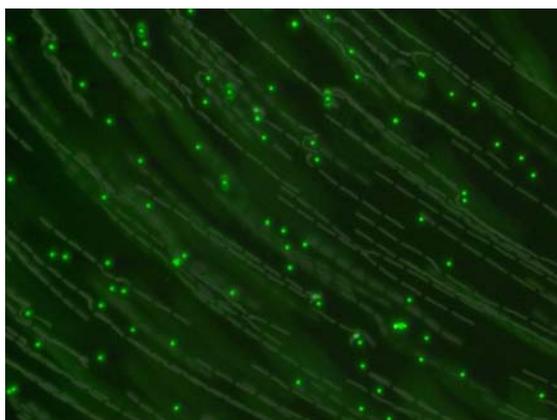
**Objectives:** The basic physics coupling stress waves to porous mass transport behavior is being investigated experimentally. The major goals are to 1) quantify the physical and chemical conditions under which stress waves influence porous fluid flow and sub-pore size (colloidal) particle transport, and 2) obtain improved experimental data that will be used to validate and quantify detailed understanding of physical mechanisms.

**Project Description:** This project is investigating how elastic waves can alter the transport of solid particles and immiscible liquids in porous media. Understanding this phenomenon will allow it to be harnessed for valuable applications, such as enhanced oil recovery and groundwater remediation. Of particular interest, the mechanism of elastic waves coupling to sub-micron particle (colloid) interactions

has been observed over a wide range of frequencies (roughly 10 Hz to 10 MHz). This mechanism can induce pore-scale colloid attachment and detachment at solid surfaces at frequencies within the range listed above, and the resulting induced redistribution of colloids in a porous matrix causes profound changes in permeability. Thus, this is an important mechanism influencing porous transport at larger scales (cm to km) as well. This project is focusing on understanding the physical, chemical, and dynamic-stress parameters that control colloid interactions with themselves (aggregation) and with solid surfaces (attachment and detachment), using advanced conceptual understandings, unique facilities and expanded capabilities developed during an earlier project. The scale dependence of these interactions is also being investigated. Microscopic colloid visualization and core-scale fluid and colloid transport experiments is being performed to accomplish this.

**Results:** Following on experiments performed in the DSSL in FY06, where Fontainebleau sandstone was injected with 1) a known suspension of 0.3-micron polystyrene micro-spheres in a solution of 0.1M NaCl, and 2) 1.0-micron microspheres suspended in deionized water (see FY06 report), a new experiment was performed where 1.0-micron microspheres suspended in 0.1M NaCl were injected into the same sample. The effects of low-frequency (10 to 100 Hz) stress oscillations on microsphere transport and core permeability were measured for all experiments. Background permeability during constant-rate flow through the core at 0.1 mL/min was measured from pressure-drop data, and production histories for microspheres released from the core were obtained by flow cytometer measurements of the effluent fluids collected. Cumulative results of these and earlier experiments indicate that low-frequency stress waves mobilize colloids and increase permeability when the trapping mechanism does not involve colloidal forces. Low ionic strength is required to detach colloids from pore walls, whereas hydrodynamic bridging of colloids at pore throats can be broken up at both low and high ionic strength. This result indicates that near-surface boundary layer (i.e., electrical double layer) forces are too strong for acoustically induced hydrodynamic forces to overcome. Particle detachment at high ionic strength may require a combination of acoustics coupled with AC electrical energy.

Microscopic visualization experiments were performed with AVMIDAS to study acoustically-induced colloidal particle behavior at very high frequencies (200-500 kHz) and at different acoustic powers and chemical conditions. Three distinct regimes of acoustically-induced particle behavior were directly observed and are being quantified: 1) aggregation via acoustic radiation (Bjerknes) forces, 2) entrapment via vorticular (Schlichting) microstreaming, and 3) entrainment via wavelength-scale Rayleigh streaming. These three types of behavior are shown in Figure 1 and represent important physical mechanisms whereby acoustic energy is capable of affecting colloid mobility and mass transport.



**Figure:** Time-lapse dynamic images showing the effects of 313 kHz acoustic energy on a suspension of 2.26-micron-diameter polystyrene microspheres suspended in deionized water (left) and 0.1 M NaCl solution (right). The field of view is 300 X 248  $\mu\text{m}$ . Rayleigh streaming is seen as faint dashed lines indicating microsphere trajectories. Schlichting microstreaming produces halos around immobile particles caused by elliptical orbiting of mobile particles. At high ionic strength, acoustics enhances aggregation by bringing microspheres close enough to each other that attractive Van der Waals forces come into play

## Summer of Applied Geophysical Experience (SAGE)

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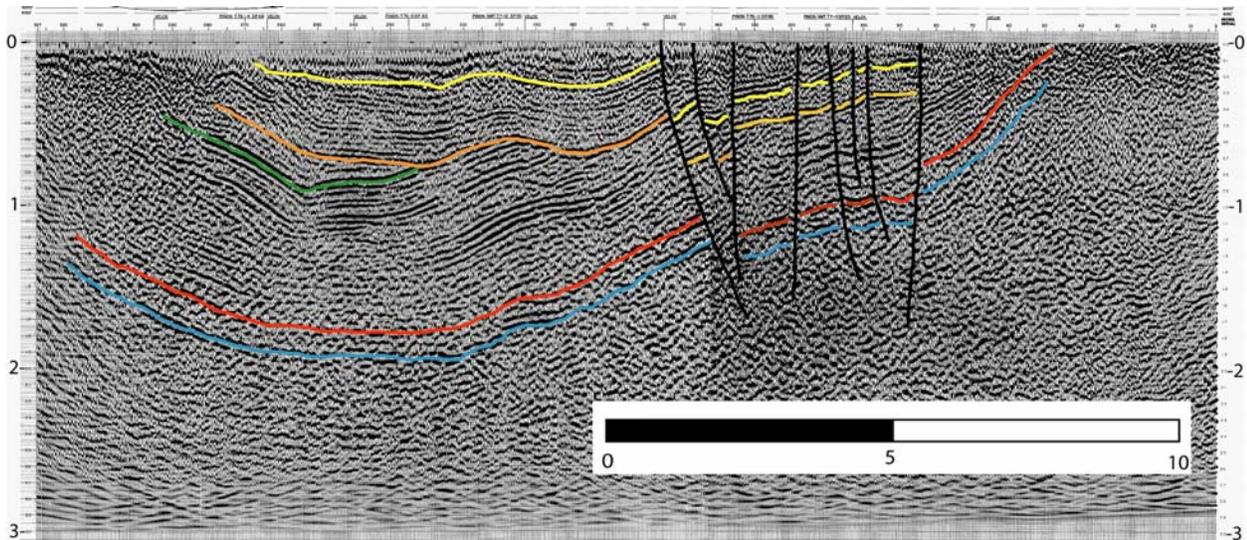
**Website:** [www.sage.lanl.gov](http://www.sage.lanl.gov)

**Objective:** SAGE provides (1) unique, hands-on training and research experience in basic and applied geophysics for 25-30 selected undergraduate- and graduate students (admission is on a competitive basis), (2) helps develop a broad, community-wide expertise in geophysics, (3) conducts leading-edge research with students on a variety of important problems, and (4) introduces students to a range of career options in the geophysical sciences. Results are expected to be important to a range of interests related to national security, including development of new energy sources, nuclear and non-nuclear waste disposal, environmental remediation, carbon sequestration, and basic research related to the structure and tectonics of continental extension.

**Project description:** The main project undertaken by SAGE 2007 was research in a new area related to the structure and stratigraphy of a complex “accommodation zone” separating two major faulted basins of the active Rio Grande continental rift. Questions being addressed by this work included the number and location of two poorly exposed faults, the Tano and West Tano faults, amount of offset along these faults, changes in offset along strike of the major La Bajada fault, geometry of relay ramps separating faults, timing of faulting, and the overall kinematics of the accommodation zone. The major methods used included seismic reflection and refraction obtained from a Vibroseis® survey, gravity, time-domain electromagnetics and controlled-source magnetotellurics, and integration with existing aeromagnetics. Six full-time faculty members from LANL and five universities, augmented by several other part-time faculty from a range of institutions and companies, instructed and supervised the students. Secondary objectives were to characterize the depth to the regional water table, and to study man-made structures and excavations using similar techniques as above (augmented by ground-penetrating radar and several EM methods) at an archaeological site. Due to the difficulty of obtaining approval to work at the Los Alamos National Laboratory, the archaeological site served as a proxy for a small-scale environmental-restoration waste-disposal site.

**Results:** Twenty six students from a wide range of large and small colleges and universities attended SAGE 2007. Participants successfully imaged subsurface strata in a new location on the downfaulted (west) side of a major north-trending, basin-bounding fault (La Bajada fault) separating the Española and Santo Domingo basins of the Rio Grande rift. The buried trace of the fault was imaged by SAGE 2005. By integrating SAGE data with proprietary industry seismic data, and building on SAGE 2005 and 2006 to correlate strata across the fault and into the basin, students in SAGE 2007 were able to determine basin shape in the field area and confirm that the vertical component of offset on the fault

exceeds 1 km. The field area is located on a northward dipping “relay ramp” adjacent to the La Bajada fault, probably with both vertical- and horizontal axis rotation. The La Bajada fault and adjacent, parallel faults (some of which are not exposed) constitute part of a northeast-trending “accommodation zone,” transferring offset laterally from the Española to the Santo Domingo basins and ultimately to the very deep Albuquerque basin of the rift. Strata on the east side of the La Bajada fault dip away from the fault zone by isostatic uplift and flexure of the footwall.



**Figure:** Migrated west to east seismic reflection section through the southern Española basin of the Rio Grande rift near Santa Fe, New Mexico, acquired by an industry survey in the 1970s. Faults are indicated as heavy dark lines. Dark orange line is the base of the Tertiary section; yellow is the base of the Espinazo Formation, a unit of particular interest as a possible aquifer. Scale bar is in kilometers. The interpretation shown here was done by SAGE faculty and students. The full lateral and longitudinal extent of the fault zone (shown right-of-center) extends beneath Santa Fe and is newly recognized by this work.

### The Uranium Decay Series at a Finer Scale

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**Objectives:** The goal of our work is to use improved U-series analytical capabilities to provide unique information on the behavior of U-series members in the environment. The emphasis is on processes that modify and alter the physical and chemical state of earth materials.

**Project Description:** Uranium-series disequilibria techniques are well-established and valuable tools for geochronology and geochemistry. Such measurements have in the past been made by decay counting; however, there are considerable advantages in using mass spectrometric techniques. The current work represents a mixture of follow-on's to our current efforts combined with new efforts to provide in-situ spatial resolution to U-series studies for geologic materials. Emphasis is on utilizing the multiple ion counting capabilities of the Isoprobe MC-ICPMS for laser ablation measurements. This

work provides information on the recent evolution of magmatic systems, human evolution, natural hazard risk assessment, climate change, and the carbon cycle.

**Results:** Our most recent work has focused on further development of U-series dating techniques for glacial ice, following our prior published studies of dusty polar ice in Antarctica. These results were presented at the 2007 Fall AGU meeting. We measured  $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$  disequilibria by mass spectrometric methods for a set of silty ice samples from the base of the GISP2 Greenland ice core, at a depth of 3040-3052 m. Samples consisted of 11 cm sections of ice core with sample weights of 340-430 g. The expected age of these samples is >150 thousand years (ka) based on counting ice layers. We separated the samples into several fractions by filtration and analyzed the < 0.05  $\mu\text{m}$  or “dissolved” fraction. This fraction had high U and Th concentrations (2.5-5 ppb U; 1.4-2.7 ppb Th). These U and Th concentrations are a factor of 1000 higher than measured for the “dissolved” ice at Allan Hills, Antarctica. Low Th/U atom ratios of 0.51-0.65 indicate that a large portion of the uranium present in the samples is truly dissolved and not associated with particles, which are expected to have Th/U ratios  $\sim 3$ . However,  $^{234}\text{U}/^{238}\text{U}$  activity ratios range from 0.972-0.992 (+/- 0.001), indicating a depletion of  $^{234}\text{U}$  relative to secular equilibrium of 1 to 3%. In addition,  $^{230}\text{Th}/^{234}\text{U}$  activity ratios are quite low (0.18-0.24), suggesting either recent  $^{230}\text{Th}$  loss and/or U addition to the samples. This recent Th/U fractionation is not consistent with a closed system age > 150 ka. Since liquid water would be characterized by  $^{230}\text{Th}/^{234}\text{U}$  activity ratios  $\ll 1$ , the low  $^{230}\text{Th}/^{234}\text{U}$  ratios likely indicate that recent melting/freezing event(s) have occurred at the base of the GISP2 core. We have modeled these results with a two component mass balance calculation, with dissolved and particulate pools for each radionuclide. Although several assumptions are required to calculate ages, results of these calculations suggest that the melting events may be as young as <10 ka. Our results are consistent with recent studies from Antarctica indicating the presence of large lakes beneath the W. and E. Antarctic ice sheets, as well as results from the nearby N-GRIP Greenland ice core in which drillers encountered active melting of ice near the basal contact with bedrock. However, further measurements of U-series disequilibria for the particulate pool are needed to verify the model and more precisely determine ages for these samples. Development of U-series dating techniques for glacial ice contributes to the general goal of establishing direct radiometric dating methods over the thousand year time scale for these types of samples, with many applications in glaciology and paleoclimatology.

### **Controls on Molecular-Scale Microbial Responses to Metals: Interactions of Bacteria, Metals and Environmental Nanoparticles**

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**Objectives:** This research effort is focused on determination of the mechanisms of microbially enhanced iron dissolution from iron-bearing minerals.

**Project Description:** Contrary to the current body of literature, the results of our experiments, discussed in this report, show that reductive dissolution is being used by an aerobic microorganism to acquire iron from Fe-bearing minerals. We show that the growth of *Pseudomonas mendocina ymp* on insoluble ferrihydrite is enhanced by exogenous reductants (ascorbate and cysteine). This enhanced growth was concurrent to increased soluble iron concentrations. *In vitro* experiments performed with the metabolites pyridine-2,6-bis(thiocarboxylic acid) (PDTC) and its carboxylic analogue pyridine-2,6-bis(monothiocarboxylate) (DPA) to examine the ability of these microbial metabolites to enhance the

dissolution of ferrihydrite revealed that these molecules dissolve iron oxide minerals by a mechanism that involves the reduction of Fe(III) to Fe(II) at the mineral surface. This work demonstrates the interplay between microbially produced reductants and siderophores in the dissolution of iron oxide minerals and the acquisition of Fe from Fe-bearing mineral phases.

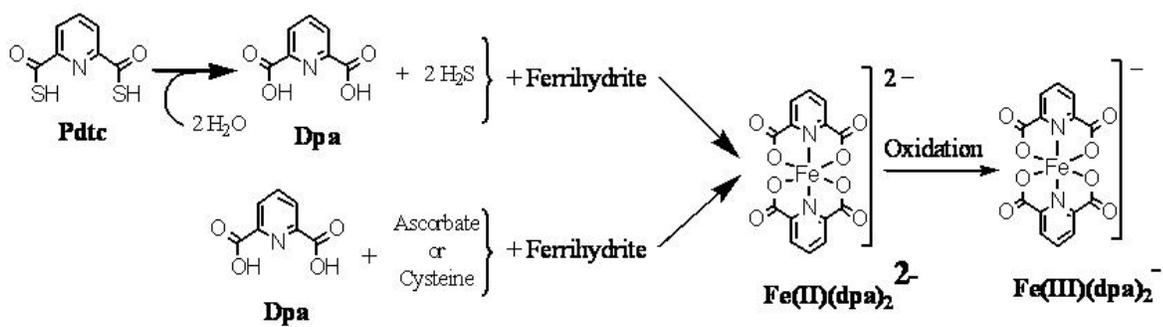
**Results:** We examined the effect of exogenous reductants on bacterial growth and iron mobilization from ferrihydrite. The bacterium used for this study, *Pseudomonas mendocina ymp*, was isolated as part of the Yucca Mountain Project from sediment in a surface holding pond of a drilling operation at the Nevada Test Site. Ferrihydrite used in these experiments was synthesized by precipitation with alkali according to methods described in the literature.

When ferrihydrite was the only source of Fe, microbial growth was observed that slightly exceeded that of the control with no iron. The total dissolved Fe analysis indicated the presence of some dissolved Fe in the media when *P. mendocina* was grown in ferrihydrite compared to the control. This observation clearly suggested Fe mobilization from ferrihydrite by the *P. mendocina*.

When *P. mendocina* was grown on ferrihydrite supplemented with external reductant a significant increase in growth and total soluble Fe was observed. The growth in these reductant supplemented media were only slightly lower than that seen when *P. mendocina* was grown in chelated Fe (67  $\mu$ M FeEDTA). A synergistic relationship between siderophores and reductants appears to be crucial to meet the microbial demand for Fe. This is the first study that shows the involvement of a reductant in environmental Fe(III)(hydr)oxide dissolution and illustrates the significance of reductants in iron mineral dissolution.

We also examined the mechanism of ferrihydrite dissolution by pyridine-2,6-bis(monothiocarboxylic acid) (PDTC) and its carboxylic acid analogue pyridine-2,6-dicarboxylic acid (DPA). PDTC was found to be efficient at dissolving ferrihydrite and the dissolution rate followed a saturation profile indicating that the mechanism of the iron mineral dissolution was controlled by the ligand binding to the surface of the mineral phase. DPA alone was unable to dissolve ferrihydrite, but the addition of small amounts of exogenous reductants (ascorbate, cysteine) significantly enhanced the dissolution rate. In the presence of exogenous reductants the rate of ferrihydrite followed a saturation profile similar to that observed for PDTC. The concentration of the reducing agent showed very little influence on the dissolution of ferrihydrite by DPA. This suggests the surface kinetics of ferrihydrite dissolution were strongly dominated by the interaction between the ferrihydrite surface and the ligand DPA, and not the reducing agent ascorbate.

MALDI-MS analysis of the final product of the dissolution experiments, showed a singly charged peak with a  $m/z = 386$  in the negative ion mode. This peak corresponds to the mass of singly charged Fe complex of DPA. This interesting observation suggests that the final dissolution product for the PDTC and DPA facilitated dissolution are identical, which is described in the scheme:



## OAK RIDGE NATIONAL LABORATORY

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PERSON IN CHARGE: D. Cole

### Nanoscale Complexity at the Oxide/Water Interface

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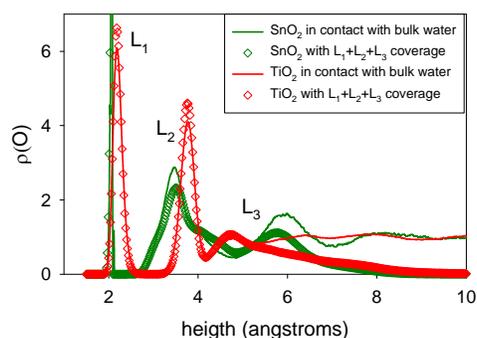
**Objectives:** We seek a complete understanding of the complex, nanoscale domain where crystalline metal oxides (including silicates) interface with aqueous solutions, over wide ranges of temperature and solution composition. Our goal is to quantitatively link atomic-scale structure and dynamics of interfaces with their macroscopic manifestations, including surface charging, ion adsorption, heterogeneous reaction kinetics and nanoparticle stability and transport.

**Project Description:** A multidisciplinary, multi-institutional effort (ORNL, Argonne National Laboratory, Vanderbilt University, Pennsylvania State University, University of Illinois) is working toward a quantitative understanding of the oxide-solution interface by coupling synchrotron X-ray and neutron scattering probes of atomic-level structure and dynamics; quantum mechanical and classical molecular dynamics simulations; experimental studies of surface protonation, ion adsorption and electrophoretic mobility; and macroscopic models of the electrical double layer (EDL) at charged interfaces, over wide ranges of solution composition and temperature. These highly-integrated efforts have been focused in recent years on the interface between aqueous solutions and the (110) surfaces of the isostructural phases rutile ( $\alpha$ -TiO<sub>2</sub>) and cassiterite ( $\alpha$ -SnO<sub>2</sub>), which exhibit modest differences in bulk and surface structures, but very different bulk dielectric properties, related to the polarizability of the valence electron orbitals of the crystalline substrate (rutile is much more polarizable). These properties of the substrate are hypothesized to exert a fundamental influence on the nature of ion adsorption (inner vs. outer sphere) and the reordering of solvent molecules near the interface.

**Results:** Synchrotron X-ray standing wave and crystal truncation rod studies on rutile and cassiterite (110) single-crystal surfaces, conducted at Argonne's Advanced Photon Source, have demonstrated significant differences in the distribution of sorbed water molecules within 1 nm of the interfaces with bulk water. These have been linked with extensive surface charging and ion adsorption studies (Rb<sup>+</sup>, Sr<sup>2+</sup>, Zn<sup>2+</sup>) on rutile and cassiterite powders with the the (110) surface predominant, as well as electrophoretic mobility studies in dilute NaCl solutions, over wide ranges of pH, temperature (10-250°C), and salinity. There is complete disruption of the bulk water structure at the interface, and the extent of dissociation of first-layer water molecules to form covalently-bonded surface hydroxyls is more extensive on cassiterite than on rutile. The Zn<sup>2+</sup> ion sorbs similarly on the two surfaces, binding as an inner sphere species at two distinct sites that are roughly equivalent to the lattice positions of Me(IV) atoms in the underlying structure. However, larger ions, like Rb<sup>+</sup> and Sr<sup>2+</sup> sorb at distinctly different sites, including inner sphere tetradentate (in contact with four surface oxygens) and bidentate sites unrelated to the bulk crystal structure. Outer sphere association Sr<sup>2+</sup> is also observed on both surfaces, but the tendency toward outer sphere sorption of these more weakly bound cations is much greater for cassiterite than for rutile. On both surfaces, increasing temperature favors inner sphere binding, a

response to the dropping bulk dielectric constant of the aqueous phase, while that of the crystalline surface remains essentially unchanged. During this period we also conducted extensive quasielastic neutron scattering (QENS) studies of the diffusional dynamics of water sorbed on rutile and cassiterite nanoparticles with the (110) crystal face predominant. These experiments were conducted using the disk chopper and high flux backscatter spectrometers at the NIST Center for Neutron Research, and using the newly commissioned BASIS backscatter spectrometer at ORNL's Spallation Neutron Source.

In **Figure 1**, the density profiles of oxygen atoms of sorbed water molecules extending outward from the crystal surface, obtained from our experimentally calibrated, and *ab initio*-optimized classical molecular dynamics (CMD) simulations of water in contact with both surfaces, are compared for a.) the case of bulk water in contact with an 'infinite slab' of the (110) surface, and b.) the case of reduced water coverage equivalent to the coverage of our QENS studies on hydrated nanoparticle surfaces. As can be seen, there is very little difference between the near surface structures, with the exception that for bulk water coverage, the water-oxygen densities rapidly decay to unit relative density, within 1 nm of the surface (i.e. bulk water structure), while the densities at reduced water coverage decay to zero over the same range. This highlights two remarkable aspects of this work, namely our optimized CMD simulations *predict* not only the level of water absorption from humid air at room temperature actually observed on our nanoparticle surfaces, but that the structure of the first and second absorbed water layers ( $L_1$  and  $L_2$ ) are essentially identical whether or not a bulk aqueous phase is present, and even the third sorbed layer ( $L_3$ ) is very similar. Furthermore, there are clearly differences in the nature of water sorption on rutile vs cassiterite, with a much thicker and more structured  $L_2$  and  $L_3$  on cassiterite.



**Figure 1.** CMD oxygen density profiles perpendicular to rutile (red) and cassiterite (green) (110) surfaces, showing three distinct structural layers,  $L_1$ ,  $L_2$  and  $L_3$ .

QENS takes advantage of the very large incoherent neutron scattering length density of the hydrogen atom, compared with nearly all other atoms, and the self-correlation of neutron scattering from the same atomic nucleus at different times, to reveal the picosecond to nanosecond translational and hindered rotational diffusion dynamics of hydrogen-bonded water molecules. We were able to quantitatively link the diffusional components of near surface water on our nanoparticle surfaces obtained from QENS with the trajectories of individual water molecules obtained from CMD simulations extending to >100 nanoseconds. Three distinct diffusional components were revealed, including local 'rattling' or hindered rotations of water molecules within nearest-neighbor cages in the 10 picosecond range throughout the interfacial region, faster picosecond coupled translational-rotational diffusion of  $L_3$  water molecules, related to their undersaturated hydrogen-bonding configurations, and a very slow, nanosecond, translational jump diffusion of  $L_2$  water molecules into  $L_3$ . The CMD simulations indicate an even slower diffusional component, in the 10s to 100s of nanoseconds, related to translations of  $L_1$  water molecules. We are currently linking inelastic neutron scattering studies and quantum mechanical molecular dynamics simulations (the latter using ORNL's leadership-class Cray XT-3 supercomputer) to investigate the vibrational dynamics and energetics of this strongly sorbed  $L_1$  water, and its influence on the thermodynamic stability and morphology of hydrated nanoparticles. Thus, we are poised to link molecular-level structure and dynamics with molecular simulations to fully model the thermodynamics and kinetics of oxide-water interface reactivity.

## Fundamental Research in Isotope Geochemistry: Experimental, Molecular-Based Simulation, and Neutron-Scattering Studies of Fluids and Minerals

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**Objectives:** The objective of this project is to address macroscopic –, molecular –, and atomic – scale aspects of isotopic effects and associated isotope fractionations in fluids and minerals under conditions relevant to earth and planetary sciences in general. Recent findings of the pressure and fluid-composition dependencies of isotopic fractionations have dramatically changed our view of what variables most influence isotopic behavior.

**Project Description:** Accurate quantification of macroscopic isotope fractionation and better understanding of fundamental causes of isotopic effects in fluids and minerals are very important. We investigate these fundamental issues, using a synergistic approach of theoretical, computational, and experimental methods, including neutron scattering techniques. A model mineral – fluid system, brucite [Mg(OH)<sub>2</sub>] – type minerals and simple molecular fluids (O<sub>2</sub>, CO<sub>2</sub>, and water, etc.), is investigated in depth, because these minerals and fluids serve as simple, yet useful analogs of more complex materials of geochemical interest. The specific goals are: (a) accurate laboratory determination of macroscopic isotopic fractionation between brucite – type minerals and water at high pressures (2 – 5 GPa), (b) molecular – based simulations and theoretical modeling for the isotopic effects of more complex molecular fluids, including water, and (c) advanced *in situ* neutron diffraction and scattering for D/H isotope effects on the structure and dynamics of brucite – type minerals at high pressures ( $\leq 10$  GPa).

**Results:** We developed an accurate, molecular-based method for calculating isotope fractionation along the liquid – vapor (L-V) coexistence curve of molecular fluids. Combining Gibbs Ensemble Monte Carlo (GEMC) and canonical molecular dynamics simulations (NVT-MD), we determined the L-V fractionation of simple homo- and hetero-nuclear diatomics (O<sub>2</sub>, N<sub>2</sub>, and CO), for which accurate intermolecular potentials and experimental data of their isotopic fractionations were available. The outcome was molecular-based expressions for the accurate prediction of isotopic fractionation, which is based solely on the measurement of either the squared-mean force or squared-mean torque obtained from neutron scattering approaches, thus avoiding entirely the need for extremely difficult measurements of volumetric phase equilibrium. Our simulation results agree quantitatively with experimental data in the literature. Our novel theoretical expression of a linear relationship between the mean squared forces and corresponding mean squared torques provides an opportunity to link molecular-based simulations and experimental determinations of the dynamic structure factors of molecules by a means of inelastic neutron scattering. We also characterized the recently proposed SPC-heavy water model *via* GEMC and canonical MD simulations for its capability to predict volumetric properties along the L-V boundary.

We have developed simple, yet accurate theoretical methods for calculating reduced isotope partition function ratios (RIPFR) at high pressures. The first approach requires only accurate equations of state (EOS) for pure isotopic end-members (H<sub>2</sub>O and D<sub>2</sub>O), which are available in the literature. In liquid and high-pressure (>20 MPa) supercritical phases, the RIPFR for hydrogen of water decreases (0.5 – 6 ‰) with increasing pressure to 100 MPa. These theoretical predictions on the RIPFR for D/H of water are consistent with our experimental data for the system brucite – water. The second method employs advanced corresponding-states principle for the development of the EOS of minor isotopologues, which

are usually unknown: D<sub>2</sub>O is an exception. The new formalism and equations were applied to H<sub>2</sub><sup>18</sup>O. Our results obtained from this novel CSP approach show that <sup>18</sup>O/<sup>16</sup>O RIPFR of liquid and supercritical waters increases about 1‰ with increasing pressure to 100 MPa. As for a combined effect of pressure and dissolved NaCl, a simple correlation method was developed for rationalizing our experimental results of combined effects of pressure and dissolved NaCl on brucite-water D/H fractionation at 380-400°C. The measured D/H fractionation shows a good linear correlation with the density of NaCl solution, and this relationship provide a simple interpolation and extrapolation method of the brucite-water D/H fractionation factor at elevated temperature and pressure.

A neutron diffraction study of brucite was initiated on both normal and deuterated compounds, using a Paris-Edinburgh high pressure cell (rated to 8 GPa). The objective is to determine the isotope effect on the lattice constants and unit cell volumes at high pressures. An initial test conducted in collaboration with ORNL neutron scientists at a neutron diffraction line (WAND) of High Flux Isotope Reactor (HFIR) of Oak Ridge National Laboratory was very encouraging.

### **Rates and Mechanisms of Mineral-Fluid Interactions at the Nanoscale**

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**Objectives:** The objective of this research is to advance our fundamental understanding of rates and molecular-level mechanisms of mineral-fluid reactions both near and far from equilibrium, over the full range of temperatures and compositions encountered in near-surface shallow crustal environments.

**Project Description:** Determination of the rates of dissolution-precipitation and isotopic exchange at variable departures from equilibrium will be coupled with a mechanistic description of the initiation of reactions at reactive surface sites. Detailed investigation of the formation of, and chemical communication across, leached layers and reaction zones, and the structure and dynamics of fluid species present in porous reacted solids will contribute to a more complete understanding of equilibrium/disequilibrium processes preserved in mineralogical record resulting from water-rock interaction. We will measure the rates of dissolution and precipitation near- and very-near equilibrium that utilizes our unique, high temperature, *in situ* pH measurement facilities. We will also interrogate the nature of porosity generation and its role in fluid transport and confinement in mineral reaction zones using advanced chemical and isotopic imaging approaches (e.g. secondary ion mass spectrometry, neutron scattering, and others) coupled with modeling and simulation.

**Results:** The dissolution/precipitation rates of boehmite, AlOOH, at 100.3°C and limited dissolution kinetics of gibbsite, Al(OH)<sub>3</sub>, at 50.0°C were measured in neutral to basic solutions at 0.1 molal (mol·kg(H<sub>2</sub>O)<sup>-1</sup>) ionic strength (NaCl) near equilibrium using a pH-jump technique with a hydrogen-electrode concentration cell. This approach allowed relatively rapid reactions to be studied from under- and over-saturation by continuous *in situ* pH monitoring after addition of basic or acidic titrant, respectively, to a pre-equilibrated, well-stirred suspension of the solid powder (an initial period of time was required for temperature stabilization and electrode response before the kinetics could be followed). The magnitude of each perturbation was small to maintain close to equilibrium conditions.

An experimental collaboration has continued with members of Penn State University's Center for Environmental Kinetics Analysis (S.L. Brantely and J.D. Kubicki, directors). CEKA Ph.D. student Michael Davis spent three months in our laboratories and we have investigated the equilibrium solubility and the very-near-equilibrium dissolution rates of quartz, SiO<sub>2</sub>, and forsterite, Mg<sub>2</sub>SiO<sub>4</sub>, in acidic and

basic NaCl brines from ambient conditions to 150°C using our unique high temperature pH measurement cells. We have demonstrated that both the equilibrium solubility and the dissolution rates of quartz in basic solutions can be determined without the need for sampling the solutions. However, unlike our boehmite dissolution kinetics study where only one aqueous phase was present, quartz dissolution yields two stable aqueous phases  $[\text{SiO}(\text{OH})_3^-]$  and  $\text{Si}(\text{OH})_4$  making the kinetics of dissolution more complex. The kinetics of forsterite dissolution suggest that initial leaching of  $\text{Mg}^{2+}$  by proton exchange is followed by expulsion of  $\text{H}^+$  due to polymerization of silica in the leached layer. This process was accompanied by formation of a minor secondary phase at the higher temperatures which we have recently interrogated with neutron diffraction experiments at NIST.

In concert with high transmission electron microscopy studies we have continued our application of SANS and USANS to interrogate the development of secondary porosity in natural materials, in this case weathered basalt clasts (with collaborators from PSU) and limestones that have experienced thermal alteration (with UTK). Results from the weathered basalts indicate the presence of micropores and mesopores with the former exhibiting surface fractal features whereas the latter exhibit mass fractal features. Similar fractal behavior was observed in the altered limestones.

The kinetics of the breakdown reaction dolomite = periclase + calcite +  $\text{CO}_2$  were investigated using cores of dolomitic marble. The samples were heated in a cold-seal hydrothermal apparatus to 650-750 °C at 100 MPa for durations ranging from 2- 59 days in the presence of  $^{18}\text{O}$ -enriched water. All experiments showed some amount of reaction regardless of duration or temperature. Reaction products occurred mainly along grain boundaries, fractures within grains, and along sample edges. Ion microprobe ion imaging and isotope-ratio analysis indicated that reaction products exchanged with infiltrating fluids. Reaction rates were calculated from measured extents of reaction, which were determined from automated EPMA modes. The extent of reaction is proportional to the square root of time, suggesting a diffusion-controlled process. A shrinking-core model for the dolomite breakdown reaction fits the grain-size data, suggesting that diffusion of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  through the mantle of reaction products controlled the rate.

While a great deal is known about the interaction between water and rhyolitic glasses and melts at temperatures above the glass transition, the nature of this interaction at lower temperatures is much more obscure. We conducted a new series of isotopic exchange experiments aimed at further elucidating this process and determining the extent to which a point-by-point analysis of the D/H or  $^{18}\text{O}/^{16}\text{O}$  isotopic composition across the hydrated rim on a geological or archaeological obsidian sample can be used as a paleoclimatic monitor. Experiments were performed by first hydrating the glass for five days in water of one isotopic composition, followed by five days in water of a second composition. Because waters of near end-member compositions were used (nearly pure  $^1\text{H}_2^{16}\text{O}$ ,  $^1\text{H}_2^{18}\text{O}$ , and  $\text{D}_2^{16}\text{O}$ ), the relative movements of each aliquot could be easily ascertained. Results suggest that, during hydration, both the isotopic composition of the waters of hydration, as well as that of intrinsic water present during the initial formation of the glass varies dramatically, and a point-by-point paleoclimatic reconstruction is not possible.

We used backscattering neutron spectroscopy to probe the dynamics of water molecules in LiCl and  $\text{CaCl}_2$  aqueous solutions confined in 2.7, 1.9, and 0.9 nm pores of various silica matrices. The pore size of 2.7 nm was found to be sufficiently large for the confined liquids to exhibit characteristic traits of bulk behavior, such as a freezing-melting transition and a phase separation. On the other hand, none of the fluids in the 0.9 nm pores exhibited a clear freezing-melting transition; instead, their dynamics at low temperatures gradually become too slow for the nanosecond resolution of the experiment. The mobility of water was suppressed the most in the  $\text{CaCl}_2$  solutions, indicating the influence of the cation charge on the dynamics of the water molecules. Quasielastic neutron scattering measurements of pure  $\text{H}_2\text{O}$  and 1

M LiCl-H<sub>2</sub>O solution confined in 1.9 nm pores revealed a dynamic transition in both liquids at practically the same temperature of 225-226 K, even though the dynamics of the solution at room temperature appeared to slow down by more than an order of magnitude compared to the pure water. The observation of the dynamic transition in the solution suggests that this transition may be a universal feature of water governed by processes acting on the local scale, such as a change in the hydrogen bonding.

## Isotopic Fractionation of Carbonate Systems Relevant to Subsurface CO<sub>2</sub>-Sequestration

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**Objectives:** The objective of this project is to understand and quantify several key reactions controlling kinetic and equilibrium isotope partitioning during the precipitation, recrystallization, and transformation of carbonate minerals (calcite, dolomite, siderite) in CO<sub>2</sub>-rich fluids at conditions encountered in various geologic settings (groundwater, deep aquifers, sedimentary basins, geothermal systems, etc.).

**Project Description:** This project is focused on: the mechanisms, rates, and isotope fractionation during three different reaction pathways leading to the formation of dolomite, the second most abundant carbonate mineral, as functions of several key variables (e.g., temperature, degree of supersaturation, ionic strength, microbial activity, inhibitor-promoter, etc.): (1) microbial and possible abiotic precipitation at low temperatures, (2) overgrowth of dolomite on seed crystals at intermediate temperatures, and (3) dolomitization of calcite and aragonite in Mg-rich solutions at intermediate to high temperatures. Microscopic- to macroscopic-scale measurement and characterization of solution chemistry and the solid phase will allow us to determine reaction mechanisms and rates as a function of time. Experimental results on oxygen and carbon isotope partitioning during the three different reaction pathways leading to the formation of dolomite will provide key information necessary for solving the “dolomite problem.”

**Results:** We have made a significant progress in determining the oxygen isotope fractionation of dolomite-water system over a wide range of temperature. Dolomite was synthesized by: (a) precipitation of protodolomite (no superstructure peaks with XRD) with the composition of Ca<sub>0.51</sub>Mg<sub>0.49</sub>CO<sub>3</sub> and a grain size of 15 nm from a mixed solution of MgSO<sub>4</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, and Na<sub>2</sub>CO<sub>3</sub> at 80°C, and (b) dolomitization of powder calcite or aragonite in Mg-Ca-Cl solutions between 100 and 300°C for durations up to 100 days. Recent literature studies of inorganic and microbial dolomite precipitation at 20-80°C (all protodolomite) and our new 80°C data of inorganic protodolomite are finally narrowing down the oxygen isotope fractionation factor between protodolomite and water at low temperatures. At 100 – 300°C, our data from dolomitization experiments are close to results by Matthews et al. (1977), rather than those by Northrop and Clayton (1966). A dolomitization experiment is currently underway up to 350°C. These new data finally start to constrain the isotope fractionation of dolomite at elevated temperatures.

To investigate the local atomic structure and cation order-disorder of sedimentary dolomite, we have initiated a neutron Pair Distribution Function (PDF) study of both natural and experimental dolomite. The neutron PDF technique is very useful for investigating both short- and medium-range ordering, using a total (Bragg and diffuse) neutron scattering. The conventional Bragg diffraction provides

information only on average, long-range ordering. Geologically young dolomite samples have excess Ca with no or weak ordering peak by XRD (protodolomite), while those of the Paleozoic and Mesozoic are nearly stoichiometric with clear ordering peaks by XRD. Neutron PDF analyses of the dolomite samples were conducted with the NPDF instrument at the Los Alamos Neutron Scattering Center (LANSCE) of Los Alamos National Laboratory, which is currently the best neutron PDF instrument in the U.S. A PDF and Rietveld refinement of the data for a hydrothermal dolomite show that the Ca and Mg sites are occupied 100% by each cation (well-ordered), and this sample serves as a reference. A Fe-rich natural dolomite show the Fe largely occupies the Mg site. A protodolomite synthesized at 80°C shows little ordering by PDF techniques as expected. Details of short- and intermediate-range ordering of these and other natural dolomites of varying ages started showing very exciting results of cation ordering. We also started a similar PDF study of pure magnetite and metal (Ni, Co, Zn)-substituted magnetite. First, a pure magnetite was hydrothermally synthesized at 600°C. Using a microbial process, copious amounts of nm-sized, single-domain, metal-substituted crystals of Fe<sub>3</sub>O<sub>4</sub> were precipitated at 25 and 60°C with varying amounts of Co, Cr, Mn, Pd, Zn, or Ni substituted into the structure. We have characterized these samples with laboratory XRD, and will soon characterize the local and medium-range distribution of these metallic elements in magnetite, using a PDF technique at LANSCE.

## PACIFIC NORTHWEST NATIONAL LABORATORY

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PERSON IN CHARGE: A. Felmy

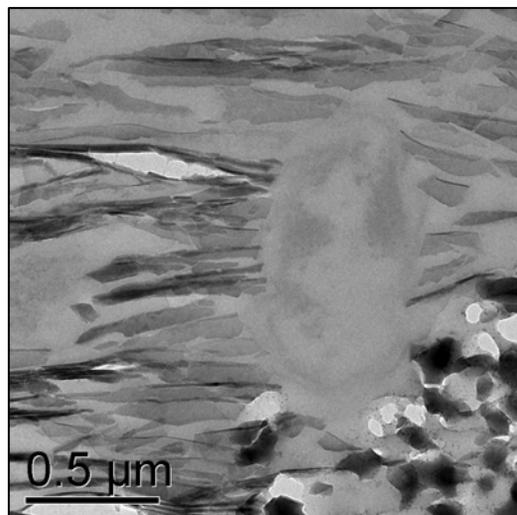
### Reductive Mineralization of Nanometer-Sized Fe(III) Oxides in Grain Coatings and Micropores

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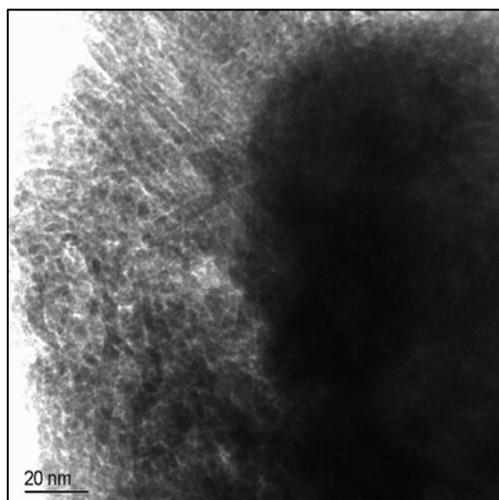
**Objectives:** Research is focused on the two following scientific questions. 1.) Can metal reducing bacteria induce the mineralogic transformation of nanometer-sized Fe(III) oxides that exhibit limited physical accessibility to whole cells, such as those that reside in microscopic fractures of lithic fragments or within the three dimensional matrix of a particle coating? 2.) Are mineral transformation pathways equivalent when the respiring cell surface does and does not contact the Fe(III) oxides undergoing reductive biomineralization?

**Project Description:** The research project is using batch suspensions of 2- and 6-line ferrihydrite and synthetic subsurface sediments where the ferrihydrite has been uniformly distributed within intragrain regions of nano-porous silica. Laboratory studies use static and dynamic-flow experimental systems with diffusible chemical reductants (ferrous iron, bioreduced anthraquinone disulfonate) and chemotactic iron reducing bacteria to evaluate whether microorganisms can access iron oxide electron acceptors in intragrain pores that are smaller than the nominal size of the cell, and to identify the nature of resulting reductive mineral products. Abiotic and biotic reduction kinetics are monitored in response to changes in experimental variables (electron donor to acceptor ratios, presence and absence of bicarbonate and phosphate), and variable temperature Mossbauer spectroscopy, conventional and synchrotron x-ray diffraction, micro-XANES spectroscopy, scanning and transmission electron microscopy, and atomic force microscopy are applied to identify reductant and microbe-induced changes to the Fe(III) oxides, and to identify the nature and properties of the product phases.

**Results:** The versatile iron-reducing microorganism MR-1 reduced intragrain Fe(III) oxides in the absence of direct contact with the outer cell envelope through the apparent production of an electron shuttle compound. This finding was unexpected because the primary biochemical agents responsible for electron transfer are believed to be anchored to the outer cell membrane, requiring both continuity with the intracellular electron transport system of the bacteria and direct contact with the Fe(III) oxide surface to be functional. Biogenic Fe(II) did not react with residual intragrain Fe(III) oxides, but diffused to the grain surface and precipitated as vivianite [Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>], often in association with microorganisms (Figure 1). Mineralization pathways were different when ferrihydrite was not localized to intragrain regions. Ferrihydrite intergrain contact, aggregation state, phosphate concentration, and Fe(II) generation/supply mechanism appeared to control whether lepidocrocite, goethite, magnetite, or other solids resulted as primary products. Mechanisms on transformation pathways and crystal growth are sought (Figure 2.)



**Figure 1.** Dramatic 10 μm-sized, radiant vivianite  $[\text{Fe}_3(\text{PO}_4)_2]$  precipitate clusters were observed on the surface of porous silica that resulted from the bioreduction of intragrain 6-line ferrihydrite. These curious precipitates were cross-sectioned by ultramicrotomy and imaged here by TEM. The porous silica is at the lower right and residual intragrain ferrihydrite appears as dark specks on and within the porous silica. Vivianite appears as horizontal plates that intersect the silica surface, often with microorganisms at their core. MR-1 is seen here as an elliptical shaped, 1 μm feature that invades the pores of the silica, and that is surrounded by vivianite plates.



**Figure 2.** High magnification transmission electron microscopic image of a reductive mineral transformation product of 2-line ferrihydrite that resulted from contact with aqueous Fe(II) for 24 h under anoxic conditions. Ferrous iron induces the rapid global recrystallization of ferrihydrite to single crystal lepidocrocite. The shown TEM cross section of a single lepidocrocite lath displays random and single crystal domains. Such results allow us to presumptively conclude that recrystallization results from highly localized dissolution-precipitation process in nm-sized internal pore spaces of randomly oriented ferrihydrite aggregates.

## Molecular Basis for Microbial Adhesion and Geochemical Surface Reactions: A Study Across Scales

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**Objectives:** The goal is to develop a molecular level description of the interactions of Gram-negative microbial membranes with subsurface materials. We are developing a better understanding of the molecular processes involved in microbial metal binding, microbial attachment to mineral surfaces, and, eventually, oxidation/reduction reactions (electron transfer) that can occur at these surfaces and are mediated by the bacterial exterior surface.

**Project Description:** The project is focused on the interaction of the outer microbial membrane, which is dominated by an exterior lipopolysaccharide (LPS) portion, of *Pseudomonas aeruginosa* with the mineral surfaces, such as hematite, and with solvated ions in the environment. It is a combined computational and experimental project (PNNL) that will enable us to generate new insights into the mechanisms of microbial attachment and validate the molecular models and computational approaches.

### Results: Molecular modeling of Lipopolysaccharides

In previous work, we have characterized the uptake of  $\text{UO}_2^{2+}$  by the LPS of *Pseudomonas aeruginosa* at neutral/slightly basic pH using potential of mean force thermodynamics integration methods. Upon uptake, the nuclide remained partly solvated at the LPS surface complexed by outer core carboxyl groups only. In contrast, experimental evidence shows that uranyl ions bind preferably to the phosphoryl groups, often also involving the participation of carboxyl groups. Interestingly all these experiments have been carried out in the pH range of 3 to 5. We have modified our LPS system to reproduce a slightly acid pH (ca. 3-5) and validated the new membrane structure against experimental data. The change in pH resulted in a lateral membrane expansion creating “water tunnels” making the phosphoryl groups of the LPS accessible (Figure 1). Molecular docking techniques (Figure 2) were used to probe

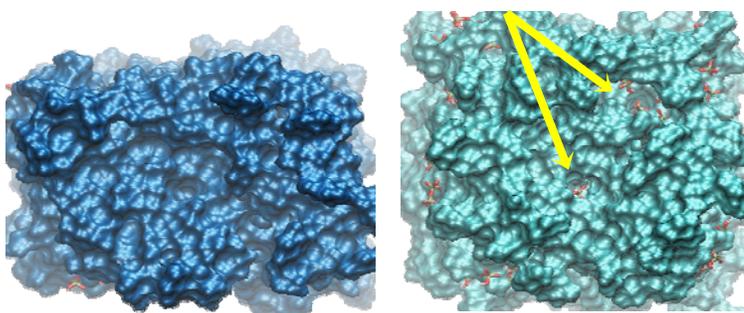


Figure 1. LPS membranes at slightly basic (left) and acid (right) pH. Membrane remodeling as a function of the pH provides accessibility to the Lipid A phosphoryl groups (shown in stick model and highlighted by yellow arrows).

the affinity of the between the LPS membrane at low pH and the uranyl ion. The results revealed the active participation of the phosphoryl groups in the complexation with  $\text{UO}_2^{2+}$  ions, where one uranyl ion may simultaneously coordinate to multiple groups in the LPS, including carbonyl groups.

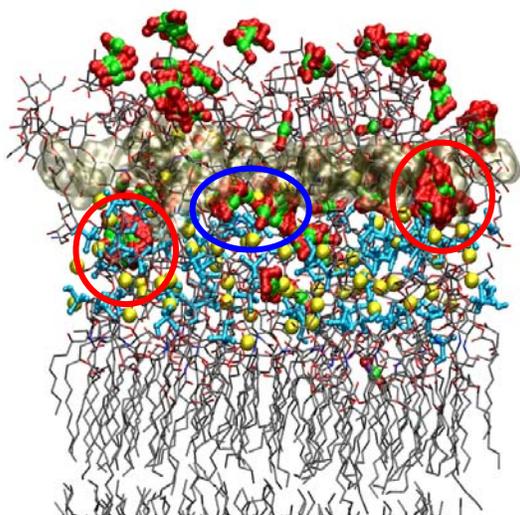


Figure 2. Docking of uranyl to the LPS membrane at low pH. The three clusters with lowest binding free energy are highlighted by circles. Lowest energy circle is shown in blue, where phosphoryl and carboxyl groups are simultaneously involved in the coordination to uranyl ions. Uranyl ions are represented in CPK model, where U: green and O: red. Carboxyl layer is shown in transparent brown surface and phosphoryl groups in blue sticks.

### *Electronic Structure Calculation*

Quantum mechanical methods have been used for the prediction of i) solvation energies and structures of ions in solution, ii) acidities of the critical groups in the sugars in the LPS, and iii) binding of metal ions to the sugar anions. An important aspect of the structure of the LPS membrane as well as ion transport in the LPS is the ability of the sugar side groups such as the carboxylic acids and the phosphates to bind positively charged ions. We have calculated the acidities of 4 critical sugars, one with a carboxylic acid, two with phosphoric acids, and one with three phosphoric acids. The first pKa of the phosphoric acid derivatives shows that these acids are stronger acids than phosphoric acid. This arises because of stabilization of the phosphate anion by internal hydrogen bonding. The second pKa for the two monophosphate derivatives makes them weaker acids than  $\text{H}_2\text{PO}_4^-$ . The second pKa of the triphosphate sugar shows that it is a strong acid. Thus, the triphosphate sugar will be doubly deprotonated under normal pH conditions and these results are being used to constrain the charge states in the molecular dynamics simulations. We have completed a similar study of the gas phase and solution phase acidities of glucose in the ring and acidic chain forms using the same approach as we developed for very strong acids.

## **Pathways for Redox Transformation of Semiconducting Minerals: The Iron Oxides**

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**Objectives:** This project aims to: 1) Determine chemical mechanisms for dissolution of specific surfaces of common electrically semiconducting minerals such as the iron oxides, 2) Establish linkages to overall macroscopic dissolution behavior, in particular for chemically and morphologically complex surfaces commensurate with those found in nature, and 3) Develop and apply analytical methods for quantifying complex surface morphologies in microscopic image data, and computational molecular methods for simulating dissolution dynamics of complex mineral surfaces.

**Project Description:** This project is a closely-coupled experimental and computer modeling study that focuses on characterizing the chemical pathways involved in the dissolution of iron oxide minerals. In

particular, this project emphasizes understanding the dynamics from initial well-defined surfaces to advanced stages of dissolution, and in linking this understanding to macroscopic behavior. This project fills gaps in knowledge of the dissolution rates and mechanisms for specific crystallographic surfaces where such information is typically only assumed. Mechanisms of iron oxide dissolution in particular entail a possible role for solid-state charge migration affecting the rate of growth and the resulting morphology of dissolution and growth features. This project relies primarily on surface-specific scanning probe microscopic observations and surface spectroscopic characterization in conjunction with molecular dynamics simulations, electronic structure calculations, and kinetic Monte Carlo simulations to help identify key mechanistic processes.

**Results:** In FY07, microscopic examination of the reductive dissolution of hematite (001), (012), (113), and (*hk*0) vicinal surfaces by Fe(II) in the presence of iron chelating ligands revealed that these crystals do not react as traditionally thought based on macroscopic measurements. Using a combination of electrochemical apparatus to measure surface potential differences, and atomic force microscopy to document surface morphologic changes, we discovered that under conditions of reductive dissolution, surface specific charge density accumulation reactions combined with bulk charge carrier diffusivity create conditions at which interfacial electron transfer reactions at one surface couple with those at another by a current through the crystal bulk. A chemically induced surface potential gradient across hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) crystals is sufficiently high and the bulk electrical resistivity is sufficiently low during reductive dissolution to link dissolution of edge surfaces to simultaneous growth of the basal plane. The finding is important in part because it is a new mechanism and in part because it demonstrates that traditional monitoring of dissolution rates using iron release rates into solution alone does not provide a sufficient basis for determining chemical mechanisms of dissolution. We are currently developing quantitative molecular models to simulate this mechanism.

### **The Influence of Mineral Surfaces on Multi-electron Reduction Mechanisms for Polyvalent Metals**

*Eugene S. Ilton, [Eugene.Ilton@pnl.gov](mailto:Eugene.Ilton@pnl.gov), Paul S. Bagus (UNT)*

**Objectives:** To better understand electron transfer reactions between Fe(II) in minerals and sorbed polyvalent metals such as U(VI). To develop *ab initio* models for the XPS and XANES of transition metals and uranium in order to help elucidate information on oxidation states and bonding environments.

**Project Description:** This project concerns reactions between minerals and toxic metal-bearing aqueous fluids. Specifically, we are exploring the mechanisms of oxidation-reduction reactions at the mineral-fluid interface involving reductants structurally bound in minerals. Key techniques used are electron microscopy, x-ray photoemission spectroscopy (XPS), and x-ray adsorption near edge structure (XANES). The project includes major theoretical efforts on the interpretation and prediction of XPS and XANES; the *ab initio* theoretical work is coupled to the experimental efforts.

**Results:** This year we demonstrated that U(V) is stabilized on the surface of magnetite after heterogeneous reduction of U(VI)aq. This extends our previous work on the interaction of U(VI)aq with ferrous micas and shows that U(V) can be stabilized on an iron oxide surface as well as on a phyllosilicates surface. Long term experiments showed that U(V) was stable for up to 2.5 months on the

magnetite surface. This is an important observation as the mica experiments that originally identified U(V) were only run for 20 hours. Further, we have obtained preliminary EXAFS results which are consistent with the XPS identification of U(V) on magnetite. EXAFS was performed with a wet paste and provides evidence that the XPS identification of U(V) is not an artifact of UHV conditions.

We extended our earlier studies on simulations of the 4f XPS for the free  $U^{4+}$  cation by calculating the U4f XPS spectrum of an embedded  $U(IV)O_8^{-12}$  cluster with the  $UO_2$  structure. While the main XPS features are similar in both cases, ligand field effects changed the multiplet structure in important ways that better simulated experimental data for  $UO_2$ . Neither initial nor final state covalency significantly reduced the 4f-5f exchange integrals; instead the differences between the atom and cluster model were due to ligand field splitting of the 5f band and increased distributions of intensity from XPS allowed to XPS forbidden peaks. The prominent 7 eV satellites associated with  $UO_2$  were absent in the simulations, which provided further evidence that these satellites are due to charge transfer and not other interatomic effects. In current work we are incorporating charge transfer (CT) configurations into the model. It is expected that these CT satellites will be sensitive to both the oxidation state and bonding environment. For additional theoretical results see the report from the University of N. Texas.

### **The Impact of Carbonate on Surface Protonation, Electron Transfer, and Crystallization Reactions in Iron Oxide Nanoparticles and Colloids**

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**Objectives:** The goal is to understand at the molecular level the formation of aqueous carbonate species and their interaction with iron and aluminum oxyhydroxide surfaces which have a high affinity for such species. The interaction of carbonate, bicarbonate, and  $CO_2$  with these materials is highly relevant to the development of processes to sequester  $CO_2$  in the subsurface in order to mitigate its impact on the environment. The isotope fractionation of  $CO_2$  and related species in the gas, aqueous and solid states is a key method to determining the  $PCO_2$  in the atmosphere over geological time scales.

**Project Description:** The experimental component of this research effort was designed to provide insight into the mechanisms through which aqueous carbonate ions are incorporated to the bulk of iron oxyhydroxide nanoparticles. We synthesized such particles by exposing aqueous solutions of ferric iron to various levels of  $PCO_2$ , pH and temperatures. The resulting particles were studied by Temperature-Programmed Desorption (TPD) and Fourier Transform Infrared (FTIR) spectroscopy to follow the sequential desorption of surface- and bulk-bound carbonate with temperature.

**Results:** The TPD-FTIR experiments enabled a clear distinction between surface- and bulk-bound carbonate in the iron oxyhydroxide particles. Experiments at large (>mM) carbonate concentrations inhibited the condensation of iron oxyhydroxide nanoparticle precursors to larger amorphous or crystallized particles. The resulting precipitates exhibited usually large fractions of interstitial water that were even resilient vacuum pumping in the TPD chamber. These particles exhibited a substantially different TPD profile than for pure goethite, which we studied in the previous year, with a notably strong dehydration peak that is concomitant to the release of both surface- and bulk-bound carbonate. Interestingly, carbon monoxide and formic acid were also formed, potentially suggesting a catalytic-like formation of these compounds by these particles, unlike the case of goethite. Finally, the mass spectrometric analysis of the  $^{13,12}C$  isotopes of  $CO_2$  throughout the TPD experiments provided an

estimate of the isotopic fractionation ratios to the solid phase. These results are currently being connected with the concurrent computational efforts of this research team.

## **First Principles Simulation of the Temperature Composition and Pressure, Dependence of Natural Fluids**

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**Objectives:** To address the problems associated with future energy strategies a much more quantitative, parameter-free interpretation of elementary geochemical processes will be required. In this program, new 1<sup>st</sup> principles simulations methods are being developed and applied to the study of the chemical behavior of metal ions, their counter ions and their oxo-hydroxo hydrolytic polyions in aqueous solutions. The understanding of the aqueous chemistry of these species is essential to the interpretation of processes such as the formation of minerals, the sequestration of CO<sub>2</sub>, the storage of nuclear waste, and the transport of toxic materials. The 1<sup>st</sup> principles based simulation methods that are being used and developed in this program allow the parameter-free prediction of the properties of these chemically complex materials over the wide range of conditions encountered in geological applications. Because of the 1<sup>st</sup> principle nature of these methods, they have very general application to the interpretation of many complex materials of interest to the BES community. In this program, special effort is being made to develop new simulation methods that will be able to exploit the full capabilities of emerging massively parallel computers and allow the simulation of new classes of materials.

**Project Description:** The results of this research will contribute to the molecular level understanding of the chemistry of processes such as ore formation, toxic species transport, mineral solubility, and absorption on mineral surfaces for sub-critical to supercritical conditions as well as provide for the more detailed analysis of the new classes of experiments such as high resolution NMR, X-ray absorption fine structure, sum frequency vibrational spectroscopy, high resolution x-ray and neutron scattering, photoelectron spectroscopy, etc., that are being used to study fundamental geochemical processes at the molecular level. Since for many of these problems the appropriate simulation methods and implementations are not yet available, an important strength of this program is our ability to develop and efficiently implement new parameter-free methods of simulation. The metals included as application targets in this research, Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Ca<sup>2+</sup>, and Ni<sup>2+</sup>, are chosen because of their geochemical importance and because they display a wide range of properties such as very different hydrolysis constants, ligand residence times, and formation of oxo-hydroxo hydrolytic polyions. In this research we endeavor to relate the properties of the ions to their chemical behavior in geological applications. The program is carried out through the very close collaboration of researchers at PNNL (co-PI Eric Bylaska) and UCSD (PI John Weare). The researchers in these two institutions collaborate in both the methods development and application aspects of the program. Collaboration is enhanced by the frequent visits of the PIs and their co-workers, the graduate students and postdoctoral students in the program to both institutions. While the closeness of the collaboration makes it difficult to assign tasks, there is more emphasis on methods development at PNNL and on chemical application at UCSD. However, every student in the program will participate in some aspect of methods and software development and in application simulation.

## Applications Results: See UCSD report (PI John Weare)

**Methods Developments Results:** Full *ab initio* molecular dynamics (AIMD) simulations are expensive and for many problems compromises must be made in the number of particles to make calculations feasible. Even though the advent of peta-scale computing, along with advances in computation algorithms, is allowing the simulation of hundreds atoms routinely, considerably larger particle numbers than is currently feasible need to be used to treat some problems such as the Al<sub>13</sub> oligomer. Fortunately, most of the problems that we are focused on are heterogeneous in the sense that there is a region of direct interest which typically has very complicated dynamics (e.g., the ion and most of the solvation region) and a much larger region in which the details of the molecular interactions are not expected to play a decisive role. For such problems QM/MM methodology offers an attractive and computationally efficient way to extend the particle scale (length scale) of AIMD simulations. QM/MM approaches based on local (e.g., GTO's, STO's) basis methods have been used for some time. However, the majority of existing calculations is limited in scope and focus to the structural optimizations of few specifically chosen states along a proposed reaction pathway. This is because the inclusion of dynamics into QM/MM simulations is determined by the efficiency of the dynamical calculation in the quantum region.

We have developed an efficient QM/MM method based on AIMD. The initial implementation of this method is general enough to include CLAYFF force field developed by Cygan *et al.*. This new development has been included in the latest release of NWChem, a quantum chemistry program package developed at PNNL. This method couples our efficient plane wave solvers of Density Functional Theory for the QM region to a molecular mechanics description of a larger region. The major difficulties with implementation QM/MM based on AIMD is the computational work involved with the calculation of the Coulomb integral over the charge density and the difficulty of charge spillover created as the electronic wave function tries to interact with the point charges outside the QM region. The spill over problem comes from the unrealistic use of point charges and the neglect of electron exchange repulsion in the MM region. These problems can be particularly difficult for a plane wave based method because the basis is very flexible. However, it can be treated by replacing the 1/r potentials of the point charges in QM/MM interaction with a representation which includes a short-range repulsion.

$$\frac{q_M}{|\mathbf{r} - \mathbf{R}_M|} \rightarrow \frac{\left( q_M |r_c^{n_\sigma+1} + q_M |\mathbf{r} - \mathbf{R}_M|^{n_\sigma} \right)}{\left( r_c^{n_\sigma+1} + |\mathbf{r} - \mathbf{R}_M|^{n_\sigma+1} \right)}$$

Using this method we have been able to show that this model is at least a 100-1000 times more computationally efficient than full AIMD simulations. For example, a UO<sub>2</sub><sup>2+</sup>+122H<sub>2</sub>O simulation takes ~10 seconds per step with 256 processors using our AIMD program, while for the QM/MM program this simulation can readily be run on a single processor.



Figure 1: Snapshot of a QM/MM AIMD simulation (QM region: UO<sub>2</sub><sup>2+</sup>+5H<sub>2</sub>O, MM region: 117 H<sub>2</sub>O).

## SANDIA NATIONAL LABORATORY/ALBUQUERQUE

CONTRACT: AL85000

PERSON IN CHARGE: J. Merson

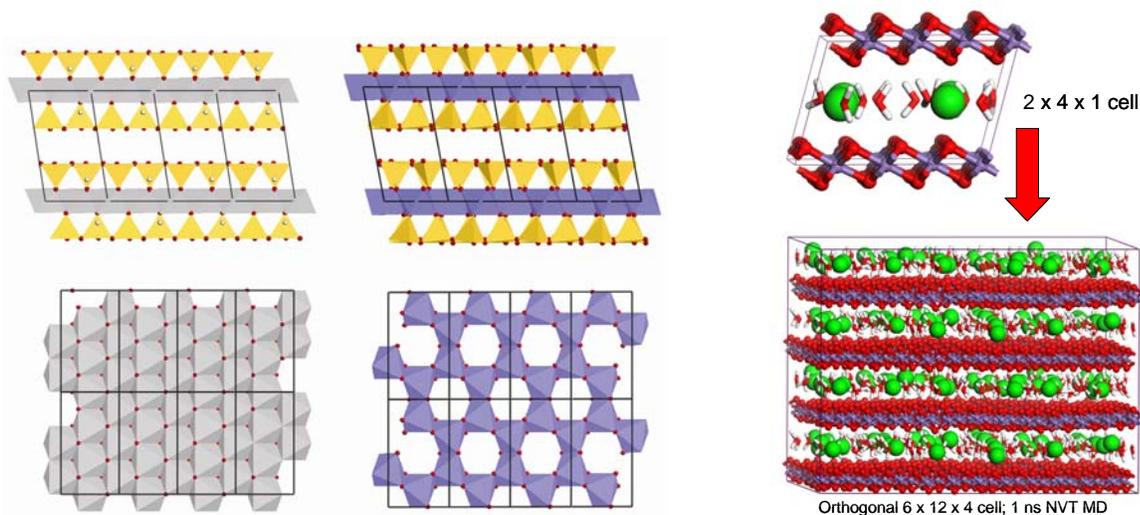
### The Nature of the Mineral-Water Interface: A Molecular Simulation and Spectroscopic Investigation

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**Objectives:** Development of computational tools for the accurate simulation of environmental processes, specifically those involving aqueous interactions with layered nanomaterials that are difficult to evaluate using conventional analytical methods. Classical and quantum simulations, along with synchrotron and specialized diffraction methods, are used to evaluate interfacial structure and dynamics of selected oxide, hydroxide, and aluminosilicate systems.

**Project Description:** In coordination with synchrotron and specialized diffraction methods, we are expanding our efforts in molecular simulation to address the atomistic behavior of the mineral-water interface. Specifically, we are investigating layered mineral systems which have received special scientific interest and widespread technological application because of their enormous surface area and strong interactions with aqueous phases and solutes. Basal and edge surfaces provide contrasting internal and surface environments that affect mineral reactivity and hydration. We are developing a second-generation energy force field for classical simulations of interfacial phenomena in mineral-water systems. These improvements will aid in the interpretation of vibrational spectra, and the addition of polarization effects in our force field will help understand the nature of the adsorption process. We are also examining the intercalation of various biomolecules in layered double hydroxides, and a combined simulation and spectroscopic study of the heterovalent manganese oxide mineral birnessite that plays a significant role in controlling heavy metals in the environment.

**Results:** The structural and vibrational properties of two uncharged phyllosilicates, talc and pyrophyllite, were investigated using quantum and classical molecular dynamics simulations. The electronic structure simulations are based on plane-wave pseudopotential density functional theory (DFT), which is shown to be sufficiently accurate in predicting the clay mineral structures and vibrational properties. The classical molecular dynamics (MD) simulations, using the CLAYFF force field, faithfully reproduce the crystal structures with relatively simple analytical functions that include primarily non-bonded interactions. The adsorption properties in these clay minerals are strongly dependent upon the disposition of the hydroxyl group in the octahedral sheet. With the assistance of molecular simulation, we explored the relationship between hydroxyl group vibrational modes and the molecular-scale structure. Overall, a detailed comparison between the *ab initio* and classical MD structural and vibrational properties provides guidance for future refinements to the empirical force field. The CLAYFF force field was also used to perform large-scale MD simulations of several birnessite minerals. The unique exchange and adsorption properties of birnessite ( $\text{NaMn}_4\text{O}_8 \cdot n\text{H}_2\text{O}$ ) are structurally related to the charge layer structure and the coexistence of heterovalent manganese in the edge-sharing octahedral layer.



Crystal structure models for trioctahedral (Mg) talc and dioctahedral (Al) pyrophyllite (left) and the expanded simulation cell for Na-birnessite (right).

## Metal-Anion Pairing at Oxide/Water Interfaces: Theoretical and Experimental Investigations from the Nanoscale to the Macroscale

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**Objectives:** The objectives of this research are to develop an approach for predicting the types of metal surface complexes that form on mineral surfaces by focusing on the role of metal-anion complexes, and to incorporate these surface complexes into thermodynamic surface complexation models to predict adsorption behavior.

**Project Description:** We combine the use of several techniques including bulk adsorption experiments, X-ray absorption, infra-red, and vibrational sum frequency spectroscopies (XAS, IR, VSGS), and molecular modeling to investigate ion-pairing in solution and at mineral surfaces. XAS provides data on how the metal binds to the surface (e.g., monodentate, bidentate), IR provides data on ion-pairing in aqueous solution, and VSGS provides data on the impact of adsorbed metal-anion pairs on water structure at the mineral surface. Molecular modeling will be used to guide spectroscopic data interpretation by providing information on water structure around ions in solution and the structure of metal-anion complexes in aqueous solution. In addition, molecular modeling can be used to provide insight into water structure at mineral surfaces, the surface sites involved in ion adsorption, and the distribution of ion pairs between aqueous solution and the mineral surface. Our studies have focused on systems involving alkaline earth metal ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ) and heavy metal ( $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ ) cations. The anions we have selected for study include  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{SeO}_3^{2-}$ . Ion adsorption and the potential formation of ternary complexes on silica (quartz, amorphous silica), alumina (corundum and gibbsite), and ferric iron (goethite) oxides are under investigation.

**Results:** Potential of mean force (PMF) calculations for the aqueous ion pairs  $\text{MgCl}^+$ ,  $\text{CaCl}^+$ ,  $\text{SrCl}^+$ , and  $\text{BaCl}^+$  were performed using a flexible SPC water model in combination with the ion-water potentials of Åqvist (1990) for the alkaline earth metals and Dang et al. (1990) for  $\text{Cl}^-$ . Association constants were determined from the PMF results and compared to the experimentally-derived association constants from Majer and Stulik (1982). These calculations give rise to a trend of increasing association with increasing metal ion size that is the opposite of the experimental trend. Surface PMF calculations were also performed between each alkaline earth metal cation and the neutral gibbsite basal surface. The free energy curves suggest that these metal cations prefer to form outer-sphere surface complexes because of large activation energy barriers associated with the removal of water molecules in the cation hydration sphere. Free energy curves for the aqueous ion pairs  $\text{MgNO}_3^+$ ,  $\text{CaNO}_3^+$ ,  $\text{SrNO}_3^+$ , and  $\text{PbNO}_3^+$  support infra-red spectroscopic observations in Allen's laboratory (OSU) regarding the preference for each cation-nitrate combination to form contact ion pairs, solvent-shared ion pairs or solvent-separated ion pairs. With Wander (SUNY), dielectric constant profiles were calculated for three goethite (110) surfaces (charge positive, negative, and neutral) in aqueous solution. These profiles show that an electric double layer forms at the interface due to water dipole orientation alone. They also exhibit clearly defined structured and diffuse layers in which the dielectric constant of water ranges from 45-80. Triple-layer model fits to experimental data for the adsorption of  $\text{Sr}^{2+}$  on amorphous silica and goethite were successfully accomplished with Carroll (LLNL) using tetradentate and monodentate  $\text{Sr}^+$  and  $\text{SrOH}^+$  complexes.

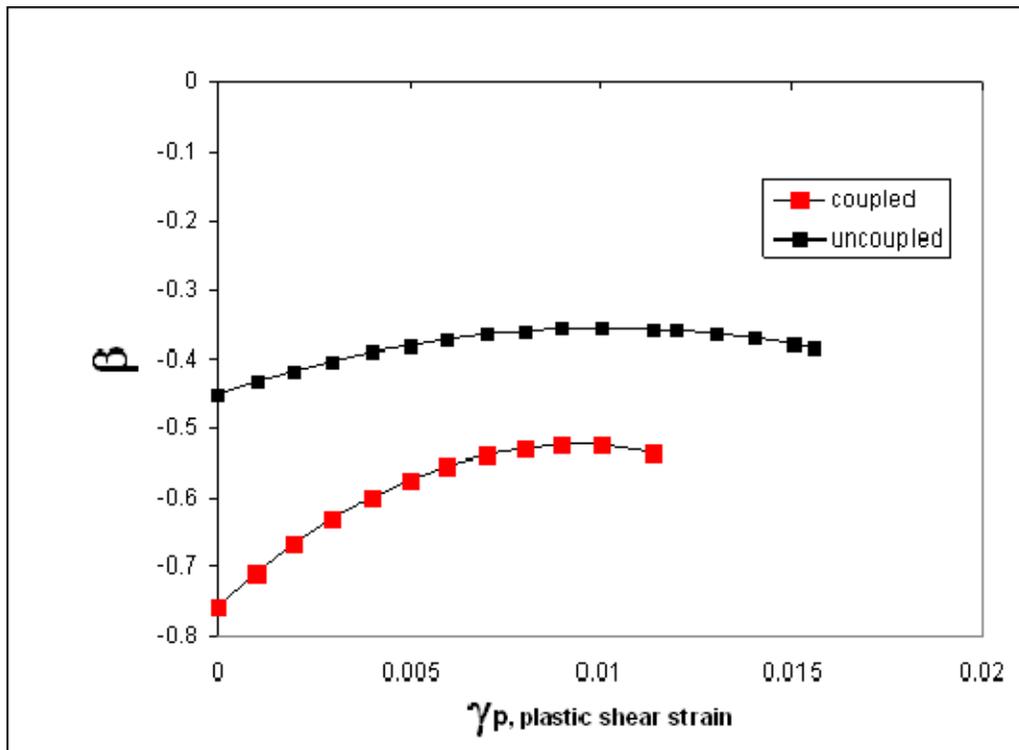
### **Approaches to Some of the Outstanding Problems in the Heterogeneous Compactive Deformation of Geomaterials**

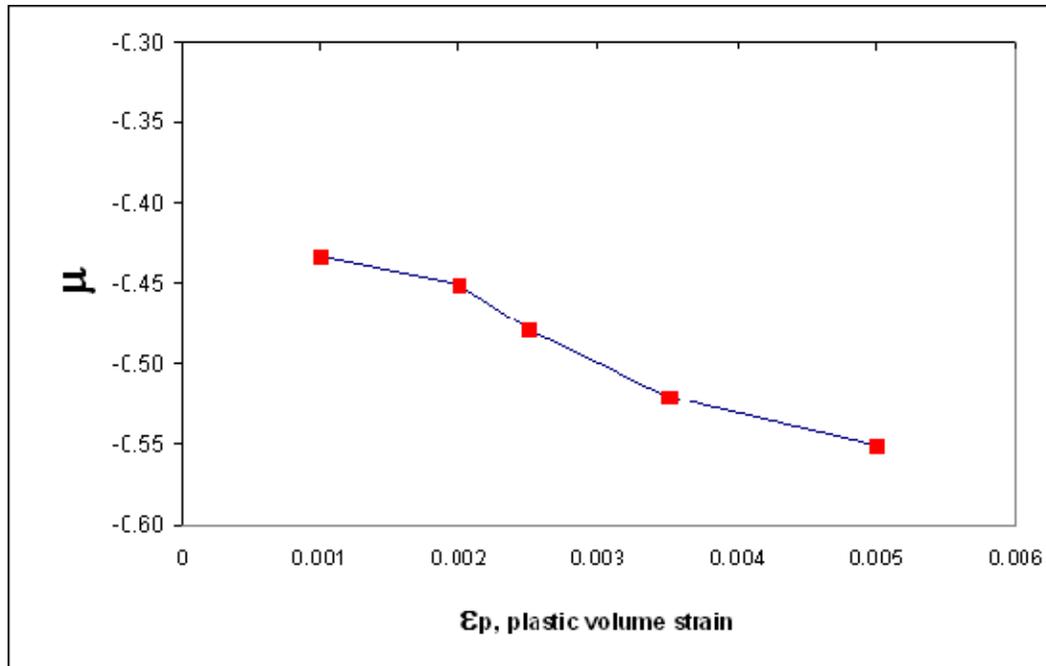
*William A. Olsson (retired 6/2006), David J. Holcomb ([djholco@sandia.gov](mailto:djholco@sandia.gov), 505-844-2157), John W. Rudnicki, Northwestern University*

**Objectives:** Many porous materials, including some sandstones, exhibit compaction localization, a bifurcation from homogeneous compaction to localized compaction under non-hydrostatic stresses. Compaction localization in porous rock is potentially of importance to industries dependent on extraction or injection of fluids into porous reservoir rocks. Our goal is to elucidate the micromechanical properties responsible for compaction localization.

**Project Description:** We are furthering this goal by seeking answers to the following questions (1) what are the connections between the various observed modes of localized compaction, (2) why do some porous rocks exhibit localized compaction while other, similar, rocks do not, (3) what controls the propagation modes and (4) which mode or modes are appropriate for describing propagation of compaction bands in geologic settings? We are approaching these questions by focusing on two areas: underlying mechanisms and propagation conditions. To gain some insight into these problems, samples of known, uniform, grain size distributions of St. Peter sand will be deformed in multiaxial compression to investigate the role played by grain size distributions in determining the occurrence of compaction localization in sand. Acoustic emission data will be used to study micromechanisms by examining focal mechanisms and energies of the grain-scale failures associated with compaction in sandstones and unlithified sands.

**Results:** Our efforts for FY07 concentrated on the analysis of an extensive body of experimental data to produce a consistent picture of the evolution of the constitutive parameters for a sandstone that exhibits shear and compaction localization. A correct computation of the parameters  $\beta$  and  $\mu$  requires separating the observed strains into components resulting from elastic processes and plastic process. Elastic moduli of rock evolve with plastic strain and are also changed by elastic processes, such as crack closure. Therefore separating the strain components necessitates the development of a complete model of the moduli evolution, accounting for the inelastic increment of strain due to modulus evolution and the stress-induced modulus changes. The data set consisted of about 30 triaxial tests conducted under either constant mean stress, constant shear stress or constant pressure, with numerous unload loops to determine elastic moduli. The entire stress space available to compressional loading was sampled by the tests. Results from the analysis showing the evolution of  $\beta$  and  $\mu$  for one test are shown in the figure. Note in particular the top figure comparing  $\beta$  calculated by properly accounting for the modulus evolution (red squares, coupled) with the values calculated using only the starting values of the moduli. The differences are large and sufficient to substantially change the predicted localization conditions. The significance of this work is that it provides the most complete data set available of the parameters used in the standard constitutive models used to study localization in porous rock.





### Quantifying the Micromechanical Effects of Variable Cement in Granular Porous Media

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**Objectives:** (1) To quantify grain-scale physical effects of variable cement quantity, composition, and location on the elastic and inelastic deformation of granular porous media.  
 (2) To use the resulting understanding of the fundamental micromechanical processes that govern macroscopic deformation to accurately capture meaningful grain-grain interactions in Discrete Element Model (DEM) simulations.

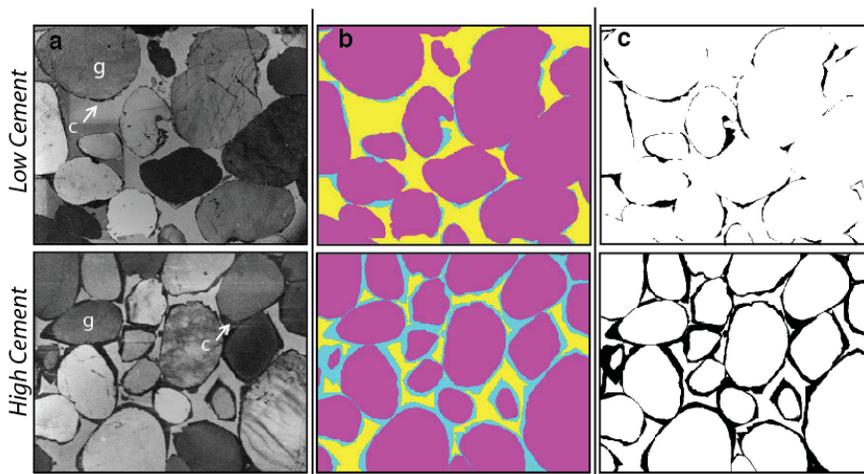
**Project Description:** The project scope requires us to develop methods of appropriately small-scale experimental deformation and structural characterization of granular porous media. We chose to work with both *natural* and *synthetic* grain-cement systems using novel approaches that provide insight into grain-scale mechanics. We will:

- 1) Develop methods for fabrication of synthetic assemblages of soda-lime silicate beads and both sodium silicate and calcium carbonate cements.
- 2) Design apparatus to test mechanical properties of synthetic grain-cement assemblages. Use nanoindentation to probe properties such as elastic modulus, hardness, and plasticity of grains and cements in both natural and synthetic systems. Use ultrasonic velocity and uniaxial deformation experiments to characterize variably cemented natural sandstone.

3) Integrate microstructural and experimental analyses to relate physical elements of progressively cemented natural and synthetic systems to their structural response to stress.

4) Develop quantitative relationships describing the stress-strain response of cemented granular systems and incorporate microscale material response into a DEM.

**Results:** Current understanding of the impact of cement on the mechanical response of granular porous media is largely based on a widely accepted conceptual model of a circular cement “bridge” between two grains. Our observations and literature review indicate, however, that this meniscus-type cement geometry is uncommon in natural materials. The UW group has therefore focused on designing an approach to quantitatively characterize, and determine the mechanical impact of, natural cement morphologies. Because quartz is the most common cement in siliciclastic sediments, our work has focused on the St. Peter Sandstone, a well sorted, quartz-cemented quartz arenite. The St. Peter exhibits considerable variation in cement abundance, with typical quartz overgrowth geometries. Quartz cement morphology changes with progressive cementation (Figure 1). Grains in low-cement samples exhibit thin, encrusting layers of quartz with isolated crystal facets. Pore spaces are relatively equant and interconnected. In contrast, high-cement samples have an interconnected network of cement with well defined facets, more angular and crack-shaped pores, and diminished pore connectivity. Cathodoluminescence (CL) images allow both cement connectivity and changes in pore geometry with progressive cementation to be quantitatively characterized.



**Figure 1:** Comparison of cement morphology and distribution of images showing areas of low (3.5%) and relatively high (15.6%) cement abundance. (a) CL images in which grains (g) are distinguished from luminescence. (b) False-color images of the same areas where cement is blue, grains are magenta, and pores are yellow. The intergranular area of the two images is roughly the same, but porosity in the high cement example is less than half that of the low cement location.

(c) Image showing only areas of cement within each sample.

The Sandia team (Figure 2) has begun to use these morphological observations to construct physically based finite element models to explore quartz cement-grain mechanical behavior. Perhaps not surprisingly, the stress distribution at our modeled grain-cement boundaries is distinctly different from that of the previously studied meniscus-type cement morphologies.

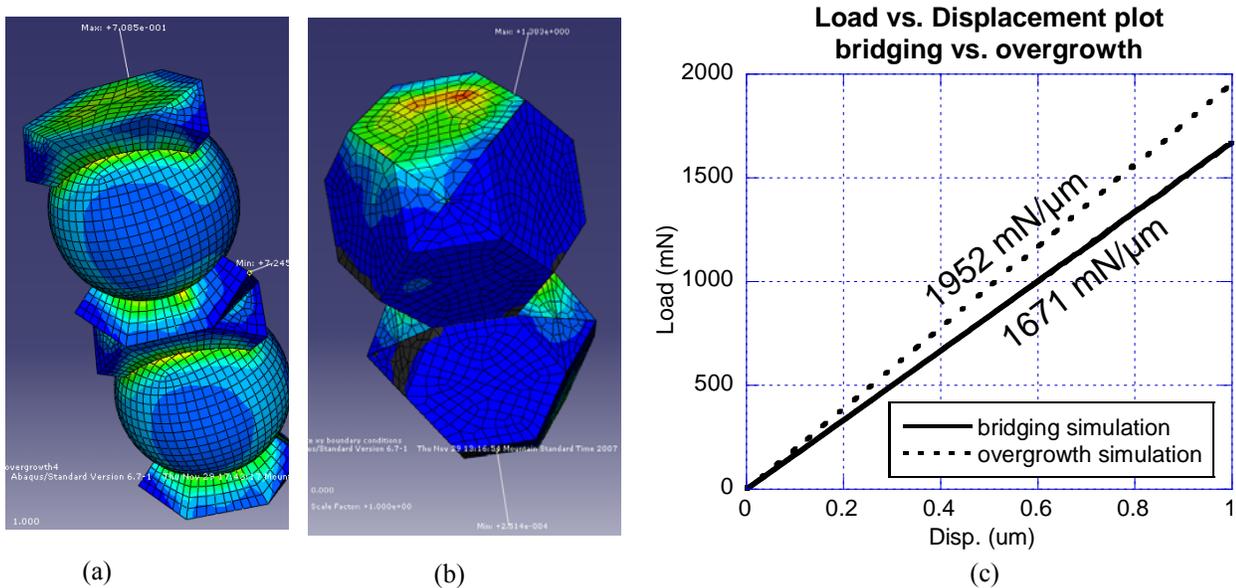


Figure 2- Stiffness comparison and stress distribution in cement "bridging" and "overgrowth" simulations. (a) simulation of cement bridging two particles, (b) simulation of cement overgrowth connecting two particles, and (c) plot showing stiffness traces of both simulations.

## The Importance of Flow-Enhanced Precipitation and Pulsatile Dispersion in Geochemical Systems

Harlan W. Stockman, [hwstock@sandia.gov](mailto:hwstock@sandia.gov)

**Objectives:** To determine the effects of fluid flow on the growth of solids in fractures.

**Project Description:** This work continues a previous study of permeability evolution in fractures, by adding numerical modeling for more aggressive conditions of oscillatory dispersion, with precipitation calculations that will be testable by experiment. The numerical simulation involves lattice Boltzmann (LB) calculations. The goal of the simulations is to design experiments capable of testing the models, via growth from gypsum seeds in Hele-Shaw cells.

**Results:** A part of the project involves the testing of models postulated by Newhouse (1941) for in-vein precipitation. Newhouse suggested that precipitates tend to form on the "stoss" or upstream side of obstacles, when the primary source of solutes is also upstream. His argument, with some qualification, is simple: the solutions encounter the upstream side first, thus first precipitate material on the upstream side. Thus growing crystals will point into the flow. There have been no real tests of this hypothesis since Newhouse's original elegant experiments. Initial LB calculations suggest there is actually a fairly limited set of conditions where the proposed behavior actually occurs; the solubility of the solid must be

high, yet the precipitation rate must be fast, and flow must be uncomplicated enough to prevent vortices from mixing the solutes. The fingering or dendritic growth is discernable best at high Damkohler number ( $Da > 10^4$ ) [Figure 1, Figure 2], and the results are most apparent from a statistical analysis of many realizations, as very slight variations in initial conditions dramatically change the pattern of dendrite growth at high  $Da$ . Even then the “fracture” surfaces must be highly regular; else one simply sees growth toward the highest flow speed, which may be a channel not coincident with the bulk flow. The precipitates at high  $Da$  tend to be porous, with long fingers that effectively stop local flow, yet fill less than 30% of the available space. The precipitates at low  $Da$  (20 or less) are more compact and non-fingered, but still show a smaller, statistically discernable tendency to grow on the upstream side. However, this measurement of growth is possible because the initial location of the seed is known; such information might not be available in geologic settings. Most geological precipitates are expected to be typical of lower  $Da$  conditions, so fingered and directional growth (observable in fractures) may actually be an anomaly.

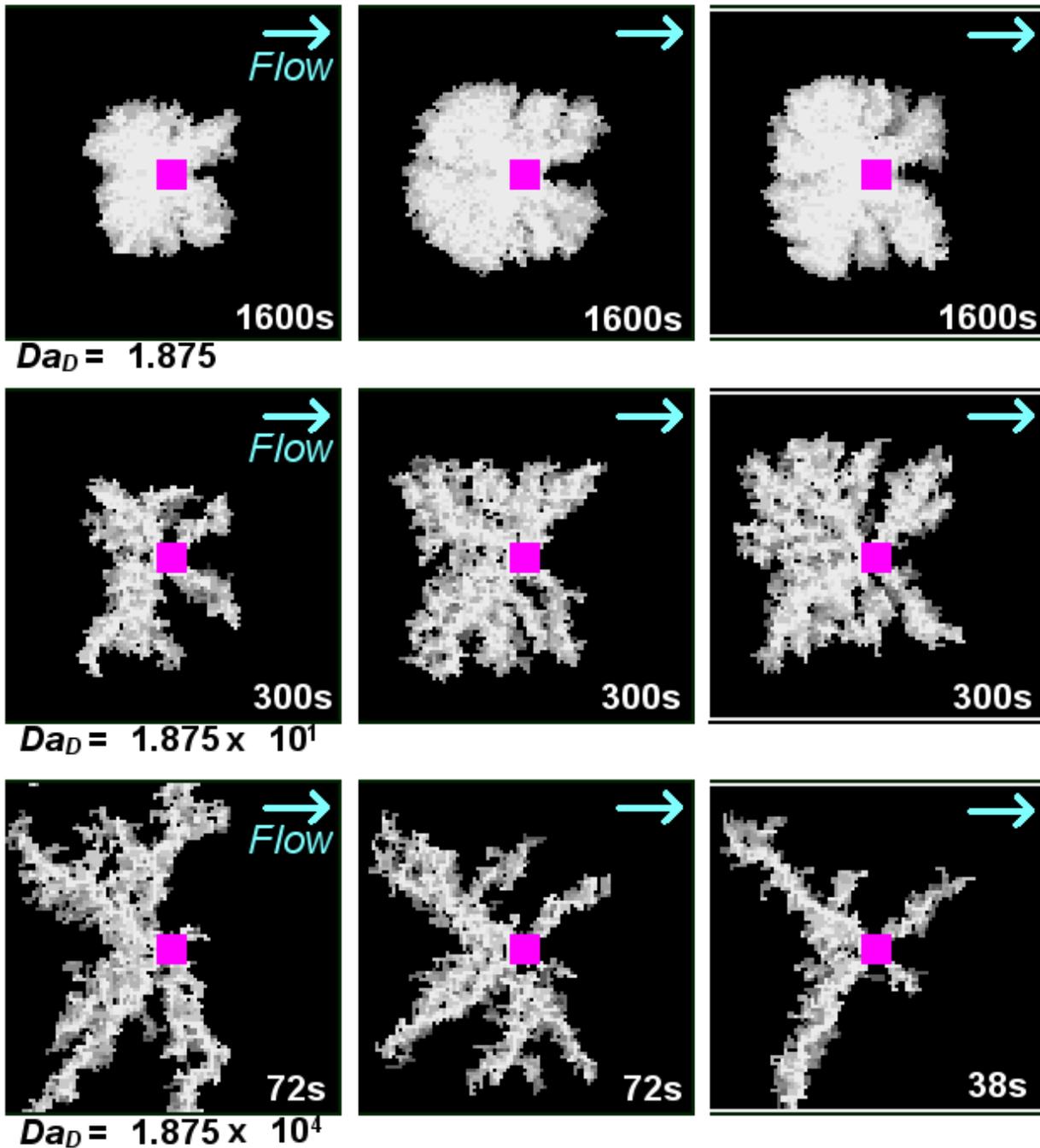


Figure 1. Simulations of multi-crystalline precipitation in a Hele-Shaw cell. Each column represents a different set of initial or boundary conditions for the simulation. As  $Da$  increases, the growth is more likely to become fingered or dendritic; at low  $Da$ , the growth is compact. Initial seed is indicated by magenta. The top row is most like conditions achievable for gypsum growth; the bottom is more like growth of  $\text{NH}_4\text{Cl}$  from supersaturated solutions.

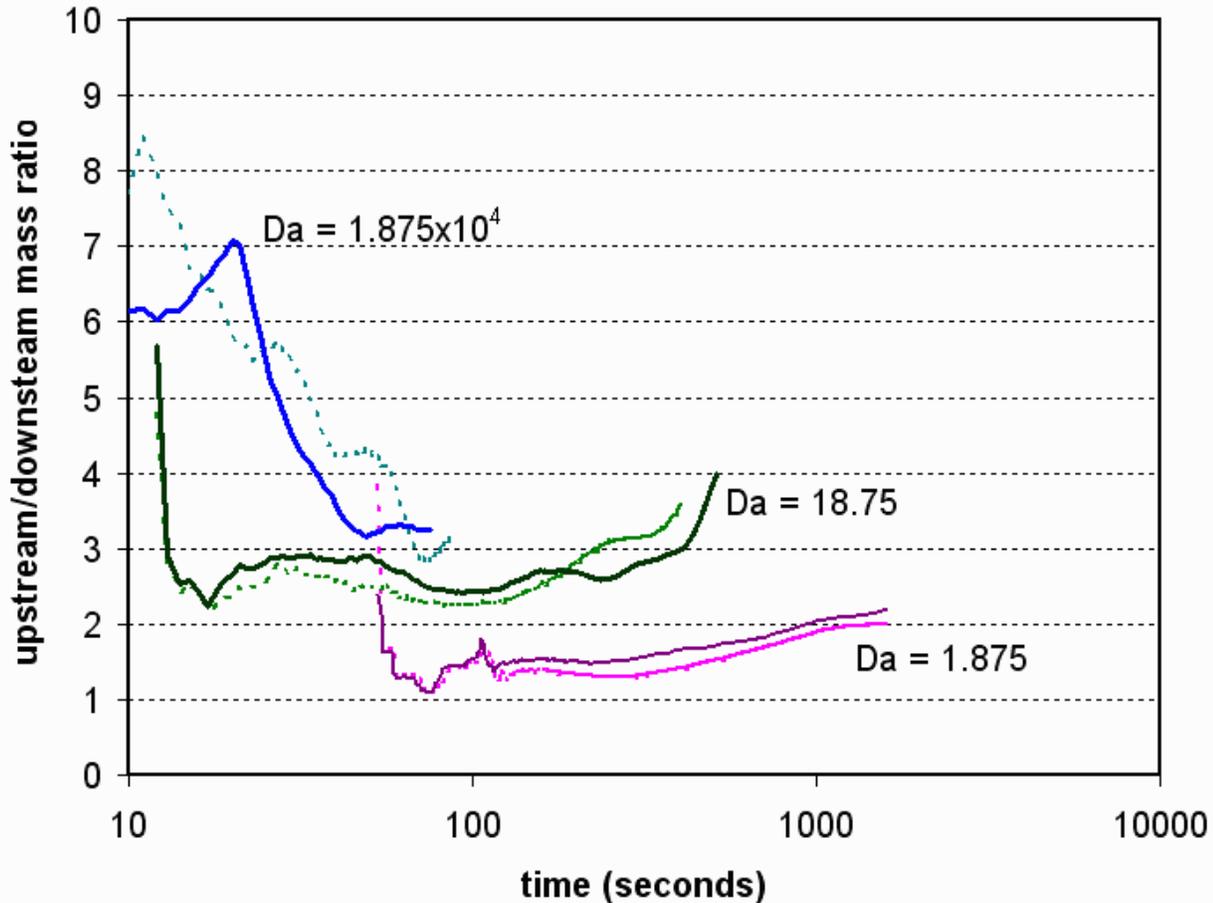


Figure 2. This plot corresponds to the conditions in the first two columns of Figure 1. The ordinate gives the ratio of mass accumulated on the upstream side, versus the downstream side of the seed. At high Da, the wrap conditions cause the dendrites to interfere rapidly, slowing growth.

### Investigation into the Relationship between Heterogeneity and Heavy-Tailed Solute Transport

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**Objectives:** The objective of this project is to characterize the influence that naturally complex geologic media has on anomalous dispersion and to determine if the nature of dispersion can be estimated from the underlying heterogeneous media.

**Project Description:** This project combines outcrop-scale heterogeneity characterization, laboratory experiments, and numerical simulations. The study is designed to test whether established dispersion theory accurately predicts the behavior of solute transport through heterogeneous media and to investigate the relationship between heterogeneity and the parameters that populate these models. The dispersion theory tested by this work is based upon the fractional advection-dispersion equation (fADE)

model. Unlike most dispersion studies that develop a solute transport model by fitting the solute transport breakthrough curve, this project will explore the nature of the heterogeneous media to better understand the connection between the model parameters and the aquifer heterogeneity.

**Results: Sandia National Laboratories**

To evaluate the influence that natural heterogeneity has on dispersion, we utilize high-resolution lidar scans that identify outcrop scale lithofacies. By comparing 2-D particle tracking simulations using lidar based heterogeneity to simulations using unconditioned and conditioned sequential Gaussian simulation (SGSIM), we quantify the difference in dispersion when using realistic and simplified representations of aquifer heterogeneity. Finally, we compare velocity distributions from simulations showing different dispersion characteristics to explore how these differences are related to heterogeneity.

From this work, we conclude that particle tracking simulations through heterogeneity based on the lidar scan has highly connected preferential pathways and distinct high and low velocity zones. Breakthrough curves show non-Fickian dispersion with heavy tailed, power law decay. Without a high degree of conditioning, SGSIM fields do not replicate dispersion as simulated through the lidar based heterogeneity. Velocity distribution analysis indicates that there is less change in velocity along a streamline when using the heterogeneity based on the lidar scan, as compared to SGSIM simulations. Because dispersion is related to the tortuous path of individual particles, standard grid-based velocity increment analysis is not a good indicator of non-Fickian dispersion. To physically test the results of these simulations, experimental design is underway to run a laboratory solute transport sand-pack experiment through media that replicates the cross-bedded nature of the outcrop.

## PART II: OFF-SITE

### THE UNIVERSITY OF ALABAMA

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**Grant:** DE-FG02-06ER15764

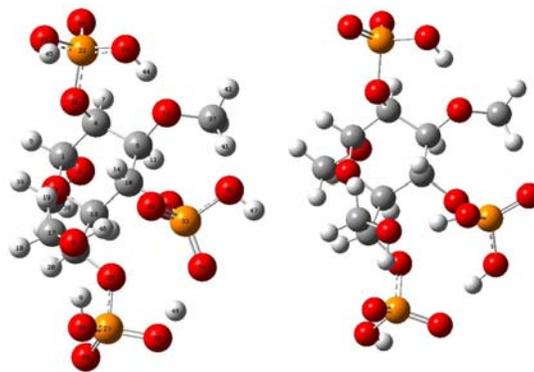
### Molecular Basis for Microbial Adhesion and Geochemical Surface Reactions: A Study Across Scales

David A. Dixon, 205-348-8441, [dadixon@bama.ua.edu](mailto:dadixon@bama.ua.edu); Tjerk P. Straatsma (PNNL), 509-375-2802, [tps@pnl.gov](mailto:tps@pnl.gov); Brian H. Lower

**Objectives:** The goal is to develop a molecular level description of the interactions of Gram-negative microbial membranes with subsurface materials. We are developing a molecular level view of microbial metal binding, microbial attachment to mineral surfaces, and, eventually, oxidation/reduction reactions (electron transfer) that can occur at these surfaces and are mediated by the bacterial exterior surface.

**Project Description:** The focus is the interaction of the outer microbial membrane, which is dominated by an exterior lipopolysaccharide (LPS) portion, of *Pseudomonas aeruginosa* with the mineral goethite and with solvated ions in the environment. It is a combined computational and experimental project (PNNL) that will enable us to generate new insights into the mechanisms of microbial attachment and validate the molecular models and computational approaches. The theoretical modeling capability will allow the transfer of the necessary fundamental information across the needed series of spatial scales, and will include molecular level simulations of small molecular clusters, molecular dynamics investigations of large biomolecular systems, and predictions of macroscopic geochemical reactions using thermodynamic models. This capability is used to gain a fundamental understanding of the processes controlling the LPS structure and function, metal uptake and transport within the outer microbial surface, and the binding of LPS functional groups to specific sites on mineral surfaces. The ability to predict bacterial attachment and detachment to/ from mineral surfaces will provide information critical for the understanding and modeling of bacterial transport in subsurface systems.

**Results:** Our computational part of the effort has three components involving the prediction of (1) solvation energies and structures of ions in solution, (2) acidities of the critical groups in the sugars in the LPS, and (3) binding of metal ions to the sugar anions. An important aspect of the structure of the LPS membrane as well as ion transport in the LPS is the ability of the negatively charged sugar side groups such as the carboxylic acids and the phosphates to bind positively charged ions. We have calculated the acidities of 4 critical sugars, one with a carboxylic acid,



Monoanion Dianion Triphosphate substituted sugar

two with a phosphoric acid, and one with three phosphoric acid substituents. The first  $pK_a$  of the phosphoric acid derivatives shows that these acids are stronger acids than phosphoric acid. This arises because of stabilization of the phosphate anion by internal hydrogen bonding. The second  $pK_a$  for the two monophosphate derivatives makes them weaker acids than  $H_2PO_4^-$ . The second  $pK_a$  of the triphosphate sugar shows that it is still a strong acid. The structure of the most stable form of the monoanion and the dianion derived from it are shown in the Figure. Thus, the triphosphate sugar will be doubly deprotonated under normal pH conditions and these results are being used to constrain the charge states in the molecular dynamics simulations. We have completed a similar study of the gas phase and solution phase acidities of glucose in the ring and acidic chain forms using the same approach as we developed for very strong acids. Comparison with experiment suggests that the sugar hydrogen bonds with solvent from the neutral remain and are not available to stabilize the anion site in glucose.

There is substantial interest in the behavior of the uranyl dication due to the role that it plays in many different technological regimes from energy production to waste storage. Previous work in this project has addressed the solvation energy of  $UO_2^{2+}$  in water. An important issue for understanding how ligands affect the vibrational spectrum of the ion is the value of each of the three fundamental vibrational frequencies of isolated uranyl. High level electronic structure calculations at the coupled cluster (CCSD(T)) and density functional theory (DFT) levels with relativistic effective core potentials and the associated large basis sets have been used to predict the isolated uranyl ion frequencies. The effects of anharmonicity and spin-orbit corrections on the harmonic frequencies have been calculated and are found to be small and usually in opposite directions. The best calculated values for  $UO_2^{2+}$  for the asymmetric stretch, symmetric stretch, and bend are 1113, 1032, and 174  $cm^{-1}$ , respectively. The separation between the asymmetric and symmetric stretch band origins is predicted to be 81  $cm^{-1}$ , which is consistent with experimental trends for substituted uranyls in solution and in the solid state.

## THE UNIVERSITY OF ALABAMA

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Grant: DE-FG02-07ER15840

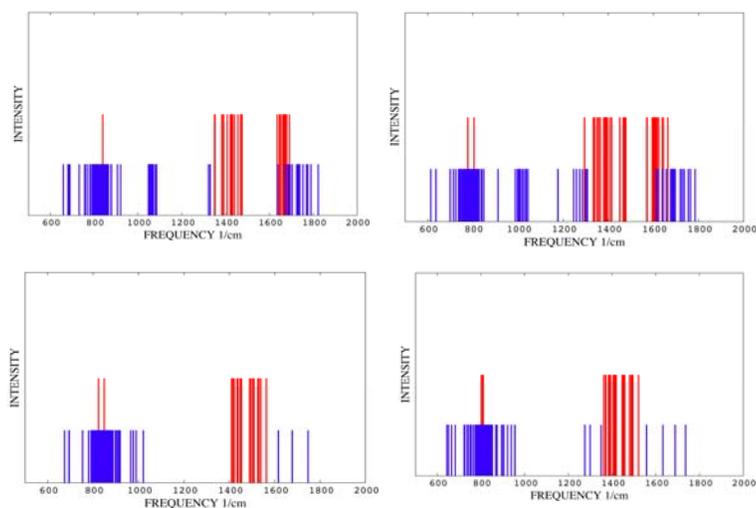
### The Impact of Carbonate on Surface Protonation, Electron Transfer, and Crystallization Reactions in Iron Oxide Nanoparticles and Colloids

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**Objectives:** The goal is to understand at the molecular level the formation of aqueous carbonate species and their interaction with iron and aluminum oxyhydroxide surfaces which have a high affinity for such species. The interaction of carbonate, bicarbonate, and CO<sub>2</sub> with these materials is highly relevant to the development of processes to sequester CO<sub>2</sub> in the subsurface in order to mitigate its impact on the environment. The isotope fractionation of CO<sub>2</sub> and related species in the gas, aqueous and solid states is a key method to determining the PCO<sub>2</sub> in the atmosphere over geological time scales.

**Project Description:** The isotopic fractionation factors between CO<sub>2</sub>(g) and the CO<sub>2</sub> component of oxyhydroxide minerals have not been directly determined experimentally. Because of the broad geochemical significance of the carbon cycle, controlled, in part, by aqueous carbonate species and carbonate minerals, we have assessed the performance of electronic structure methods for predicting carbon-isotope fractionation in the CO<sub>2</sub>(g)-CO<sub>2</sub>(aq)-HCO<sub>3</sub><sup>-</sup>(aq)-CO<sub>3</sub><sup>2-</sup>(aq)-carbonate mineral (calcite, aragonite, and dolomite) system. We have used density functional theory and molecular orbital theory to predict the <sup>12</sup>C/<sup>13</sup>C isotopic fractionation factors. We have developed and tested a range of methods for such predictions including implicit solvation, super-molecule cluster approaches, and the accuracy of current exchange-correlation functionals in combination with various basis sets.

**Results:** The calculations of the isotope fractionation factors resulted in the following conclusions. (1) In large clusters with around 30 water molecules forming two solvent shells, conformational variability associated with about 10 configurations gives standard errors in the fractionation factors, which are small compared to nonsystematic errors resulting from the choice of computational method. (2) Solvated clusters involving around 30 water molecules, without additional treatment of solvation effects, and with frequencies calculated at the PBE/6-31G\* level, are capable of giving qualitative calculation of



**Figure.** Modes making contributions to the fractionation factor at the 0.1 (red) and 0.01 (blue) levels, for HCO<sub>3</sub>(H<sub>2</sub>O)<sub>32</sub><sup>-</sup> (above) and CO<sub>3</sub>(H<sub>2</sub>O)<sub>32</sub><sup>2-</sup> (below). The graphs on the left are calculated using the B3LYP functional and those on the right are calculated using the PBE functional.

isotopic fractionation in the gas-phase, aqueous, and solid-state carbonate system with errors  $\leq 3$  per mil. Our calculations suggest that this error could be reduced to approximately 1 per mil at the B3LYP/aug-cc-pVDZ level. The calculated temperature dependence of the fractionation factors agrees well with experimental measurements. Calculations with smaller numbers of water molecules cannot achieve the level of accuracy of 1 mil, and calculations using only continuum solvent are not even qualitatively correct, regardless of the type of solvation model employed. (3) There is a mixing of the modes of the ion with the solvent leading to more than the minimal number of vibrational modes in the ion being important in determining the isotope fractionation factor. This needs to be further explored experimentally and computationally. One possibility is to measure  $^{12,13}\text{C}$  isotope fractionation factors in  $\text{D}_2\text{O}$  and compare them to measurements in  $\text{H}_2\text{O}$ . We have initiated high level computational studies of the kinetics of formation of carbonate and bicarbonate from  $\text{CO}_2$  in aqueous solution by using coupled cluster methods (CCSD(T)), solvation models, and transition state theory.

## ARIZONA STATE UNIVERSITY

School of Earth and Space Exploration

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**Grant:** DE-FG02-04ER15505

### **A SIMS Study of the Chemical Dynamics of Organic/Inorganic Interactions in Sedimentary Basins**

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**Objectives:** Stable isotopes (Li & B) and trace element contents (Li, B, & N) in kerogen and diagenetic clays are being studied as a tool to monitor oil and gas migration through sedimentary basins. The goal is to determine the temperature of release of these elements from the organics and any fractionation occurring between fluids and solids.

**Project Description:** Analyses of kerogen and clays by secondary ion mass spectrometry (SIMS) can reveal organic/inorganic interactions. SIMS allows analysis of trace elements and isotope ratios *in situ*, eliminating chemical extractions that may induce isotopic fractionation. Changes in B and Li isotopes in kerogen and diagenetic illite may be a more useful tracer of the hydrocarbon related fluids in sedimentary systems than major elements (e.g., C, O) because fewer minerals incorporate these elements at the reaction temperatures of oil and gas maturation, while major elements are involved in a variety of diagenetic reactions. This integrated trace element and isotopic study of kerogen and clays tests the hypothesis that diagenetic illite records the pulses of isotopically light fluids related to the movement of hydrocarbons through sedimentary basins. The results should lead to a better understanding of mass transfer between organic and inorganic phases during hydrocarbon migration.

**Results:** Our evaluation of light element isotopic tracers culminated this year in the discovery that Li, B, and N contents and Li and B isotopes are fractionated as a function of distance from a thermally mature source region. Our measurements of N, B and Li contents were made on three size fractions of illite crystals, where dates indicate that the smallest fraction crystallized earlier than the coarser fractions. In all cases, there is a trend showing anomalously high N (as  $\text{NH}_4^+$ ) fixed in the illites associated with oil producing regions in the SW, B is anomalously high along the central basin axis, and Li is anomalous to the far NE in Estonia (Fig. 1). The B and Li isotope composition of the illites also varies significantly along this trend. The isotopic distribution is complicated by the fact that illitization occurred across a temperature gradient from SW (185°C) to NE (125°C). The fluid composition required to produce the illite isotopic ratios observed suggests that isotopically light Li was taken up first by illite near the hydrocarbons. Since Li diffuses through water 6 times faster than B,  $^7\text{Li}$  accumulated farthest from the source (Estonia) where abundant methane reserves are found.

Boron (in kerogen), is not as mobile as Li, and thus its influence on clays near a reservoir would be detected at a later time during thermal maturation. Indeed, the data show that  $\delta^{11}\text{B}$  does not decrease (i.e., reflect hydrocarbon migration) until *after* nucleation of the smallest crystals. Lower values of  $\delta^{11}\text{B}$



## **BOSTON UNIVERSITY**

Department of Physics and Center for Computational Science  
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**Grant:** DE-FG02-95ER14498

### **Collaborative Research: Understanding Multi-Scale Space-Time Patterns in Crustal Deformation Processes: Towards Ensemble Forecasting in Complex Tectonic Systems**

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**Objectives:** To develop a physical understanding of the origins of space-time patterns and statistical correlations occurring in geomechanical and tectonic systems, and use these to forecast future activity that may produce disasters affecting a variety of critical energy facilities, such as nuclear power plants, oil refineries, and national laboratories.

**Project Description:** The complex earth system generates a variety of phenomena that are highly nonlinear and operate over a broad range of spatial and temporal scales. Signatures of these processes include scaling (fractal distributions), global and local self-organization, intermittency, chaos and the emergence of coherent space-time structures and patterns. We are using massively parallel simulations to model geodynamical effects observed in earthquake systems in order to determine the origin of these phenomena. These investigations and the theoretical efforts done in parallel are particularly aimed at quantifying the limits of predictability for disasters such as earthquakes that occur within the earth system. We are currently continuing our development of the theoretical and computational tools that allow us to both obtain sufficient data on realistic models and to analyze the data we obtain. From these simulations we will then predict geodetic and other deformation associated with impending earthquakes to be tested against Global Positioning System, Synthetic Aperture Radar, seismicity and other field data.

**Results:** Statistical Models: We have looked carefully at the effect of inertia and real friction on the behavior of simple models of earthquake faults and fault systems. We find that for velocity weakened forces that the size and frequency distribution of earthquake events depends strongly on the parameter that governs the weakening. For systems with little weakening we find critical phenomena like behavior such as Gutenberg-Richter (GR) scaling. For systems with strong weakening we find characteristic events which do not exhibit GR scaling. Our conclusion is that fault systems and individual faults may have different properties from one another depending on the details of the friction force and hence the details of their morphology.

Pattern Analysis: We have carried out a detailed analysis of the space-time information content of global earthquake catalogs. We have also developed a variety of new testing algorithms, including a simple Chi-square approach, to understand the space-time error inherent in forecasts as a function of the forecast area fractional coverage (false alarm rate). Tests such as these are critical to the development of successful ensemble forecast methods. In collaboration with K. Tiampo (UWO, Canada), we also analyzed the ergodic properties of sequences of California earthquakes as well as sequences on other fault systems in Canada and Spain. We found that some systems had what we refer to as punctuated ergodic behavior. That is, the system

behaves as if it is an equilibrium state until a large event forces it out of equilibrium. The system then reestablishes itself in equilibrium until the next main event. The punctuated ergodicity seems to be related to the ability of certain algorithms to accurately forecast earthquake events.

Physics of Near Mean-Field Systems: Since earthquake faults have long range elastic forces we studied the morphology of fluctuations (earthquakes) in long range force systems. We find that the fluctuations have a very different form than fluctuation in short range stress transfer systems and that the transition from small fluctuations (earthquakes) to large ones has a specific signature that may aid in forecasting and understanding scaling laws such as the Omori law, Gutenberg-Richter scaling and the power law increase of Benioff strain before a large event. This work was done in collaboration with Harvey Gould (Clark University), Kristy Tiampo (University of Western Ontario) and Natalie Gulbahce (Los Alamos National Laboratory).

## CALIFORNIA INSTITUTE OF TECHNOLOGY

Division of Geological and Planetary Sciences  
Pasadena CA 91125

**Grant:** DE-FG02-06ER15773

### Experimental Petrology and Geochemistry of Volatile-Bearing Silicate Melts

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**Objectives:** The focus of this project is the application of experimental petrology and geochemistry to problems in petrology and geochemistry, with particular emphasis on understanding the behavior and properties of the principal volatile components, H<sub>2</sub>O and CO<sub>2</sub>, and trace elements such as P in magmatic systems.

**Project Description:** The goal of Part 1 is the definitive determination of the diffusion coefficient for water ( $D_{H_2O}$ ) in basaltic, andesitic, and rhyolitic melts in order to understand its compositional dependence, including water content. Profiles of water concentration in hydration and diffusion couple experiments have been analyzed by Fourier transform infrared spectroscopy (FTIR) using a computer-automated stage on the microscope attached to the FTIR spectrometer.  $D_{H_2O}$  values were determined from FTIR profiles using both direct calculations (i.e., Boltzmann-Matano methods) and models assuming specific relationships between diffusivity and water content. Part 2 is the study of the zonation of phosphorus in olivines. Using electron microprobe, we have characterized the complex (and often oscillatory) phosphorus zoning in natural olivines from basalts, andesites, dacites, komatiites, and igneous meteorites. We have generated similar P, Al, and Cr zoning in olivines grown experimentally at 1 atm with cooling rates of 15-30°C/hr in a synthetic Hawaiian basalt. We have also begun measuring Al and P chemical diffusivities in olivine.

**Results:** *Part 1:* We have completed our pilot study of diffusion of water in silicate melts: 16 hydration and diffusion couple experiments with compositions of high-Al basalt, haplobasalt, and haploandesite. Various functional models for the dependence of  $D_{H_2O}$  on water content agree well with direct calculations of  $D_{H_2O}$ . The relationships between  $D_{H_2O}$  and water content examined include constant  $D_{H_2O}$ ,  $D_{H_2O}$  proportional to water content,  $D_{H_2O}$  proportional to the logarithm of water content, and  $D_{H_2O}$  of molecular water constant with immobile hydroxyl groups. Averaging the results from these various methods for several samples for each composition, we have determined that a generalized exponential function of  $D_{H_2O}$  with respect to H<sub>2</sub>O content can reproduce the analyzed profiles. The gray curve in Figure 1 shows the generalized exponential curve for haploandesite, compared with the functional models and direct calculations of  $D_{H_2O}$ . We have begun to analyze a new set of 42 samples with small gradients in H<sub>2</sub>O content. Couple experiments were generated by juxtaposing glasses produced with water saturation levels for pressures varying by only 10-60 MPa. Hydration experiments were produced by exposing a hydrated glass to P<sub>H<sub>2</sub>O</sub> only slightly greater than that used to make the original glass. Initial results, shown as large dots in Figure 1a, are consistent with the previous results and will allow us to refine the exponential relationship. We have begun to use secondary ion mass spectrometry (SIMS) technology to improve noise levels in the diffusion profiles. Although we are using calibration based on the FTIR results, calculation of diffusion coefficients is not sensitive to this. Modified Boltzmann-

Matano analysis of both the FTIR and SIMS profiles produce very similar values for  $D_{H_2O}$ , within approximately 15%.

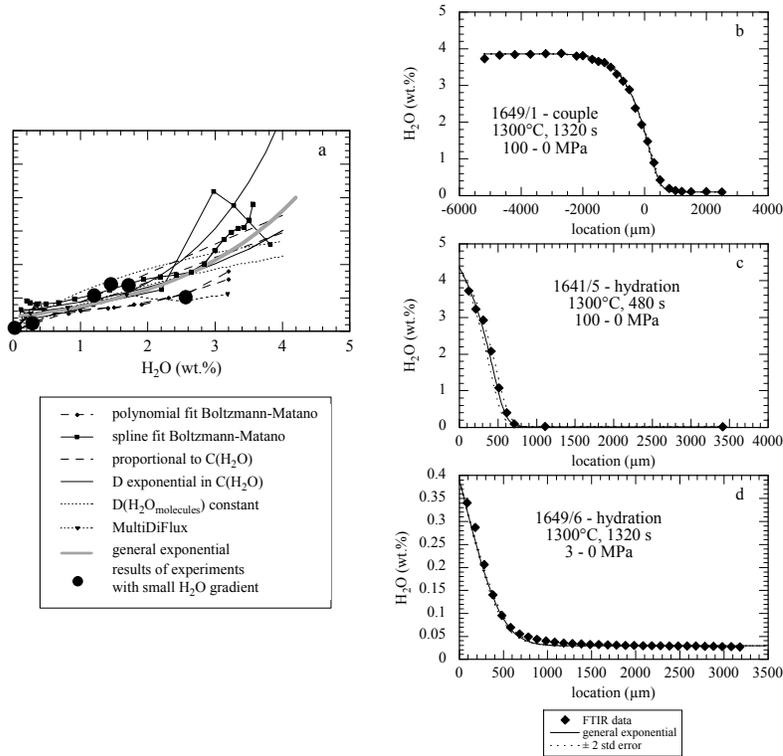


Figure 1. Results for haploandesite. Panel (a) shows the relationship between  $D_{H_2O}$  and  $H_2O$  content for various functional models and direction calculations. Large dots indicate diffusion coefficients determined by experiments with small gradients in  $H_2O$  content. Panels (b), (c), and (d) show how well forward calculations using the general exponential curve, from panels a and b, fit the profiles determined by FTIR.

*Part 2:* Our study indicates that phosphorus zoning is a widespread feature of igneous olivines, occurring in all samples studied (basalt, andesite, dacite, komatiite). P zonation is found in olivines with no correlated zonation in major or minor divalent cations, although it frequently correlates spatially with Al and Cr. The incorporation of P into olivine at the observed levels appears to be a disequilibrium process reflecting rapid crystal growth and the observed zoning patterns may be potential indicators of magmatic processes. Olivine zonation occurs in many different patterns, including oscillatory and sector zoning, high-P cores surrounded by lower P olivine, and replacement of P-rich regions with low-P olivine. Not all natural samples exhibit Al or Cr-zonation, specifically those samples thought to have been held at high temperature for extended periods following crystallization. This suggests that retention of zoning is related to the diffusive reequilibration time for each element and that  $D_{Al} > D_{Cr} > D_P$  for P-correlated cations. We have begun to study the generation of P-zonation through a series of controlled cooling rate experiments (1-30°C/hr) and produce P, Cr, and Al zoning similar to those observed in natural olivines under even the slowest rates, consistent with the zoning being ubiquitous in natural samples. In addition, we are analyzing a suite of cumulate, slowly cooled, olivines to constrain the chemical diffusivities of P, Cr, and Al and the reequilibration timescales necessary to perturb zonation. This analytical work is paired with experimental studies of lab-generated diffusion couples to better quantify the chemical diffusivities.

## CALIFORNIA INSTITUTE OF TECHNOLOGY

Division of Geological and Planetary Sciences  
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### Isotope Tracer Studies of Diffusion in Silicates and of Geological Transport Processes Using Actinide Elements

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**Objectives:** This project addresses understanding the transport of chemical species in nature by focusing on three general areas of study: actinide transport, platinum group elements and Re in deep sea sediments, and B and Ca isotopes in corals.

**Project Description:** The major efforts of this phase of the project have been directed toward the high precision measurement of Ca isotopic abundances in both terrestrial materials and in meteorites and lunar samples. The purpose of this study was to measure the evolution of  $^{40}\text{Ca}$  as recorded in carbonate deposits due to the input of Ca from the continental crust and from mantle sources. A wide variety of samples have been obtained and the materials subjected to analysis.

**Results:** This report covers the research activities during a period of no cost extension. The effects being investigated were the increase of  $^{40}\text{Ca}$  due to the decay of  $^{40}\text{K}$ . A base line would be the  $^{40}\text{Ca}/^{42}\text{Ca}$  in early formed meteorite samples which have almost no K, lunar samples of very high age with no K, mantle samples with very low K/Ca and carbonates from marine deposits with ages ranging from 3.5 Gyr to recent marine deposits and MORB glasses. The experimental difficulties have proven quite great. The effects are at the 1 epsilon level in  $^{40}\text{Ca}$ , which is also the major Ca isotope.

We presented an abstract at the Dec. 2006 AGU meeting claiming the resolution of effects. However, it is now clear that this claim can not be justified as drifts in the results are found to be about 1 epsilon unit. The idea is great, but the real quality of the measurements is not. We have been pursuing this problem and the technical difficulties associated with it. At the present time, it is not evident where the problem lies. The precise measurement of Ca isotopes has proven to be a difficult problem for all serious investigators and we have found, to our discomfort, that the solution is not apparent to us even using the best available detector systems. The results of our efforts are now being put into final form & we will submit a note for publication on our efforts. We will continue this work for some time using Institutional resources available to Dr. D. A. Papanastassiou at Caltech using the instrument at JPL.

Extensive research has been conducted on the stellar sources of a wide variety of nuclides. In particular, it has been found that the "standard model" for r-process nucleosynthesis associate with massive stars (>11 solar masses) is incorrect and a new site for the heavy r-process is found to be low mass SNeII (8-10 solar masses). A further effort to explain the extra mixing in low mass AGB & Red giant stars has been made considering the effects of magnetic buoyancy. A presentation of this new approach was made by Wasserburg at the IX Torino workshop on nuclear processes in AGB & red giant stars. He also served on both the Scientific Steering Committee & local (CALTECH) organizing committee for the international meeting celebrating the 50th anniversary of nuclear astrophysics & presented a scientific paper on short lived nuclei in the early solar system.

## UNIVERSITY OF CALIFORNIA, BERKELEY

Department of Earth and Planetary Science  
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**Grant:** DE-FG02-01ER15218

### How Do Interfacial Phenomena Control Nanoparticle Structure?

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**Objectives:** The objective of this project is to understand how and why the molecular environment at a nanoparticle surface influences the internal structure and properties of the material.

**Project Description:** Nanoparticles are important components of natural systems, arising as the result of physical, chemical, and biological processes. Due to their small size and enhanced reactivity, they may play unexpected roles in the environment. However, nanoparticles are not necessarily static. Rather, some are able to respond quickly to changes in their surroundings. Thus, prediction of nanoparticle behavior requires understanding of how the presence of molecules such as water or organics can influence their structure and surface reactivity. The approach taken in this study is to combine nanoparticle synthesis with experimentation, characterization using a suite of methods, and molecular simulation and prediction tools. Our work includes analysis of how specific classes of molecules at nanoparticle surface influence particle behavior and has made use of high-pressure experimental methods to perturb nanoparticles and learn about how they respond to changes in their physical and chemical environments.

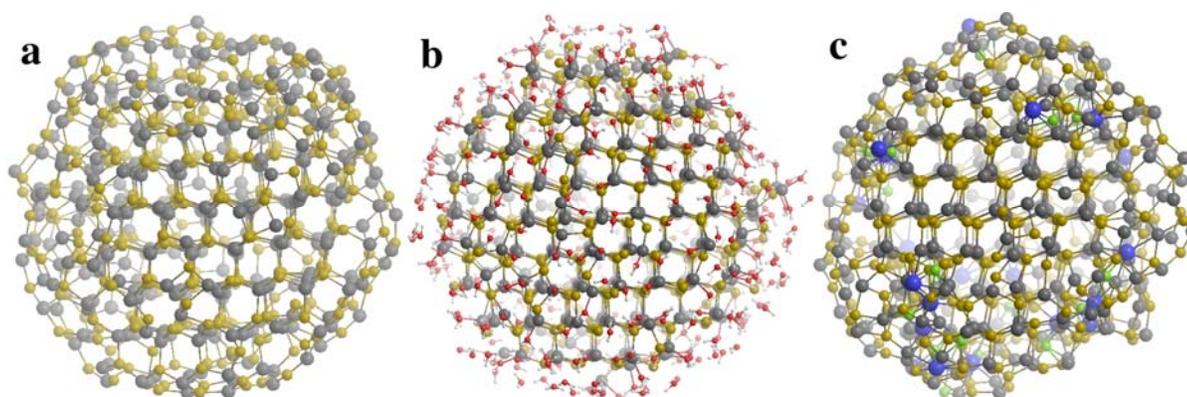
**Results:** In order to interpret and understand the experimentally determined structural responses of small ZnS nanoparticles (~ 3 nm) at different surface environment (methanol and methanol plus chlorobenzene, water, thiophenol, sodium sulfate, calcium chloride and sodium chloride, respectively), we used first-principle calculations and molecular dynamics simulations to investigate the interaction strength between the surface species and ZnS nanoparticles. Results from our plane-wave electronic structure calculations showed that the binding energies (Table 1) of surface species on a ZnS surface strongly correlate with the nanoparticle-surface species interaction strength.

**Table 1.** Calculated parameters for surface species-ZnS (100) surface interaction.

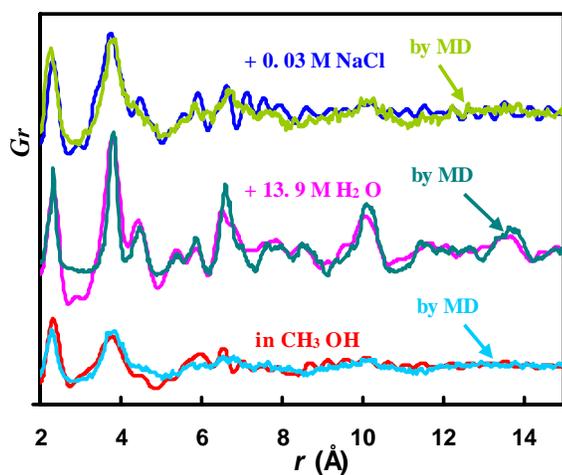
Surface species	Interacting atomic pair	Equilibrium distance (Å)	Binding energy (kJ/mol)
Na <sub>2</sub> SO <sub>4</sub>	O-Zn	2.083	134.7
NaCl	Cl-Zn	2.332	124.7
C <sub>6</sub> H <sub>6</sub> S	S-Zn	2.446	89.8
H <sub>2</sub> O	O-Zn	2.140	66.7
C <sub>6</sub> H <sub>5</sub> Cl	Cl-Zn	2.869	78.5
CH <sub>3</sub> OH	O-Zn	2.963	36.8

Molecular dynamics (MD) simulations of representative systems (Figure 1) confirm that that stronger surface binding and more surface coverage by surface species largely compensate for the disruption of the periodic structure of the ZnS nanoparticles at the surfaces. This results in a more crystalline

nanostructure and hence more and/or higher PDF (pair-distribution function) peaks (Figure 2).



**Figure 1.** Snapshots of the structures of a 3 nm ZnS (sphalerite) particle in the molecular dynamics simulations. (a) MD in vacuum, (b) MD of nano-ZnS with adsorption of 362 H<sub>2</sub>O molecules, and (c) MD of nano-ZnS with adsorption of 24 Na<sup>+</sup> and 24 Cl<sup>-</sup> ions. Zn: gray; S: dark yellow; O: red; H: light gray; Na: blue; and Cl: green.



**Figure 2.** Comparisons between experimental and MD calculated PDFs ( $G_r$ ) of  $\sim 3$  nm ZnS nanoparticles suspended in methanol, methanol plus water, and methanol plus NaCl.

## UNIVERSITY OF CALIFORNIA, BERKELEY

Department of Earth and Planetary Science  
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**Grant:** DE-FG02-04ER15507

### Microbial Metabolism and the Nature of Metal Sulfide Biomineralization Products

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**Objectives:** The primary question investigated in our work is “How does the activity of sulfate reducing microbial consortia impact the size, aggregation state, and behavior of metal sulfide nanoparticles, including their mobility in the environment”.

**Project Description:** Microbial activity can strongly influence the form and distribution of metals in the environment. In this project we are studying the ways in which microbial sulfate reduction removes metals from solution by inducing the precipitation of metal sulfide nanoparticles. We have experimentally evaluated the ways in which solution chemistry impacts the rate of sulfide production, quantifying the effect in terms of thermodynamic controls on microbial activity levels. Using the ability to control sulfate reduction rates, we have investigated how microbial activity impacts aggregate size and aggregation rate and conducted experiments to study particle transport in microfluidic systems. We used nanoSIMS to show that natural metal sulfide nanoparticle aggregates contain substantial concentrations of protein and conducted experiments to test the ability of a suite of amino acids to promote nanoparticle aggregate development.

**Results:** This report covers the fourth year of a three-year grant (no cost extension with no remaining funding). Thus, the primary activities involved data analysis, manuscript preparation, responding to reviews etc. The major focus of the final period of the grant involved publication of the Ph.D. research of John Moreau. The second part of this, a collaboration with Peter Webber (LLNL) and Michael Martin (LBNL) and others, included *in situ* isotopic and biochemical analyses of natural nanoparticle aggregates formed by sulfate-reducing bacteria using secondary ion mass spectrometry (NanoSIMS, ~50 nm probe spatial resolution) at Lawrence Livermore National Laboratory and synchrotron Fourier transform infra-red spectroscopy (SR-FTIR, ~10  $\mu\text{m}$  spatial resolution) at the Advanced Light Source of Lawrence Berkeley National Laboratory. Significant organic nitrogen concentrations within aggregates were attributed to polypeptides on the basis of SR-FTIR data. Based on experimental results, it was estimated that approximately 14% of the aggregate volume is occupied by proteins. We also completed the analysis of an experimental study of the role of proteins and amino acids in generating dense (non-fractal) aggregates of metal-sulfide nanoparticles, in collaboration with Ben Gilbert (LBNL). Results of the characterization and aggregation study were published in *Science* in 2007. The other collaborative LLNL study involves an effort to document isotopic gradients in sulfide within the same nanoparticle aggregates. Although preliminary data indicate the existence of these features, ongoing work at LLNL is required to validate the findings prior to publication.

**Laboratory experiments:** We continued experiments on sulfate reduction (~ 9 mM sulfate) and sulfide biomineralization by subsurface microbial consortia using column experiments. Sediments and exposed to complex anaerobic, metal-bearing (Zn, Cu, U, Se, V) containing 3 mM acetate. Columns were

monitored via solution geochemistry, mineralogical characterization, and using molecular 16S rRNA gene analysis of the microbial community during the onset of sulfate reduction. Columns established for this study are being used in ongoing experiments with Rifle, CO, sediments for work relevant to the Rifle IFC, for studies of the sensitivity of geophysical methods to sulfide biomineralization (Ken Williams Ph.D. research) and for studies of the activity of specific organisms during iron and sulfate reduction.

## UNIVERSITY OF CALIFORNIA, BERKELEY

Department of Earth and Planetary Science  
Berkeley CA 94720

**Grant:** DE-FG02-03ER15418

### **Diffusion/Dispersion Transport of Chemically Reacting Species**

*Harold C. Helgeson (d. May 28, 2007); H.-R. Wenk, 510-642-7431, [wenk@berkeley.edu](mailto:wenk@berkeley.edu)*

**Objectives:** The principal aims of this research project are (1) calculation of the thermodynamic consequences of incongruent melting of kerogens in hydrocarbon source rocks and (2) calculation of the thermodynamic properties of biochemical reactions coupled to organic and inorganic oxidation/reduction reactions at high pressures and temperatures.

**Project Description:** Thermodynamic models of incongruent melting of kerogens to produce hydrocarbons can be used to predict the composition and quantity of petroleum generated from hydrocarbon source rocks. Although the formation of hydrocarbons may be found initially in water-absent regions, interactions between hydrocarbons and aqueous solutions are likely during expulsion and transport to reservoirs. The consequences of biochemical reactions coupled to organic/inorganic reactions at the oil/water interface can be assessed using thermodynamic models that take into account temperature, pressure, oxidation state and other chemical properties of the system.

**Results:** The results of investigations obtained during FY 2007 are connected with two major research areas: development of a chemical and thermodynamic model for oil generation in the earth, and documentation of the energy and chemical mass transfer consequences of chemical reactions among biomolecules and organic and inorganic species at the oil-water interface.

The results of Gibbs energy minimization computer experiments carried out during this investigation together with thermodynamic analysis of phase relationships in the system C-H-O indicate that incongruent melting of kerogens in source rocks to produce predominantly aliphatic hydrocarbons is favored at temperatures at or above  $\sim 140$  °C. With increasing temperature, the metastable speciation of liquid hydrocarbon mixtures in equilibrium with kerogens becomes increasingly aromatic. By combining the calculated volumes of hydrocarbons and of pore space produced by the chemical reactions with kerogen richness (H/C) and source rock thicknesses, it can be shown that the results of thermodynamic calculations are consistent with known quantities of reservoir oil in the Los Angeles and North Paris basins and in other reservoirs. A paper describing this model has been accepted for publication.

Calculations of the consequences of non-ideal mixing on the speciation of hydrocarbon mixtures have been carried out using the PFGC (Parameters from Group Contributions) equations of state. These equations and parameters were incorporated into the Gibbs energy minimization software package known as HCh. The initial results of Gibbs energy minimization with non-ideal mixing of hydrocarbons show that this model can be used to more realistically predict the compositions of oils found in reservoirs; in particular, the dominance of aromatic species at high temperatures in the ideal calculations is lessened considerably by incorporating the activity coefficient calculations. The overall applicability

of this thermodynamic approach can also be extended by including groups to account for non-ideal interactions involving nitrogen and sulfur species. This work is being written up for publication.

Progress in FY 2007 in the area of coupled biomolecular-inorganic reactions is represented by the publication of a thermodynamic model for coupling electron transfer (driven by exergonic oxidation-reduction reactions) to the formation at high temperatures and pressures of representative metabolic species in microbes. The biochemical species included adenosine triphosphate (ATP), adenosine diphosphate (ADP) and oxidized and reduced nicotinamide adenine dinucleotide (NADox and NADred). It can be shown that the formation of NADred at the expense of NADox is favorable when coupled to the oxidation of glucose or of hydrogen at 25°C, but with increasing temperature to ~120°C the reaction coupled to glucose oxidation becomes increasingly favored while that coupled to hydrogen oxidation becomes less favored. Quantifying the energies associated with these representative reactions may be essential to prediction of the limits of microbial metabolism in a variety of subsurface environments.

#### **Website/Thermodynamic Data:**

Further information about this research is available on the website for the Laboratory of Theoretical Geochemistry and Biogeochemistry, which was launched in March 2006. The website provides links to the online versions of the publications cited here as well as related thermodynamic data files and software. The thermodynamic data files were generated using data produced in this laboratory for inorganic and organic species, including liquid hydrocarbons and aqueous biomolecules. Throughout FY 2007 the primary data file was updated multiple times with thermodynamic data taken from these and other sources the recent literature; the file now contains over 2500 species entries. The data file is available in a format that is compatible with the widely-used SUPCRT92 software package for calculating standard molal thermodynamic properties of species and reactions and has also been successfully imported into a Windows-interface being developed for SUPCRT92 known as OrganoBioGeoTherm (OBIGT). Both of these software packages are available for free download from the website.

## UNIVERSITY OF CALIFORNIA, BERKELEY

Department of Earth and Planetary Science  
Berkeley CA 94720

**Grant:** DE-FG02-05ER15637

### **Extracting Geological Stresses and Anisotropy from Rocks by Means of Neutron Diffraction**

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**Objectives:** The goal is to develop reliable methodologies to determine the influence of stress on anisotropy in polycrystalline sedimentary rocks, such as chert, shales and limestones, where seismic anisotropy is crucial for geophysical prospecting. Initially focus was on neutron diffraction but the approach has been broadened to include synchrotron X-ray scattering.

**Project description:** Understanding geological stresses and anisotropy in sedimentary rocks is of great concern in structural geology, geophysics and, particularly, geophysical exploration of sub-surface structures. Information is very limited because of the complexities and poor crystallinity of polyphase materials such as shales. New tools - time-of-flight neutron and synchrotron X-ray diffraction - offer the possibility for probing the internal structure of geomaterials and to quantify micro-to-nano scale stress-induced changes in rocks. Research relies on advanced diffraction experiments at National laboratories (LANSCE, APS, ALS) and sophisticated data analysis (Rietveld method and FEM modeling). Based on observations on natural and experimental samples a comprehensive model can be derived that links macroscopic physical properties to the internal structure and the formation process.

**Results:** The general approach is to irradiate bulk rock samples with neutron and hard X-rays, record diffraction patterns and analyze these for phase, composition, preferred orientation and lattice strain with the crystallographic Rietveld method developed specifically for this investigation and made available to the broader user community.

*Quartz* emerged as a fascinating material where mechanical twinning can be used to elucidate paleostresses. New experiments explored the influence of temperature and stress on the twinning activity. In situ neutron experiments with the strain diffractometer SMARTS at LANSCE document changes in structure as a material is deformed at stresses ranging from 100 to 500 MPa and currently the behavior during the trigonal-hexagonal phase transformation under stress is being investigated. With this new information we can now calibrate the quartz twinning pattern and use it as a paleopiezometer in natural situations such as tectonic deformation and meteorite impacts. Current investigations include sedimentary quartz-bearing rocks from the San Andreas fault drill core and analyses with the microfocus Laue technique at ALS suggest that indeed there may be preserved lattice strains induced by deformation events (collaboration with M. Kunz and N. Tamura).

Preferred orientation of clays is a primary ingredient for anisotropy in *shales* that has never been quantitatively characterized. A most exciting result of the research was the fact that, after developing the hard synchrotron X-ray technique, we can now investigate very complex shales such as those from European nuclear waste repositories with 6 major phases. Preferred orientation of illite-smectite, kaolinite, chlorite and calcite produce strong anisotropy. Preferred orientation varies with geological setting, mineralogical composition and depth. This is further explored with experiments to quantify the

influence of compaction pressure and mineral content (quartz/clay mixtures) (collaboration with N. Mondol, K. Bjørlykke, Univ. Oslo and T. Vanorio, Stanford). Figure 1 illustrates how illite preferred orientation increases with pressure and weakens as quartz is added to the mixture.

The new observations add constraints and also open a whole range of new questions. In looking forward, priorities are to concentrate on understanding the mechanisms of mechanical twinning and texture memory in quartz-bearing rocks by further neutron diffraction experiments at LANSCE, involving also analog materials such as low symmetry metals with twinning such as titanium and uranium. A systematic investigation of twinning patterns in naturally deformed quartz rocks is underway and preliminary results are very revealing. On shales we are now studying experimental material and, in collaboration with C. Sayers are now refining a theory to understand the contribution of different factors such as single crystal properties, preferred orientation, porosity distribution on polycrystal elastic properties. Uncertainties about single crystal elastic properties of clay minerals are a major limitation and we are working with L. Stixrude (now UCL) to obtain elastic properties of illite/smectite from first principles.

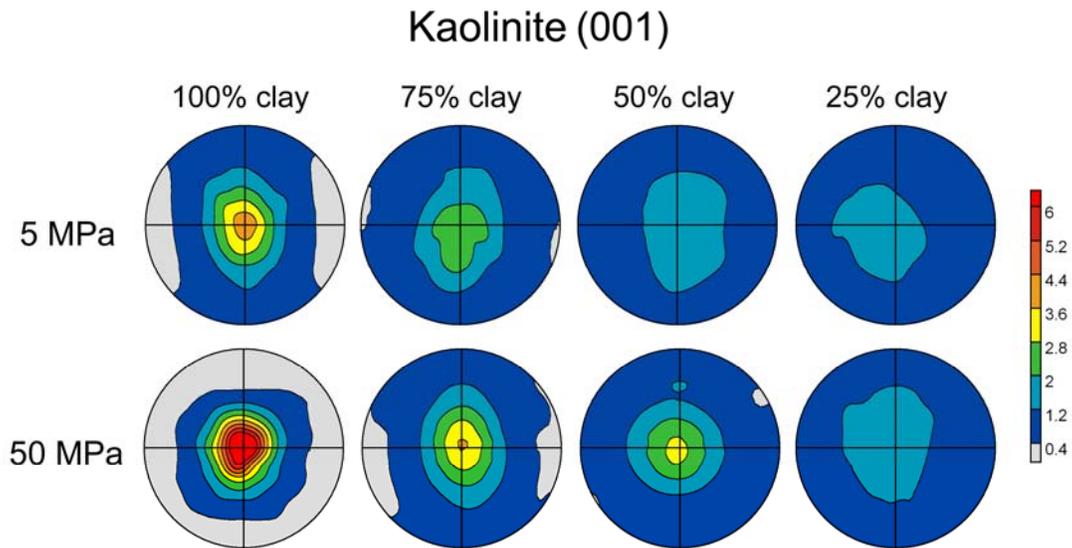


Figure 1. (001) pole figures of kaolinite in experimentally compressed illite-kaolinite-quartz mixtures as function of pressure and clay content. Equal area projection. Pole densities in multiples of a random distribution.

## UNIVERSITY OF CALIFORNIA, DAVIS

NEAT ORU

4440 Chemistry Annex

Davis CA 95616

**Grant:** DE-FG02-97ER14749

### Thermodynamics of Minerals Stable Near the Earth's Surface

*Alexandra Navrotsky, 530-752-3292; [anavrotsky@ucdavis.edu](mailto:anavrotsky@ucdavis.edu), Peter A. Rock  
(Thermochemistry Laboratory)*

**Objectives:** Using specialized calorimetric techniques, we obtain thermochemical data for bulk and nanoscale minerals and apply the findings to geochemical problems in the Earth's critical zone.

**Project Description:** Minerals at or near the Earth's surface have complexity of structure, metastability, hydration, and variable crystallinity. They are carriers of and sinks for pollutants. This project measures, systematizes and interprets the thermodynamic properties of a variety of complex mineral phases using oxide melt solution calorimetry and related techniques. Systems currently under study include hydrated sulfates, iron oxyhydroxides, hydrotalcites, other phases related to acid mine drainage, phosphates, arsenates, and heavy metal containing minerals.

**Results:** An extensive calorimetric study of iron oxides and oxyhydroxides is almost complete. It shows that maghemite,  $\gamma\text{-Fe}_2\text{O}_3$ , although metastable with respect to hematite,  $\alpha\text{-Fe}_2\text{O}_3$ , when coarsely crystalline, becomes thermodynamically stable at the nanoscale because of lower surface energy. This energy crossover is similar to that seen in  $\text{Al}_2\text{O}_3$ . Furthermore, iron oxyhydroxides have lower surface energies than anhydrous oxides, leading to thermodynamic stabilization of the hydrated nanophases to higher temperatures than for the equilibrium dehydration of coarse goethite to hematite. The ferric oxyhydroxide polymorphs show a complex set of energy crossovers, see Fig. 1. At particle sizes  $<50\text{nm}$ , goethite, akaganeite, lepidocrocite, and ferrihydrite become very similar in enthalpy (and probably free energy), explaining their common occurrence. The  $\text{Fe}_2\text{O}_3$  and  $\text{FeOOH}$  data support previous systematics found for  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ . Polymorphs having higher enthalpies as bulk phases have lower surface energies. Hydrous phases have lower surface energies than anhydrous phases. Hydrated surfaces have lower surface energies than anhydrous surfaces. As part of this work, we have developed an accurate method that simultaneously measures the adsorption isotherm and heat of adsorption of water on oxide powder surfaces. The work on iron oxides is being completed and a review article is being written.

Work has started on the effect of crystallinity and particle size on the energetics of layered stable hydroxides.

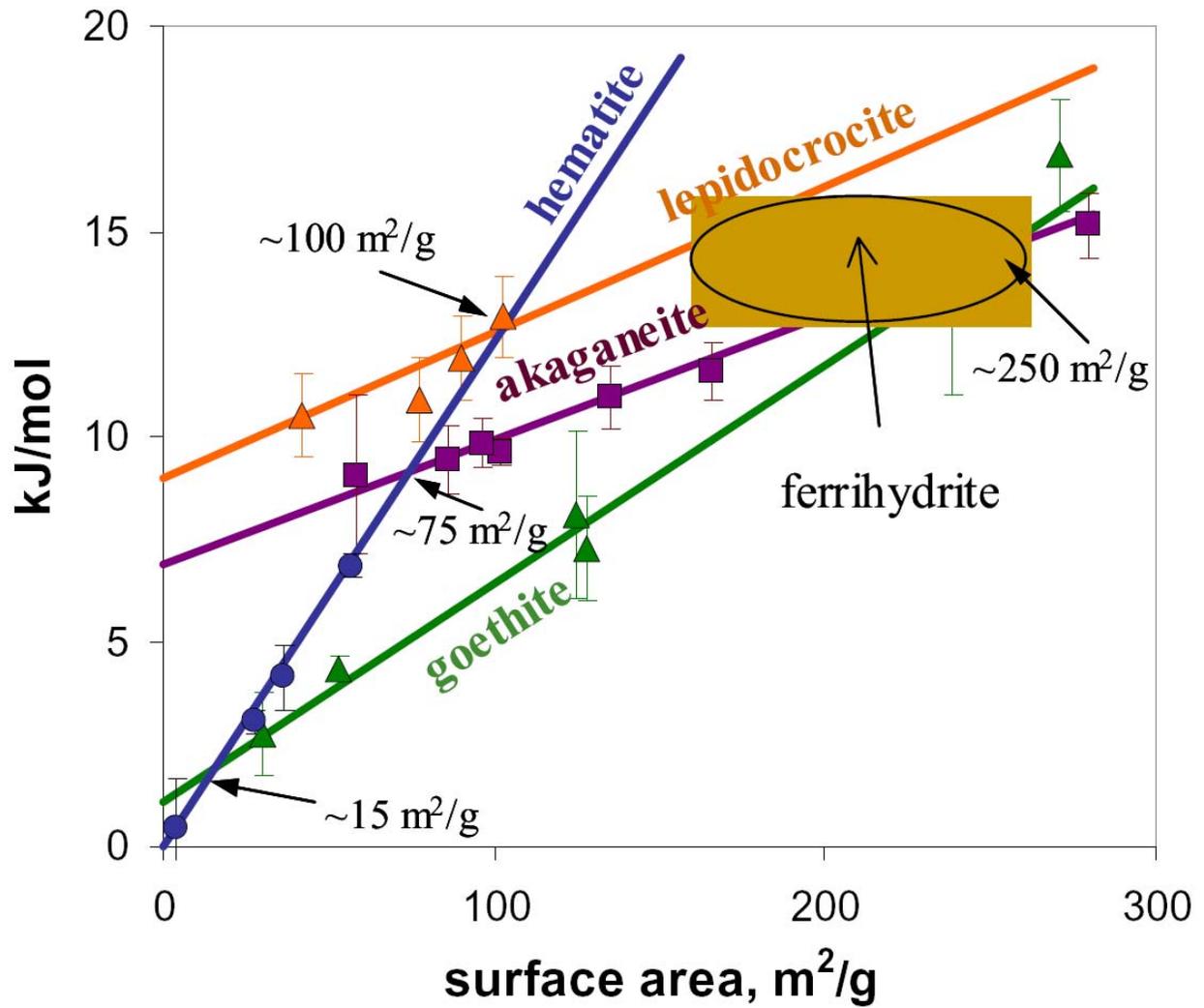


Fig. 1. Calorimetrically measured enthalpies relative to coarse hematite plus liquid water  $\frac{1}{2}(\text{Fe}_2\text{O}_3 + \text{H}_2\text{O})$  for oxyhydroxides and fine grained hematite versus surface area ( $\text{m}^2/\text{g}$ ). The points are experimental data and the ellipse indicates the range for various ferrihydrite samples studied.

## UNIVERSITY OF CALIFORNIA, DAVIS

Department of Geology

Davis CA 95616

**Grant:** DE-FG02-04ER15498

### **The Impact of Carbonate on Surface Protonation, Electron Transfer, and Crystallization Reactions in Iron Oxide Nanoparticles and Colloids**

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**Objectives:** The goal is to understand at the molecular level the formation of aqueous carbonate species and their interaction with iron and aluminum oxyhydroxide surfaces which have a high affinity for such species. The interaction of carbonate, bicarbonate, and CO<sub>2</sub> with these materials is highly relevant to the development of processes to sequester CO<sub>2</sub> in the subsurface in order to mitigate its impact on the environment. The isotope fractionation of CO<sub>2</sub> and related species in the gas, aqueous and solid states is a key method to determining the PCO<sub>2</sub> in the atmosphere over geological time scales.

**Project Description:** The isotopic fractionation factors between CO<sub>2</sub>(g) and the CO<sub>2</sub> component of oxyhydroxide minerals have not been directly determined experimentally. Because of the broad geochemical significance of the carbon cycle, controlled, in part, by aqueous carbonate species and carbonate minerals, we have assessed the performance of electronic structure methods for predicting carbon-isotope fractionation in the CO<sub>2</sub>(g)-CO<sub>2</sub>(aq)-HCO<sub>3</sub><sup>-</sup>(aq)-CO<sub>3</sub><sup>2-</sup>(aq)-carbonate mineral (calcite, aragonite, and dolomite) system. We have used density functional theory and molecular orbital theory to predict the <sup>12</sup>C/<sup>13</sup>C isotopic fractionation factors. We have developed and tested a range of methods for such predictions including implicit solvation, super-molecule cluster approaches, and the accuracy of current exchange-correlation functionals in combination with various basis sets.

**Results:** Quantum chemical calculations on large supermolecular carbonate-water and carbonate mineral clusters are used to predict equilibrium constants for <sup>13,12</sup>C isotope-exchange reactions between CO<sub>2</sub>(g), aqueous carbonate species, and the common carbonate minerals. For the aqueous species, we evaluate the influence of the size and conformational variability of the solvation shell, the exchange-correlation functional, and the basis set. The choice of exchange-correlation functional (PBE vs. B3LYP), the basis set (6-31G\* vs. aug-cc-pVDZ), and solvation shell size (first shell only vs. first shell and a partial second shell) each produce changes of ~5-10 per mil in the reduced partition function ratio. Conformational variability gives rise to a standard error of ~0.5 per mil using ~10 solute-solvent conformations. The best results are obtained with the B3LYP/aug-cc-pVDZ combination, but because the improvements in the basis set and exchange correlation functional drive the reduced partition function ratios in opposite directions, reasonably good results are also obtained with the PBE/6-31G\* combination. To construct molecular clusters representative of mineral environments, a new method is introduced based on conservation of Pauling bond strength. Using these clusters as models for minerals, calculations of mineral-gas and mineral-aqueous carbon-isotope fractionation factors, are in good agreement with experimental measurements. Carbon-isotope fractionation factors for gas, aqueous and mineral phases are thus integrated into a single theoretical/computational framework.

## UNIVERSITY OF CALIFORNIA, DAVIS

Department of Geology

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**Grant:** DE-FG02-04ER15639

### How Do Interfacial Phenomena Control Nanoparticle Structure?

*James R. Rustad, 530-754-6021; [jrrustad@ucdavis.edu](mailto:jrrustad@ucdavis.edu), Jillian F. Banfield (UC Berkeley), Glenn Waychunas (Lawrence Berkeley National Laboratory)*

**Objectives:** Nanomaterials may have particularly heterogeneous surface structures owing to their high interfacial curvatures. Crystal structures of the hydrated salts of Al and Fe oxide nanoparticles exhibit a wide variety of structural environments with different accessibility of solvent and counterions at various regions on the particle surface. It is important to know how much variation this causes in site reactivity and what factors most strongly influence reactivity in nanoparticle environments.

**Project Description:** Water exchange rates are the most fundamental measure of the kinetics of water-mineral interaction. This project uses molecular dynamics methods to simulate chemical reactions on nanoparticle surfaces. The predictions can be compared to rate measurements in the literature, often at a site-specific level. These include the  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  monomer; the  $\epsilon$ -Keggin ion  $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+/8+}$  (**Al<sub>13</sub>**); the  $[\text{Al}_2\text{O}_8\text{Al}_{28}(\text{OH})_{56}(\text{H}_2\text{O})_{26}]^{18+}$  (**Al<sub>30</sub>**) aqueous polyoxocation; the surfaces of Al-oxyhydroxide minerals boehmite ( $\text{AlOOH}$ ) and gibbsite ( $\text{Al}(\text{OH})_3$ ); and the aluminosilicate mineral kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ). Calculations use rare events molecular dynamics methods to calculate both the free energy barrier in the potential of mean force and the transmission coefficient. These are combined to generate the overall rate of reaction.

**Results:** To evaluate the pathways of water exchange reactions, we have simulated exchange of inner-sphere and bulk water molecules for different sizes of  $\text{Al}^{3+}(\text{aq})$  clusters,  $\text{Al}(\text{H}_2\text{O})_6^{3+} + n\text{H}_2\text{O}$  for  $n = 0, 1, 6$  or  $12$ , with *ab initio* and molecular dynamics simulations, in order to understand how robust the *ab initio* method is for identifying hydrolytic reaction pathways. This elementary reaction is particularly simple and well constrained by experiment. Nevertheless, we find that a rich array of parallel reaction pathways that depend sensitively on the details of the solvation sphere and structure, and that larger clusters are not necessarily better. Inner sphere water exchange in  $\text{Al}^{3+}(\text{aq})$  may occur through two dissociative pathways, one in which the incoming and outgoing waters are *cis*, the other in which they are *trans* to one another. A large majority of exchanges in the molecular dynamics simulations occurred via the *trans* mechanism, in contrast to the predictions of the *ab initio* method. In  $\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O}$ , the *cis* mechanism has a transition state of 84.3 kJ/mol, which is in good agreement with previous experimental and *ab initio* results, while the *trans* mechanism has only a saddle point with two negative frequencies, not a transition state, at 89.7 kJ/mol. In addition to the exchange mechanisms, dissociation pathways could be identified that were considerably lower in energy than experiment and varied considerably between 60-100 kJ/mol, depending on the particular geometry and cluster size, with no clear relation between the two. *Ab initio* calculations using large clusters with full second coordination spheres ( $n = 12$ ) were unable to find dissociation or exchange transition states, because the network of hydrogen bonds in the second coordination sphere was too rigid to accommodate the outgoing inner sphere water.

## UNIVERSITY OF CALIFORNIA, DAVIS

Department of Chemistry, Department of Geology  
Davis CA 95616

**Grant:** DE-FG-02-05ER15693

### **Proton Exchange Rates and Other Elementary Reactions in Large Aqueous Molecules: A Combined Experimental and Simulation Project**

*Dr. William H. Casey, 916-752-3211; [whcasey@ucdavis.edu](mailto:whcasey@ucdavis.edu)*

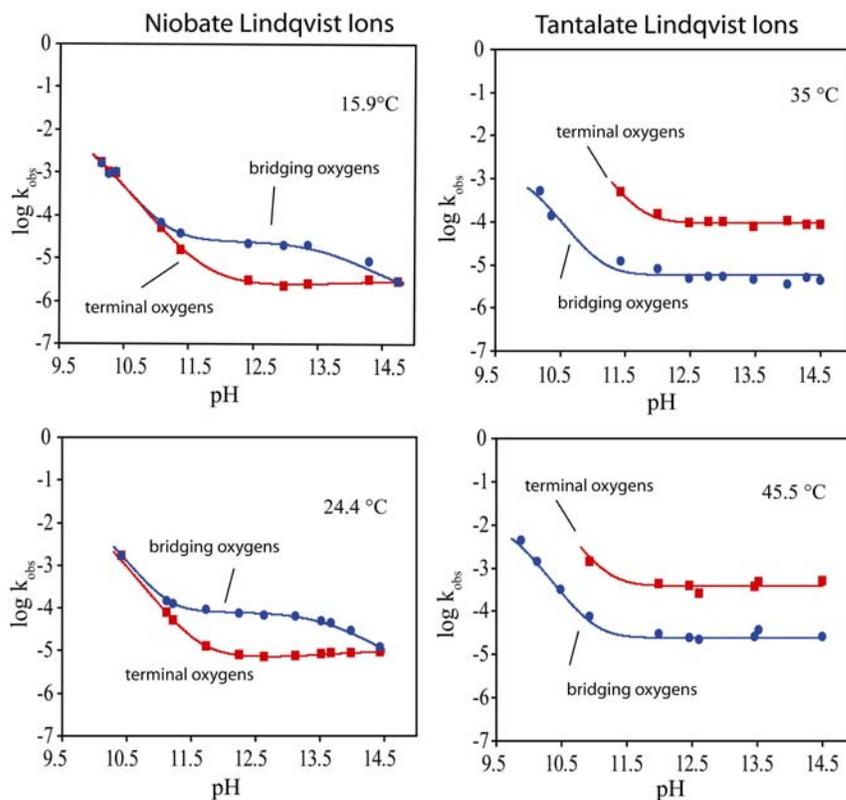
**Objectives:** We want to be able to accurately assign reactivities to the various structural elements in oxide materials and particularly at their interfaces with water.

**Project Description:** Geochemists have been trying to understand the aqueous-mineral interface at the molecular scale through computer simulations and experiment. Even simple proton-enhanced dissolution, however, has no clear consensus because molecular pathways cannot be identified in experiment. Nanometer-size oxide ions can answer many of the questions, such how protons affect labilities, how individual oxygen sites react with water and how fast. Unlike surfaces, these nanometer-size clusters allow one to follow reactions at individual structural oxygens and to separately identify the dissociation pathways. We can also assess the accuracy of our computer methods.

We are studying sets of oxide clusters and follow these elementary or near-elementary reactions using  $^{17}\text{O}$ -NMR spectroscopy and electrospray-ionization mass spectrometry. These methods allow us to follow oxygen-isotope-exchange reactions at specific structural sites, which is otherwise impossible.

**Results:** We reported residence times for protons on the bound waters and two sets of  $\mu$ -OH bridges for the  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  nanocluster. These results provide one of the only constraints for proton residence times for mineral surfaces, which the clusters resemble. We also extended the work to other nanometer-size clusters including Lindqvist ions, which are a superoctahedron of  $\text{M}(\text{O})_6$  octahedra that are all linked at a single inert  $\mu_6$ -oxo. They have a central  $\mu_6$ -O site, twelve  $\mu_2$ -O bridges, and six terminal  $\eta=\text{O}$  sites, all of which are observable in  $^{17}\text{O}$ -NMR. The structures of Nb(V) and Ta(V) Lindqvist ions are virtually identical because of the Lanthanide contraction that nearly equalizes the  $\langle\text{M}-\text{O}\rangle$  bond lengths. Metals in the two structures have a closed-shell electronic configuration and primarily differ by the full shell of  $4f^{14}$  electrons in the Ta(V) version of the Lindqvist ion [Figure 1]. We show that the relative rates of isotopic exchange of the  $\eta=\text{O}$  and  $\mu_2$ -O sites *invert* as one goes from Period 5 [Nb(V)] to Period 6 [Ta(V)], although these molecules are virtually isostructural and nearly isoelectronic. These observations challenge our understanding of reaction pathways in aqueous solutions and provide key test cases for computer simulations of reaction dynamics in aqueous solutions.

**Figure 1:**  $^{17}\text{O}$ -exchange rates for the  $[\text{H}_x\text{Nb}_6\text{O}_{19}]^{(8-x)-}$  (**left**) and  $[\text{H}_x\text{Ta}_6\text{O}_{19}]^{(8-x)-}$  (**right**) Lindqvist ions. The data for the  $\mu_2\text{-O(H)}$  are in blue circles and the data for the  $\eta=\text{O}$  are in red squares. The lines correspond to fits of a rate law to the data.



## UNIVERSITY OF CALIFORNIA, DAVIS

Department of Physics and Geology, and Center for Computational Science and Engineering  
Davis CA 95616

**Grant:** DE-FG02-04ER15568

### **Collaborative Research: Understanding Multi-Scale Space-Time Patterns in Crustal Deformation Processes: Towards Ensemble Forecasting in Complex Tectonic Systems**

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**Objectives:** To develop a physical understanding of the origins of space-time patterns and statistical correlations occurring in geomechanical and tectonic systems, and use these to forecast future activity that may produce disasters affecting a variety of critical energy facilities, such as nuclear power plants, oil refineries, and national laboratories.

**Project Description:** The complex earth system generates a variety of phenomena that are highly nonlinear and operate over a broad range of spatial and temporal scales. Signatures of these processes include scaling (fractal distributions), global and local self-organization, intermittency, chaos and the emergence of coherent space-time structures and patterns. We are using massively parallel simulations to model geodynamical effects observed in earthquake systems in order to determine the origin of these phenomena. These investigations and the theoretical efforts done in parallel are particularly aimed at quantifying the limits of predictability for disasters such as earthquakes that occur within the earth system. We are currently continuing our development of the theoretical and computational tools that allow us to both obtain sufficient data on realistic models and to analyze the data we obtain. From these simulations we will then predict geodetic and other deformation associated with impending earthquakes to be tested against Global Positioning System, Synthetic Aperture Radar, seismicity and other field data.

**Results: Theoretical Models:** We have developed a variety of models for magmatic intrusions in the La Palma volcano in the Canary Islands. These computations indicate that a highly massive magmatic body is active underneath the central region of Cumbre Vieja. We also developed a series of models for earthquake seismicity known as the Branching AfterShock Sequence, or BASS. BASS is also applicable to material damage and defect mechanics, the primary subject of our further work for DOE/OBES. This model realistically simulates the diffusion of seismicity as well as the scaling properties obtained from a statistical physics analysis of the underlying processes.

**Pattern Analysis:** We have carried out a detailed analysis of the space-time information content of global earthquake catalogs. We have also developed a variety of new testing algorithms, including a simple Chi-square approach, to understand the space-time error inherent in forecasts as a function of the forecast area fractional coverage (false alarm rate). Tests such as these are critical to the development of successful ensemble forecast methods. In collaboration with K. Tiampo (UWO, Canada), we also analyzed the ergodic properties of sequences of California earthquakes.

**Numerical Simulations:** During this period, we have developed a variety of acceleration algorithms for use on parallel computers for our system-wide earthquake simulation. We have also developed a series of data mining and pattern analysis techniques that can be directly exported to real fault data. Finally, we

have constructed new and much more topologically detailed models for use at finer scales of resolution in space and time.

## UNIVERSITY OF CALIFORNIA, SANTA BARBARA

Department of Earth Science  
Santa Barbara CA 93106

**Grant:** DE-FG02-96ER14620

### **Physiochemical Evidence of Faulting Processes and Modeling of Fluid Flow in Evolving Fault Systems in Southern California**

*James R. Boles, (805)893-3719; [boles@geol.ucsb.edu](mailto:boles@geol.ucsb.edu), Grant Garven, Johns Hopkins University (now at Tufts University)*

**Objectives:** This is a collaborative study to quantify basinal fluid flow, submarine methane migration and diagenetic effects within deforming faults in a transpressional setting that is seismically active. Most of the work deals with faulted basins of California.

**Project Description:** We have mainly targeted active faults and young petroleum fields in southern California for study including the Refugio Fault in the Transverse Ranges, Ellwood Fault in the Santa Barbara Channel, and the Newport-Englewood Fault in the Los Angeles Basin. Subsurface core samples, outcrop samples, well logs, reservoir properties, pore pressures, fluid compositions and published structural-seismic sections are being studied to characterize the tectonic/diagenetic history and degree of compartmentalization for these known fault networks. We are also investigating the geochemical signatures in carbonate that characterize rapid CO<sub>2</sub> degassing. These data provide constraints for finite element models that are being developed to predict fluid pressures, flow patterns, rates and patterns of deformation, subsurface temperatures and heat flow, and geochemistry associated with large fault systems.

**Results:** We have recently been completing our study of disequilibrium effects during calcite crystallization as a result of rapid CO<sub>2</sub> degassing. Our goal has been to develop a quantitative understanding of this phenomenon in order to interpret geochemical signatures, including both isotopic and trace element compositions, of fault zone cements. Well tubing scales and speleothems that have grown at rates of 1 mm per year or greater, show covarying carbon-oxygen isotopic values with slopes up to + 5.  $\delta^{18}\text{O}$  oxygen is at least several per mil more positive than expected from equilibrium. Scales are also enriched in heavy carbon up to 28 per mil, due to CO<sub>2</sub> degassing. Scales from the Lost Hills field have up to 16 wt % Mg substitution and are out of isotopic equilibrium with formation waters, which is attributed to rapid calcite crystallization. Scales from other fields, however, do not appear to have this unexpected Mg substitution. Growth rate-related Mg-substitution in calcite may have important implications for interpreting Mg/Ca ratios in calcite used for temperature interpretations in paleoclimate studies. Calcite in fault zones from Southern California do not show the distinctive isotopic and trace element signatures of well scales. From this we infer that fault zone cementation is not a result of rapid precipitation during a rupture event but rather a slow post-seismic infilling of newly created fault void space.

We continue to study the South Ellwood fault and wells in the South Elwood field where we have calculated fault permeability from the rate of seawater influx into an underpressured reservoir. We are currently investigating the effect of the influx on reservoir water chemistry and communication between

compartments and will be testing our calculations in other wells from down hole pressure-temperature sensors. The installation of these sensors has been delayed until 2008, at which time we should be able to obtain accurate downhole pressure and temperature data.

In the Los Angeles basin, Mike Ryan, current UCSB Masters student, is analyzing formation water samples from uncontaminated deep zones along the Newport-Englewood Fault in the Los Angeles Basin that will allow us to explore the hydrology of this important transpressional fault zone. From this same zone, we have recently acquired core samples and electric well logs (including image) from 40 deep wells recently drilled by Plains Exploration and Production. Mr. Ryan has begun x-ray diffraction and petrographic analysis of these samples. These wells have penetrated an igneous body, previously unknown anywhere in the LA basin. The igneous rock is associated with the termination of the NI fault and appears to have caused significant diagenetic and thermal effects on the reservoir sands.

The planning stages of an oil company-sponsored well designed to core the N-I fault zone near the southern end continue to progress. We have begun talks with the Southern California Earthquake center and are discussing permanent monitoring of the hole and additional projects on the core from the fault zone and adjacent unfaulted rock. It is anticipated the well will be drilled and cored in 2008. The collaboration between UCSB and Tufts University (formerly JHU) continues to be strong and successful, and we are incorporating new collaborators when opportunities appear as described in the modeling work summary by Garven.

## UNIVERSITY OF CALIFORNIA, SANTA CRUZ

Institute of Geophysics and Planetary Physics  
Santa Cruz CA 95064

**Grant:** DE-FG02-04ER15530

### **High Resolution/High Fidelity Seismic Imaging and Parameter Estimation for Geological Structure and Material Characterization**

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**Objectives:** Develop new, improved methods for wave equation migration-imaging and extend these methods for estimating impedance contrasts and material properties at boundaries. The work focuses on three general areas: (1) development of new, more efficient, more accurate, wave-equation-based propagators and imaging conditions for migration imaging; (2) developments toward true amplitude imaging that allows estimation of the reflection as a function of angle at an interface; and (3) study of wave propagation in heterogeneous, elastic media. These efforts are all focused on obtaining more reliable quantitative information about rock properties from seismic data and images resulting from seismic data.

**Project Description:** High-resolution/high fidelity seismic imaging is critically important for both energy resource management (oil/gas exploration/production) and monitoring CO<sub>2</sub> sequestration. We propose to exploit natural advantages of our method for providing reflection amplitude vs. angle information that can be used to infer *in situ* parameters like rock properties and fluid type and content. We also propose to develop imaging methods using multi-component elastic data. Conventional Amplitude vs. Offset (AVO) analysis to obtain material properties has had limited success in geologically complex regions. Thus, new methods of obtaining material property information are needed. Wave-equation based approaches have shown some promise for providing information about material properties but additional effort is needed to develop and fully exploit the capabilities of such methods.

#### **Results:**

##### *(1) Multi-scale seismic migration/imaging*

Standard seismic migration using a Ricker source wavelet is close to a single-scale imaging, and is essentially a high-frequency imaging to the structures of interests. The low-wavenumber components of many important structures, such as salt domes, are lost in the imaging. In this study we propose a multi-scale seismic imaging scheme to reconstruct the full spectra of the heterogeneities, including the low-wavenumber information. We decompose the medium heterogeneities into multi-scale representation by multi-resolution analysis using dyadic scaling. The multi-scale images by one-way beamlet migration using the band-passed data (octave bandwidths) of the SEG/EAGE salt model correspond well with the relative structures after the dyadic scaling of the original model. The final image by summing up all the

scales has much richer low-wavenumber components and is much closer to the original model than the standard one-way wave migration.

*(2) Wavelet transform and its applications in seismic migration, illumination and true reflection imaging*

We develop a new decomposition scheme for wavefield using local harmonics. Beamlet migration using the local harmonic propagators has the same efficiency as LCB propagator but has direction localization built in the propagators. Preliminary tests for prestack depth migration using the synthetic data of the 2D SEG/EAGE salt model demonstrate the good imaging quality and the ability of direction localization.

In the original acquisition aperture correction in the local-angle domain, the image is directly formed using the wavefields in the local-angle domain, which is very time-consuming due to the computationally demanding angle-domain decomposition. Based on the efficient local-wavenumber domain decomposition of the wave fields, we propose a fast method to obtain the image in the local-angle domain with shot summation in the local-wavenumber domain. For a given frequency the images in the local-wavenumber domain can be efficiently formed for each shot and then summed up to form the image for all shots in the local-wavenumber domain. This summed image for all shots for a given frequency is then interpolated to form the image in the local-angle domain. By similar strategy, the amplitude correction factor in the local-angle domain can be obtained too. With the image matrix and amplitude correction factor matrix in the local-angle domain, same acquisition aperture corrections can be applied as in the original method. In 2D SEG/EAGE salt model, the new method shows similar results to the original method, including the image and amplitude correction factor in the local-angle domain and the final corrected total strength of the image, but the new method is far more efficient.

*(3) The finite-frequency sensitivity analysis for migration residual moveout and its applications in migration velocity analysis*

We derive a broadband sensitivity kernel relating the residual moveout in prestack depth migration to velocity variations in migration velocity model. We then validate this sensitivity kernel by comparing it with the residual moveout directly measured from the migration image. Based on this sensitivity kernel, we propose a new tomography method for migration velocity analysis. Numerical examples are used to demonstrate the potential applications of this broadband sensitivity kernel in migration velocity updating. We use the fast one-way propagator and the one-return approximation to calculate the sensitivity kernel. The new method is formulated for the shot-record prestack depth migration and shot-index common image gather. Thus no time consuming angle domain analysis is required. The new approach is a wave-equation based method which naturally incorporates the wave phenomena and is best teamed with the wave-equation based migration method for velocity analysis.

## UNIVERSITY OF CALIFORNIA, SAN DIEGO

Department of Chemistry and Biochemistry  
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**Contract:** DOE DE FG02-06ER15767

### **First Principles Simulation of the Temperature Composition and Pressure, Dependence of Natural Fluids**

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**Objectives:** 1<sup>st</sup> principles simulations methods are being developed and applied to the study of the chemical behavior of metal ions, their counter ions and their oxo-hydroxo hydrolytic polyions in aqueous solutions. The understanding of the aqueous chemistry of these species is essential to the interpretation of processes such as, the formation of minerals, the sequestration of CO<sub>2</sub>, the storage of nuclear waste, and the transport of toxic materials. The 1<sup>st</sup> principles based simulation methods that are being used and developed in this program allow the parameter free prediction of the properties of these chemically complex materials over the wide range of conditions encountered in geological applications.

**Project Description:** The results of this research will contribute to the molecular level understanding of the chemistry of processes such as ore formation, toxic species transport, mineral solubility, and absorption on mineral surfaces for sub-critical to supercritical conditions as well provide for the more detailed analysis of the new classes of experiments such as, high resolution NMR, X-ray absorption fine structure, sum frequency vibrational spectroscopy, high resolution x-ray and neutron scattering, photoelectron spectroscopy etc. that are being used to study fundamental geochemical processes at the molecular level. Since for many of these problems the appropriate simulation methods and implementations are not yet available, an important strength of this program is our ability to develop and efficiently implement new parameter free methods of simulation. The metals included as application targets in this research, Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Ca<sup>2+</sup>, and Ni<sup>2+</sup>, are chosen because of their geochemical importance and because they display a wide range of properties such as very different hydrolysis constants, ligand residence times, formation of oxo-hydroxo hydrolytic polyions. In this research we endeavor to relate the properties of the ions to their chemical behavior in geological applications. The program is carried out through the very close collaboration of researchers at PNNL (co-PI Eric Bylaska) and UCSD (PI John Weare). The researchers in these two institutions collaborate in both the methods development and application aspects of the program. Collaboration is enhanced by the frequent visits of the PIs and their co workers, the graduate students and postdoctoral students in the program to both institutions. While the closeness of the collaboration makes it difficult to assign tasks, there is more emphasis on methods development at PNNL and on chemical application at UCSD. However, every student in the program will participate in some aspect of methods and software development and in application simulation.

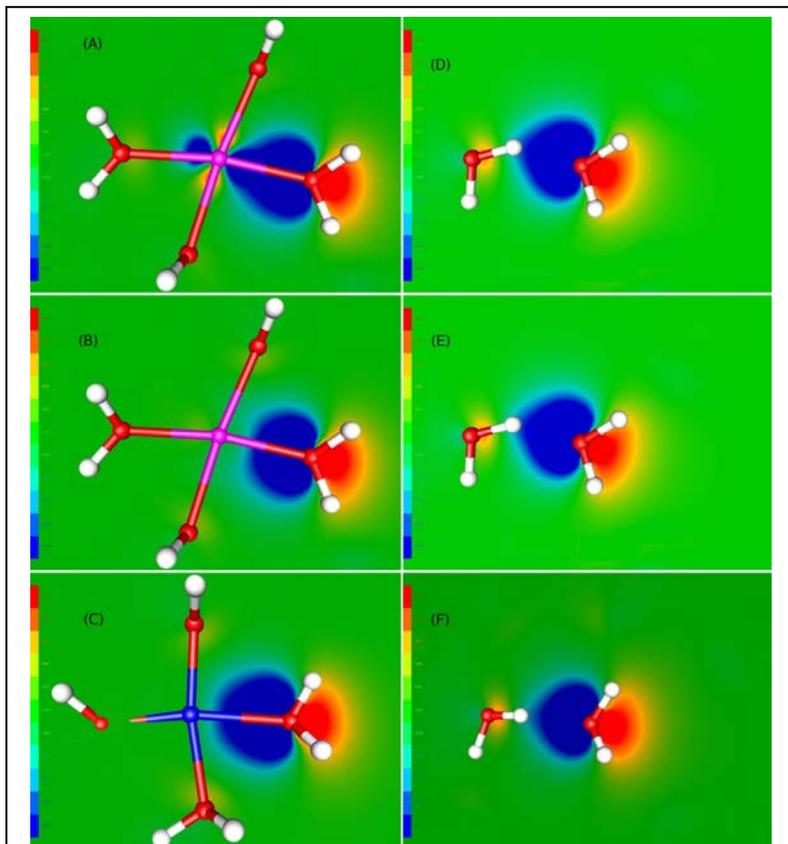


Figure 1. Cross-section of Lone Pair (L.P.) Wannier orbitals. A, B show 1<sup>st</sup> shell spin up and spin down L.P. of Fe<sup>3+</sup>, C gives the restricted first shell L.P. of Al<sup>3+</sup>. D,E show spin up and spin down L.P. for 2<sup>nd</sup> shell water of Fe<sup>3+</sup>, F shows the restricted 2<sup>nd</sup> shell L.P. for Al<sup>3+</sup>. The value of the Wannier orbital density is given by the inset color scale (blue = -0.1, red = 0.1, final = 0.02). Some surrounding waters have been removed for clarity.

**Applications Results:** Highly charged ions in aqueous solutions interact strongly with neighboring water molecules forming very stable 1<sup>st</sup> and 2<sup>nd</sup> hydration shells. The primary interactions are Coulombic. Therefore, many thermodynamic and dynamic properties roughly scale with the ion size and charge. However, within a particular charge type (e.g. Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, etc.) there may be very significant differences in behavior. A well known example is the ligand field stabilization enthalpy,  $\Delta H_{hyd}$ , in which the enthalpy of metal ion hydration varies with the d electron occupation moving through the transition metal series. The common interpretation is that the octahedral symmetry of the 1<sup>st</sup> hydration shell splits the degeneracy of the d electron ion valance orbitals. The excess stability of the hydrated species is assumed to be due to the partial filling in these orbitals. This is based on a purely electrostatic treatment of the interaction between the d electrons and the ligands. However, experimental evidence has recently been presented for the covalent interaction of the ion orbitals with those of the solvated water molecules. No such interaction is observed in the similar charged species, the Al<sup>3+</sup> ion. A significant advantage of the

*ab-initio* molecular dynamics methods that we have been developing is the availability of electronic structure information. These simulations show that the electronic densities of the localized Wannier representations of the spin down lone pair electrons of the hydrating waters of 3d<sup>5</sup> (spin up) Fe<sup>3+</sup> interact strongly with the with the unoccupied spin down orbitals of the ion center. This results in the significant d-type structure displayed in Fig. 1A. It is interesting to observe that the spin up Wannier orbitals do not share density with the spin up orbitals of the spin up polarized ion, Fig. 1B, presumably because of exchange repulsion. This d-type interaction is not displayed by the restricted lone pair of the Al<sup>3+</sup> first shell (compare Fig. 1C with B and D-F). In Fig. 1D-F the spin up and spin down Wannier orbitals of a second shell water of hydration of the Fe<sup>3+</sup> ion (D and E, respectively) and Al<sup>3+</sup> (F) are also plotted, showing that the spin perturbation does not go beyond the first hydration shell.

**Methods Developments Results:** See PNNL report (Co PI Eric Bylaska):

## UNIVERSITY OF CHICAGO

Center for Advanced Radiation Sources  
5640 S. Ellis Avenue  
Chicago IL 60637

**Grant:** DE-FG02-94ER14466

### **GeoSoilEnviroCARS: A National Resource for Earth, Planetary, Soil and Environmental Science Research at the Advanced Photon Source**

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**Objectives:** GeoSoilEnviroCARS is a national consortium of earth scientists whose goal is to design, construct and operate, as a national user facility, synchrotron radiation beam lines at the Advanced Photon Source, Argonne National Laboratory.

**Project Description:** Instrumentation for the following techniques is provided for earth and environmental science research: (1) x-ray absorption fine structure spectroscopy; (2) fluorescence microprobe analysis and microtomography; (3) powder, microcrystal and surface diffraction; (4) high-pressure crystallography with diamond anvil cells and multi-anvil presses, and (5) radiography at high pressure in the multi-anvil press. Research areas include phase transitions in mantle minerals; the properties of the Earth's core; migration and remediation of toxic metals and radioisotopes in contaminated sediments; structure, reactivity and sorption at the mineral-water interface; the chemical nature of hydrothermal fluids and magmas; and flow dynamics of fluids and solids.

**Results:** Two hundred fifty seven (257) beam time proposals were received, 302 unique users conducted experiments, and 60 papers were published. Published research included the following (lead collaborators in parentheses): Structure of the hydrated hematite ( $1\bar{1}02$ ) surface (K. Tanwar); Transformations of mercury, iron, and sulfur during the reductive dissolution of iron oxyhydroxide by sulfide (A. Slowey); Air-water interfacial areas and interfacial partitioning tracer tests (M. Brusseau); Effect of CO<sub>2</sub> on the speciation of bromine in low-temperature geological solutions (K. Evans); Microstructure of granular materials (R. Al-Raoush); Microscale heterogeneity in biogeochemical uranium cycling (M. Ginder-Vogel); Long-term stability of organic carbon-stimulated chromate reduction in contaminated soils (T. Tokunaga); Structure of the hydrated ( $10\bar{1}4$ ) surface of rhodochrosite (Y.-S. Jun); Low-pressure decomposition of chrysotile (P. Candela); Thallium compartmentalization in *Iberis intermedia* (K. Scheckel); Eu/HNO<sub>3</sub> aqueous solutions and Nb-bearing silicate melt phases coexisting with hydrothermal fluids (R. Mayanovic); Magnetite scavenging and the buoyancy of bubbles in magmas (G. Gualda); Hydrated  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> ( $1\bar{1}02$ ) surface structure: Role of surface preparation (K. Tanwar); Cobalt storage mechanism in hyperaccumulator *Alyssum murale* (R. Tappero).

## UNIVERSITY OF CHICAGO

Center for Advanced Radiation Sources  
5640 S. Ellis Avenue  
Chicago IL 60637

**Grant:** DE-FG02-92ER14244

### **Synchrotron X-ray Microprobe and Microspectroscopy Research in Low Temperature Geochemistry**

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**Website:** <http://www.bnl.gov/x26a/>

**Objectives:** The objectives are to apply a synchrotron-based x-ray microprobe for determinations of the compositions, structures, oxidation states, and bonding characteristics of earth materials with trace element sensitivity and micrometer spatial resolution.

**Project Description:** The project aims to develop and utilize the x-ray fluorescence microprobe on Beamline X26A at the National Synchrotron Light Source (Brookhaven National Laboratory). Available spatially-resolved analytical techniques include x-ray fluorescence, x-ray absorption fine structure spectroscopy, fluorescence microtomography and x-ray diffraction. Research focuses on scientific problems in geochemistry and environmental science including the cycling of contaminants in organic/inorganic systems, biogeochemistry of actinides and metals, crystal chemistry of energy-relevant elements, and oxidation states of igneous systems.

**Results:** Fifty (50) unique users conducted experiments within the past year and 15 papers were published. Published research included the following (lead collaborators in parentheses): (1) long-term stability of organic carbon-stimulated chromate reduction in contaminated soils and its relation to manganese redox status (T. Tokunaga et al.); (2) influence of sources on plutonium mobility and oxidation state transformations in vadose zone sediments (D. Kaplan et al.); (3) macroscopic and spectroscopic characterization of arsenate adsorption and incorporation mechanisms by calcite (V. Alexandratos et al.); (4) real-time speciation of uranium during active bioremediation and U(IV) reoxidation (J. Komlos et al.); (5) alteration of iron-rich lacustrine sediments by dissimilatory iron-reducing bacteria (S. Crowe et al.); (6) simultaneous x-ray absorption spectroscopy of uranium, iron, and manganese in contaminated sediments during bioreduction (T. Tokunaga et al.). Ongoing research projects included (1) correlations between elemental microdistributions and coral skeleton micro-architecture (E. Hendy and A. Lanzirotti); (2) arsenic oxidation state heterogeneity and correlations with mineralogy in mine waste solids from Yellowknife and Nova Scotia (H. Jamieson et al.), (3) uranium fate and transport during saline waste solution infiltration into Hanford vadose zone sediment (J. Wan et al.).

## UNIVERSITY OF CHICAGO

Department of the Geophysical Sciences  
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**Grant:** DE-FG02-01ER15254

### **Kinetic Isotope Fractionation by Diffusion in Liquids**

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**Objectives:** The major objective of our research effort is to continue documenting and quantifying kinetic isotope fractionations during chemical diffusion in a variety of liquids ranging from silicate melts to water. A significant part of the effort involves developing and validating high-precision isotope measurements of Ca, Fe, K, Li, Mg, and Si by multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) on purified solutions or by laser ablation. We are also using the CAMECA 1280 multicollector ion microprobe at the University of Wisconsin to make high-precision Si and Mg isotopic measurements on spots as small as 10 microns.

**Project Description:** Diffusion couples juxtaposing rhyolite and basalt are run in a piston cylinder assembly for various lengths of time at a pressure of about 1GPa to avoid problems with gas bubble migration. The thermal diffusion experiment are also run in a piston cylinder but in this case the assembly contains only basalt and is offset from the hot spot so as to produce a 100 – 150 °C temperature difference across the molten sample. The experiments for diffusion of dissolved salts in water involve diffusion from a small spherical container into a much larger volume of water producing a system that we have shown to be a Rayleigh fractionator from which the relative diffusivity of elements or isotopes can be determined. The run products are measured by multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) or with the CAMECA IMS-1280 ion microprobe at the University of Wisconsin.

### **Results:**

**(I) Diffusion in Silicate Liquids:** A new series of diffusion couples juxtaposing mid-Ocean ridge basalt and natural rhyolite glass have been run for measuring the isotopic fractionation of Ca, Fe, Mg during diffusion. The diffusion couples were annealed in a piston cylinder apparatus at 1.2 GPa, and held at temperatures in the range 1350°C-1450°C for times ranging from 10-15 hours. Profiles of the major element concentrations have been measured along the length of the diffusion couples using a JEOL JSM-5800LV scanning electron microscope equipped with an Oxford Link ISIS-300 energy dispersive microanalytical system. The profiles show very well developed diffusion profiles, which we will use to guide the isotopic measurements by laser ablation MC-ICPMS. Once the laser ablation measurements were completed, the diffusion couples were sectioned, dissolved and the various elements separated using ion exchange columns. The purified solution were measured using a nebuliser as input to the MC-ICPMS and isotopic compositions re-measured using methods we have already shown yield high precision results. In this way we determine the isotopic fractionation during diffusion and validate the precision of the measurements made by laser ablation MC-ICPMS. Mg isotope fractionation by chemical diffusion was found to be twice as large as that of Ca on a per atomic mass unit difference.

**(II) Isotope Fractionation by Thermal Diffusion:** We have recently published a paper on the extraordinarily large isotopic fractionations of Mg that arise when an initially homogeneous basalt melt is subjected to a temperature difference of about 100°C, where we only showed data on Mg isotope fractionation due to temperature differences of 100°C. We now have similar fractionation data on Fe, Ca, Si, and O; all of which show very large fractionations relative to our analytical precision. The paper on the thermal diffusion isotopic fractionation of all these major elements of a basalt (except for Al that has only one stable isotope) is almost complete and will be submitted within the next month.

**(III) Diffusion in Water:** Experiments specifically designed to measure the ratio of the diffusivities of ions dissolved in water were used to determine  $D_{Li}/D_K$ ,  $D_{7Li}/D_{6Li}$ ,  $D_{25Mg}/D_{24Mg}$ ,  $D_{26Mg}/D_{25Mg}$ , and  $D_{37Cl}/D_{35Cl}$ . The measured ratio of the diffusion coefficients for Li and K in water ( $D_{Li}/D_K = 0.6$ ) is in good agreement with published data, providing evidence that the experimental design being used resolves the relative mobility of ions with adequate precision to also be used for determining the fractionation of isotopes by diffusion in water.

A new set of experiments involving isotope fractionations by diffusion in both water and in methanol (a less dielectric fluid than water) have been carried out and are in the process of being measured for the fractionation of Li, Mg, Ca, and Fe. We anticipate submitting a manuscript with the results by early summer.

**(IV) Development of Analytical Techniques:** We continue perfecting methods for making high precision isotopic measurements of Mg by laser ablation MC-ICPMS and find that there is a small (~1‰ per amu), but easily corrected, matrix effect as the Mg content goes from 15 wt% to 1 wt%. New methods for measuring K isotope compositions using the MC-ICPMS at Lawrence Berkeley National Laboratory are also being developed. The most exciting new development in high precision isotope measurements involves using the CAMECA 1280 multicollector ion probe at the University of Wisconsin where we have been able to make Mg and Si isotopic measurements with a precision of 0.1 per mil on spots as small as 10 microns. We are in the process of submitting a paper on Si isotope fractionations of evaporation residues that were measured with the 1280. The 1280 will be a tremendous asset when we measure isotopic fractionations in natural samples that we expect will be on small scales (i.e., zoning of cumulate crystals).

## CLARK UNIVERSITY

Department of Physics  
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**Grant:** DE-FG02-02ER15367

### **Physics of Channelization: Theory, Experiment, and Observation**

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**Website:** <http://physics.clarku.edu/~akudrolli>

**Objectives:** We seek a fundamental understanding of the physical processes that erode channels and create drainage networks, by integrating theoretical models, laboratory experiments, and field observations.

**Project Description:** We address two aspects of the erosion problem: the “two-phase phenomenon” of water-driven granular flow, and the growth and interactions of channels. We study the former problem in the laboratory and the latter problem in both the laboratory and the field. In both cases we combine our empirical studies with theoretical analysis.

We specifically address the problem of erosion driven by subsurface “seepage” flows. As in the more commonly studied problem of erosion by overland flow, an understanding of the two-phase flow of water and grains is required to predict the conditions under which material is eroded and subsequently transported by rivers and streams. Compared to the case of overland flow, however, the growth of seepage channels is relatively decoupled from topographic roughness. Channel networks driven by groundwater flow instead reflect more purely their competition for water. We seek to better understand the conditions necessary for the initiation of erosion, the mechanisms that govern the growth of seepage-driven channels, and the processes that determine the geometry of seepage networks.

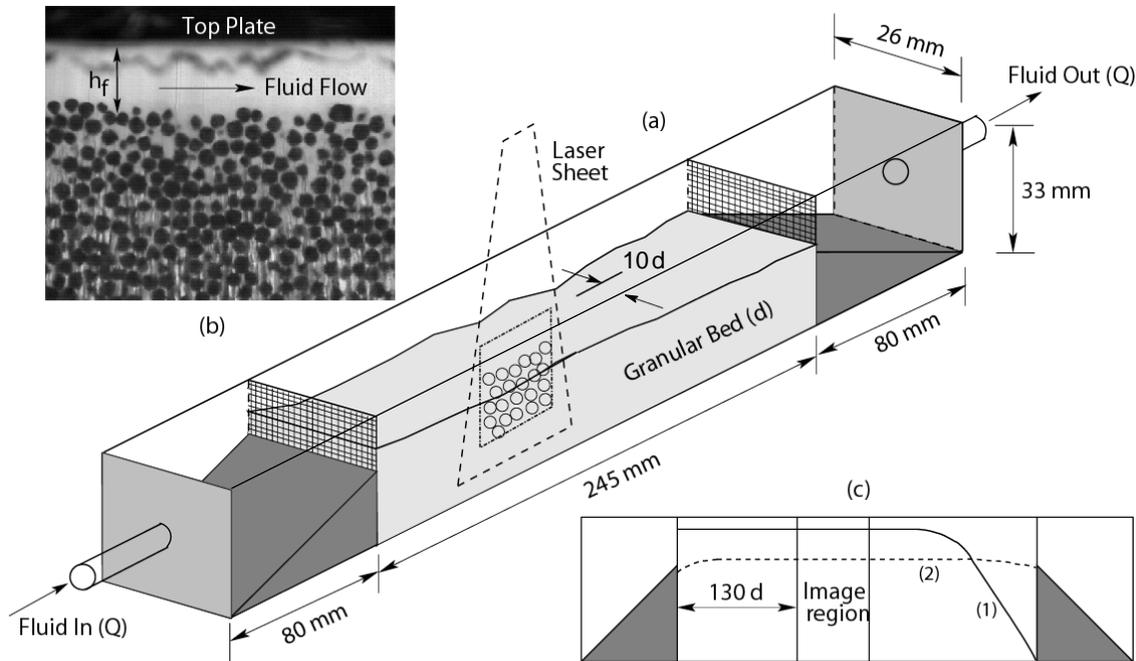
#### **Results:**

**Field study.** We have studied how the flow of subsurface water shapes the “steephead channels” that drain into the Apalachicola River near Bristol, Florida, on the Florida Panhandle. The channels are cut through 65-m thick surface deposits of sand, and are about 100 m wide and up to 4 km long. Groundwater emerges at the base of each conical channel head. The channel network is characterized by regularly spaced channels with a rough orthogonal structure. To determine how the flow of groundwater interacts with the growing channel network, we collected three-dimensional ground-penetrating radar (GPR) data in the vicinity of highly bifurcated channels. Our results suggest that the subsurface sands through which the channels are cut are effectively homogeneous at length scales comparable to or greater than a typical channel width. We conclude that the ordered, regular structure of this channel network derives from dynamics rather than subsurface heterogeneity.

**Theory.** Numerical simulations of fully three-dimensional subsurface flow into a side branch show that the vertically integrated flux into a channel's tip is roughly proportional to the planar surface area that is closer to the channel tip than to any other point on the main channel or the side branch. This *geometric area* can therefore be used to approximate the true, hydrodynamic, drainage areas and drainage

densities. We use this approximation to construct a model in which channel tips grow at a velocity proportional to the water flux they attract, and new channel tips nucleate at a rate proportional to the local drainage density. A characteristic length scale is then the typical distance  $l$  traversed by growing channels between nucleation events. The structure of the resulting network is then determined by the dimensionless ratio  $l/H$ , where  $H$  is the distance to the groundwater divide. Results show that as  $l/H$  becomes large, channels “screen” each others’ growth and the typical dimensionless distance  $d/H$  channels decreases to a constant, thus providing a tentative explanation of the ordered structure of seepage networks.

**Experiments.** The large-scale interactions between channels ultimately derive from the microscopic mechanisms that drive erosion within a single channel. A fundamental problem is to predict the granular flux for a known fluid flow. To explore this problem in the laboratory, we have constructed a new apparatus (Figure 1) that provides visualization of the grain-scale and fluid motions that occur near the critical Shields number, i.e., when the shear stresses on a granular bed are just sufficient to mobilize grains. Our flow geometry, in which the depth of the fluid gap gradually increases as the grains are eroded, results in the cessation of granular flow and thus allows for an unambiguous definition of the Shields threshold condition. By varying the fluid flux through the cell, we have verified the hypothesis that the boundary viscous shear stress is sufficient to predict cessation of granular flow.



**Figure 1:** (a) Schematic diagram of our experimental apparatus for exploring grain-scale motions at the threshold for erosion. (b) Sample image of the refractive index matched beads in a plane away from the side walls. (c) Side view of the experimental apparatus.

## CLAY MINERALS SOCIETY

3635 Concorde Pkwy  
Chantilly VA 20151

**Grant:** DE-FG02-07ER15873

### **Enchanted Clays: 44<sup>th</sup> Annual Meeting of the Clay Minerals Society**

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**Objectives:** The primary purpose of the Clay Minerals Society is to stimulate research and to disseminate information relating to all aspects of clay science and technology. Through the 2007 annual meeting in Santa Fe, the society offered individuals a means of following the many-sided growth of the clay sciences and of meeting fellow scientists with widely different backgrounds and interests. Clay Minerals Society members include clay mineralogists, crystallographers, physicists, chemists, geochemists, soil scientists, agronomists, ceramic scientists, civil engineers, petroleum geologists and engineers, and industrial scientists in fields involving products ranging from catalysts to sorbent materials.

**Project Description:** “Enchanted Clays: 44<sup>th</sup> Annual Meeting of the Clay Minerals Society” was held June 2-7, 2007 in beautiful and historic Santa Fe, New Mexico, USA. Santa Fe provided an idyllic location in the southwestern United States for the attendees to enjoy technical and social sessions while soaking up the diverse culture and wonderful climate of New Mexico—The Land of Enchantment. Over 180 scientists from around the globe attended the meeting and shared knowledge and ideas on the latest advances in clay mineral science while enjoying the historic and enchanted environs of Santa Fe. The meeting included three days of technical sessions, three days of field trips to clay and geological sites of northern New Mexico, and a full day workshop on the stabilization of carbon by clays. Details are available at the meeting web site: [www.sandia.gov/clay](http://www.sandia.gov/clay).

**Results:** The scientific sessions of the meeting kicked off on Monday morning with words of welcome from the mayor of Santa Fe, from the society president Richard Brown, and from the meeting organizer Randall Cygan. Co-organizers of the meeting included Jeffery Greathouse, George Guthrie, and Dewey Moore. Paul Schroeder was the recipient of the Marion L. and Chrystie M. Jackson Mid-Career Clay Scientist Award. The Pioneer in Clay Science Lecture was presented later by Spencer Lucas. Sessions on various clay mineral topics followed over three days. These included Carbon sequestration and stabilization by clays; Characterizing clay minerals; Clays in soils and sediments; Clays and environmental processes; Clays and archeology; Clays as nanomaterials; Clays in extreme environments; Clays in oil shale and kerogen-bearing sediments; General session; Molecular simulations of clays; and Zeolites. One hundred and three oral presentations were made during the technical sessions. Also, thirty-three technical posters were highlighted on Tuesday at a general poster session. As is customary for CMS meetings, there was a special workshop on Sunday before the formal meeting. The workshop was titled “Carbon Stabilization by Clays in the Environment: Process and Characterization Methods”, and was organized by David Laird and Javiera Cervini-Silva. Field trips to the Cerrillos Hills and Española Basin were held on both Saturday and Thursday. These were led by Dewey Moore with assistance from Paul Nadeau. There was also a visit to the Harding pegmatite, once

the primary source of beryllium for the United States. A demonstration in the art of making adobe bricks was held on Tuesday. Various administrative meetings and business lunches were held throughout the week of the conference. Finally, there was a special reception for students held on Monday evening to recognize the future leaders of the society. The financial support from the Geosciences Program of the Office of Science helped greatly to achieve the success of Enchanted Clays.

## COLORADO SCHOOL OF MINES

Center for Wave Phenomena  
Green Center  
Golden CO 80401

**Grant:** DE-FG02-05ER15739

### **Prestack Amplitude Analysis of Wide-Azimuth Seismic Data for High-Resolution Reservoir Characterization**

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**Objectives:** The goal of the project is to develop an efficient methodology for prestack amplitude analysis and inversion of multicomponent seismic data acquired over azimuthally anisotropic fractured formations. The project results will be instrumental in seismic characterization and dynamic monitoring of fractured reservoirs. In particular, seismic amplitude inversion will help in estimating the fracture orientation and density, analyzing the local stress field and assessing the capacity of a fractured medium to sequester a fluid.

**Project Description:** Since reflection coefficients carry local information about the medium properties at the top and bottom of the reservoir, amplitude-variation-with-offset (AVO) analysis can provide a much higher vertical resolution than traveltimes methods. The main focus of the project is on the joint AVO inversion of wide-azimuth PP, PS, and SS (if available) data for realistic orthorhombic and lower-symmetry reservoir models. To mitigate amplitude distortions in the overburden, we are devising a moveout-based correction for anisotropic geometrical spreading that does not require knowledge of the velocity model. The anisotropic parameters obtained from the amplitude inversion are being used for evaluating the physical properties of heterogeneous, fractured reservoirs.

#### **Results:**

##### **1. Field-data application of the anisotropic geometrical-spreading correction.**

The moveout-based anisotropic spreading correction (“MASC”) developed within the framework of the project was applied to 3D wide-azimuth P-wave data acquired above a fractured gas-sand reservoir at Rulison field, Colorado. The azimuthally varying AVO gradient (AVO ellipse) from the bottom of the reservoir revealed two major fracture-related anomalies, one of which became much more pronounced and spatially coherent after application of MASC (Figure 1).

##### **2. Geometrical-spreading correction for converted waves.**

We extended the algorithm of the moveout-based anisotropic spreading correction to mode-converted PSV-waves acquired in vertical symmetry planes of anisotropic (e.g., orthorhombic) media. Testing on full-waveform synthetic data generated by the reflectivity method confirms that MASC accurately reconstructs the PS-wave reflection (conversion) coefficient in layered anisotropic models.

### 3. AVO analysis of multicomponent data for tilted transversely isotropic (TI) media.

We developed concise approximations for PS-wave reflection coefficients in TI media with a tilted symmetry axis and compared them with exact numerical results. Our solutions provide a foundation for extending AVO-inversion algorithms to reservoirs with dipping fracture systems.

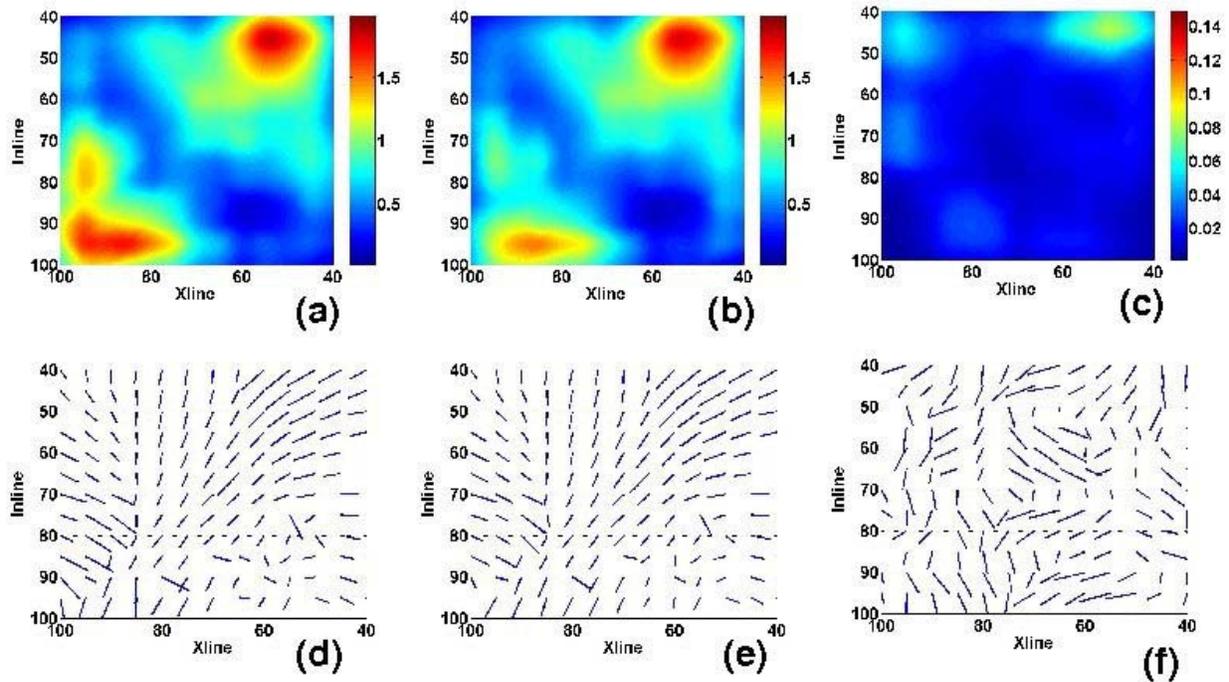


Figure 1: Results of azimuthal AVO and moveout analysis for the fractured reservoir formation at Rulison field, Colorado. AVO ellipses (a, b) were computed for the bottom of the reservoir using MASC (a) and the conventional gain correction (b); (c) shows the interval NMO ellipses in the reservoir. The color scale in plots (a, b, c) corresponds to the eccentricity of the ellipses computed by subtracting unity from the ratio of the semi-major and semi-minor axes. The bottom row displays the azimuth of the semi-major axis of the AVO (d, e) and NMO (f) ellipses; the length of the ticks is proportional to the eccentricity. Application of MASC helped to identify and focus the AVO anomaly in the lower left corner of the survey (compare plots a and b).

## COLORADO SCHOOL OF MINES

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**Grant:** DE-FG02-06ER15778

### **Monitoring the Subsurface with Multiple Scattered Waves and Quasi-Static Deformation**

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**Objectives:** Use of seismic data to monitor temporal changes in the subsurface. In this segment of the work, data analysis and wave propagation modeling have been applied to study temperature changes around a heated tunnel within the Yucca Mt., NV nuclear waste storage facility. Changes in P and S velocities correlate to changes in temperature and groundwater content, and indicate permanent change in the rock due to high temperatures.

**Project Description:** The 1998-2002 Yucca Mt. heated drift experiment used a specialized system of heaters to simulate stored nuclear waste and effects of radioactive decay heating on the tunnel, surrounding rock, and groundwater flow. While calibration shots were recorded on a seismic array installed around the tunnel, wall temperatures approached 200° C for one year, and the system was left to cool. The tunnel was bored into local homogeneous tuff, and measures 40 meters in length by 5 meters in diameter.

Receiver gathers show classic wave propagation behavior as verified in the literature for pulses incident upon cylinders (the tunnel). Wavefields around the tunnel consist of healed wavefronts, reflected waves, and creeping waves for both P and S wave input pulses. P-S and S-P converted waves exist with angular dependencies resulting in directivity effects. Individual wavelets are complicated by the proximity of the source mechanism to the tunnel wall, resulting in a complex series of incoming P and S pulses.

The addition of heat, and resulting groundwater dryout causes direct and reflected P-S arrival changes in the surrounding tuff. 2-D waveform simulation coupled with well-constrained thermal models has consistently replicated receiver data in the plane of the calibration source (barring 3-D effects). Modeling and experimental work from literature have also shown the presence of a "Franz" wave that propagates perpendicular to the tunnel wall within the transition zone at low velocities. This wave is also present in field and model data at speeds that vary with thermal input. Because this correlates with groundwater content it may be effective for monitoring the radius of intruding groundwater.

Data also show that the same waveforms effectively do not change during the two-year cooling cycle. LANL array data were preprocessed to remove spurious samples and coherent noise, and then time-aligned to the first-break of the P-wave arrival. The accompanying figure shows two sets of shear wave arrivals at a receiver located opposite the source and below the tunnel at a radius of 13 meters. The top set shows waveforms collected during the year-long heating phase. These waveforms clearly show gradual time shifts due to changing velocities resulting from addition of heat. The lower set shows

waveforms from the same receiver over a two-year cooling period. These waveforms clearly overlap, indicating that local velocities do not return to previous values.

Lack of change in the waveforms occurring during the two year cooling period infers permanent change has occurred in the rock matrix, or that long-term hysteresis effects are present. These effects have been observed analytically on large and small samples of other rock material (granite, sandstone, etc.). Unheated cases may be short-lived as the rock imbibes fluid, returning wave speeds to previous values. However, heated cases exist where the hysteresis path does not form a complete cycle, and wave speeds are permanently changed.

This hysteresis effect as seen in seismic corresponds to micro-fracturing that most likely in the superheated region directly next to the tunnel surface. These fractures tend to close only when oriented perpendicular to the local stress field.

**Results:** P-S separation and Franz wave velocity are therefore potential tools for seismically measuring the diameter of groundwater saturation around tunnels at Yucca Mt., or similar installations. Changes in arrivals observed in the data indicate potential long-term change or permanent damage to the tunnel rock/structure caused by heating and dryout.

Heating phase waveforms (top), Cooling phase waveforms (bottom), CH4

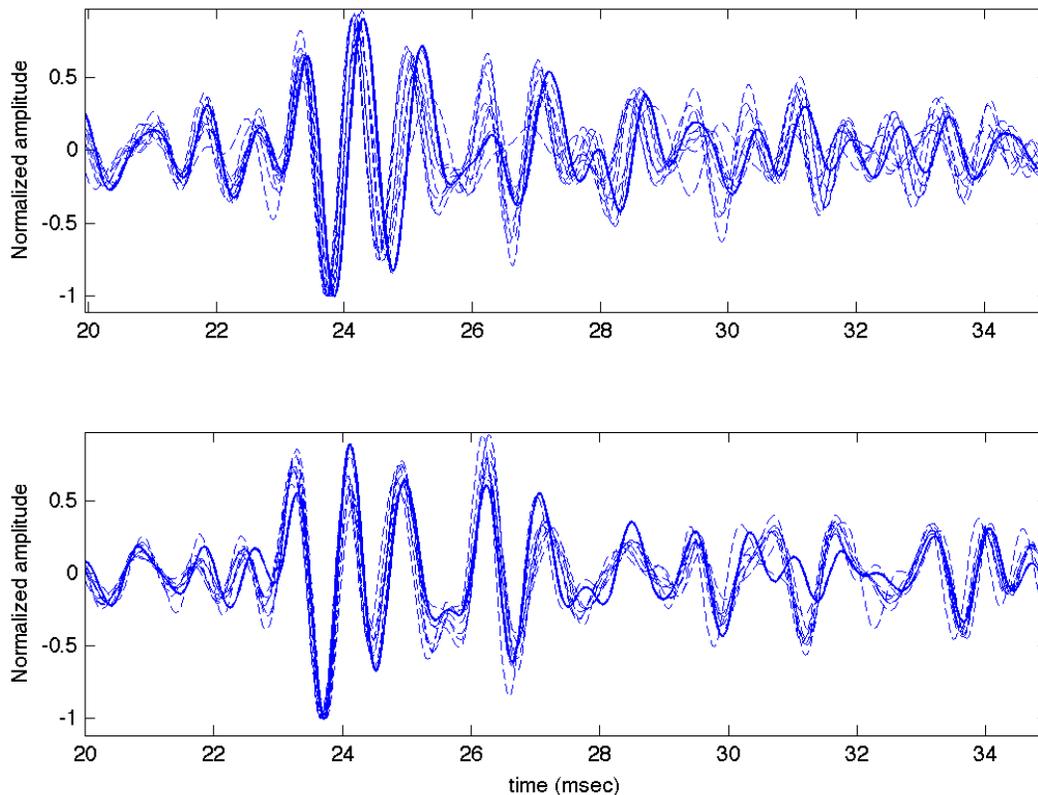


Fig. 1: Shear waves from 1-year tunnel heating phase (top), and 2-year cooling phase (bottom). Note changes in arrivals due to heating, and lack of change over longer term cooling. Minor variations due to irregular source mechanism.

## COLORADO SCHOOL OF MINES

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**Grant:** DE-FG02-07ER15841

### Investigation into the Relationship between Heterogeneity and Heavy-Tailed Solute Transport

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**Objectives:** The objective of this project is to characterize the influence that naturally complex geologic media has on anomalous dispersion and to determine if the nature of dispersion can be estimated from the underlying heterogeneous media.

**Project Description:** This project combines outcrop-scale heterogeneity characterization, laboratory experiments, and numerical simulations. The study is designed to test whether established dispersion theory accurately predicts the behavior of solute transport through heterogeneous media and to investigate the relationship between heterogeneity and the parameters that populate these models. The dispersion theory tested by this work is based upon the fractional advection-dispersion equation (fADE) model. Unlike most dispersion studies that develop a solute transport model by fitting the solute transport breakthrough curve, this project will explore the nature of the heterogeneous media to better understand the connection between the model parameters and the aquifer heterogeneity.

**Results:** Our work this year was broken into the following questions: 1) Can multi-scale geologic variability be accounted for by classical methods, and if not, can the nonlocal fractional-order equations provide better predictions?; 2) Are the fractional transport equations more accurate at the field scale?, and 3) Can the fractional-order equations be parameterized by some simple observable geologic features?

**1) Multi-scale variability:** We investigated the transport of solutes through multi-scaling fractal fields and found that plume growth is always between perfectly stratified and Fickian rates, and highly non-Gaussian. This refutes the analytic results postulated over a decade ago. We also found a simple explanation for the apparent anomalous growth of dispersivity without a need for universal structure of aquifers. The development of non-local equations required a large effort in the basic mathematics of non-local transport, leading to a new set of equations and theories for non-local, heavy-tailed transport. The transport parameters in the non-local equations can be completely arbitrary functions of space and time – just like within the classical ADE (Eq. 1). We developed a stochastic model to solve the non-homogeneous space-time nonlocal equations, and in the process showed the exact particle-tracking algorithm for all mobile/immobile formulations.

**2) Large-scale transport and fractional ADEs:** Our investigations into field-scale transport returned to the MADE site in Columbus, Mississippi. We computed the growth of the first five integer moments predicted by several theories (continuous time random walks [CTRW], fractional mobile/immobile, and space-time fractional equations). We found that the space-fractional component is key to predicting fast-moving solute, and that a fractional mobile/immobile (fractal time) component is required to predict

the decay of mobile mass. Therefore, a governing equation that makes accurate predictions at the MADE site is:

$$\frac{\partial C}{\partial t} + \beta \frac{\partial^\gamma C}{\partial t^\gamma} = -\nabla \cdot (vC - D\nabla_M^\Lambda C) \quad (1)$$

where  $C(x,t)$  is total resident concentration,  $\beta(x)$  is the immobile capacity coefficient,  $0 < \gamma < 1$  is the fractal mobile/immobile coefficient,  $t$  is time,  $v(x,t)$  is mean velocity,  $\Lambda$  is the direction-dependent fractional derivative matrix, and  $M(\theta v(x,t))$  is the mixing measure, which is essentially a three-dimensional dispersion coefficient.

**3) Parameters from Geologic Information:** The predictions at the MADE site required the estimation of a number of parameters. Some were gained from an observation of the plume itself (particularly those in the time operator on the left-hand side of eq. [1]), which amounts to fitting instead of prediction. The parameters for the space operator (order of derivative and mixing measure) were gleaned from the  $K$  distribution, with an assumption the the high- $K$  deposits originated from a braided stream environment. To investigate the ability to estimate the time parameters from geologic information, we simulated a large number of aquifers using Markov-Chain facies simulators and compared these to an analytic expression for the late-time tailing of an ensemble plume. Our results show that the fractal parameters  $\beta$  and  $\gamma$  can be very accurately estimated from boring logs by simply looking at the distribution of low- $K$  unit thicknesses. If the solute sequestered in these units is released primarily by diffusion, then the predictions of late-time tailing and remediation are very accurate.

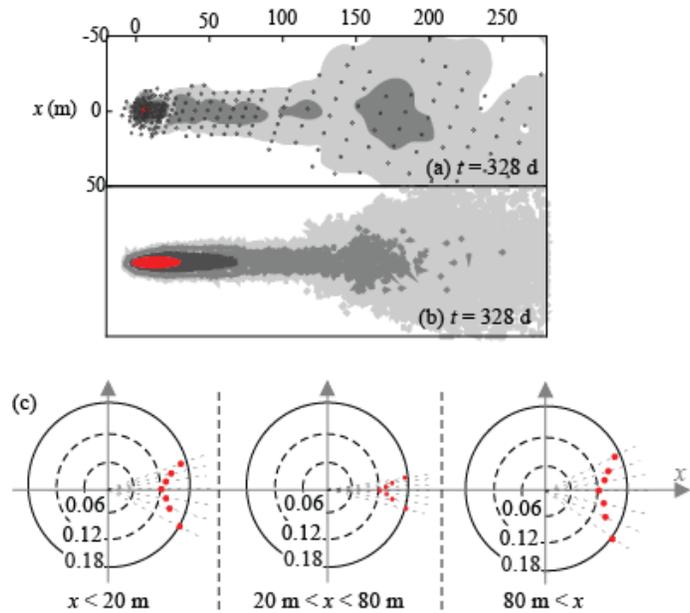


Figure 1. a) Measured and b) simulated tritium concentrations at the MADE-II test. c) Mixing measures  $M(\theta)$  used for prediction, which came from idealized braided stream patterns.

## UNIVERSITY OF COLORADO

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**Grant:** DE-FG02-04ER15589

### Monitoring the Subsurface with Multiple Scattered Waves and Quasi-static Deformation

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**Objectives:** To investigate the use of quasi static deformation in the detection of changes in the subsurface caused by the infiltration of fluid contaminants.

**Project Description:** We are exploring a new technology that is based on using low-frequency strain data to monitor changes in fluid saturation conditions in porous media. Laboratory experiments have shown that strain data can reveal changes in complex moduli, which are caused by hysteresis in meniscus movement (changes in surface tension, wettability) when a pore containing two fluids is stressed at very low frequencies (< 10 Hz).

This technology has potential applications to monitoring changes in (1) leakage at buried waste sites, (2) contaminant remediation, and (3) flooding during enhanced petroleum recovery.

A three year field study at the Maricopa Agricultural Center of the University of Arizona involved two six-week irrigation periods of a 50m by 50m area. The first irrigation was with water only and the second with water containing a bio-surfactant. Data from three tiltmeters, which had been installed along an East-West line, are being analyzed. Solid Earth tides provide an uninterrupted low frequency deformation to test our theory. We compare theoretical tidal tilts with the tilts measured at the three progressively more distant tiltmeter locations.

**Results:** Tidal tilts have maximum amplitudes of less than  $\pm 100$  nano-radians. We resolve tilts down to one nano-radian (1 micron over 1 km). Long-term tilts (many months) resulting from the relaxation of the instrumented holes are on the order of 100 micro-radians, those from routine agricultural activities, such as nearby irrigation, are as large as  $\pm 5$  microns and an Earthquake in Alaska on November third in 2002 caused a permanent tilt offset of 1 micro-radian. The tidal tilt signals are hidden in this large background noise. Special care is taken in the removal of this background noise. Since tidal signals have periods of about 12 and 24 hours and because irrigation is often done on a daily basis, thus with similar periods, we cannot simply apply narrow band filtering to remove the noise. Yet, for example, the irrigation signals are recognizable by their distinct exponential tilt characteristic and can be fit individually with specially designed functions and thus removed. The theoretical tidal signal is used as a guide in selecting the start and end points for fitting the unwanted signal, avoiding whenever possible to subtract any tidal parts of the signal.

To date we have completed the analysis over two periods, one each in the autumns of 2003 and 2004, each starting in early September and finishing at the end of January of the following year, each contained a period of irrigation. The recorded signals are spliced together, then splined to conform to the theoretical signal at 300s intervals. Then spurious background signals are removed, some, such as high frequency spikes or steps, are removed with conventional filtering, others, such as those from irrigation

or other agricultural activities, are removed individually. A simple example of an isolated irrigation signal is shown in the inset of the figure. The duration of the signals in the inset is approximately 3 days. The small, blue, sinusoidal looking trace is the theoretical tidal tilt signal, the red signal is the measured signal and the green signal is the measured minus the theoretical signal. It is the latter signal that is fit and removed. The exponential nature of the signal results from the cone of depression that forms in the groundwater when a pump is started and the recovery when the pump is shut off.

The times chosen for the irrigations were in the autumns for a multitude of reasons; human comfort and fewer agricultural activities were the main ones. The relatively low noise level in the tilt signals confirms the wisdom of these choices. After the removal of much of the noise from the measured signals, they and the theoretical signal are filtered with a 4<sup>th</sup> order zero phase-shift Butterworth filter with bandwidths from 9 hours to 16 hours and 15 to 26 hours to capture the 12 and 24 hour tidal periods respectively.

In the figure we show the residuals from the means when amplitudes of the theoretical signals are subtracted from those of the measured ones. A 14 day sliding window was advanced in steps of 3.5 days and only tidal signals that exceeded 30% of the signals at high tide were used in calculating the means. The data in the figure suggest that indeed the irrigation with the surfactant affected the tidal strain signal. It took about two weeks to see the effect, a reasonable time, which corresponds to the time for the first irrigation water to reach the groundwater level.

We are now engaged in noise removal for the entire period from October 2002 to April 2005 to see if the apparent effect we see is fortuitous or if it is associated with the surfactant irrigation. The noise levels are particularly high during late spring and the summer months when agricultural activities are at their peak.

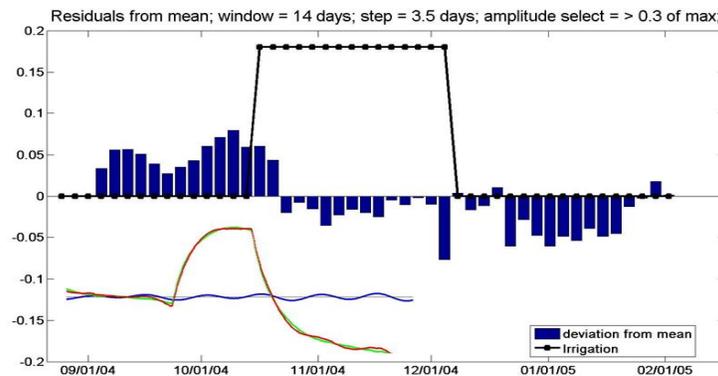


Figure Caption: The effect of irrigation (black line) on the relative amplitudes of measured and theoretical tilts are shown. The measured signals, which was cleaned and filtered for the selection of the tidal tilt around a 12 hour period, are compared with the filtered theoretical signal. Their mean amplitudes were calculated in sliding 14 day windows and the residual of measured-minus-theoretical plotted. The windows were advanced by 3.5 day steps. Because of the relatively high noise level at low tides, only tidal tilt values that exceeded 0.3 of the maximum values were used in the analysis. The inset shows a three day period, which contains an irrigation event. The small sinusoidal signal is the theoretical tilt for that period.

## UNIVERSITY OF CONNECTICUT

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**Grant:** DE-FG02-95ER14528

### **Air-Derived Noble Gases in Sediments: Sites and Mechanisms for Trapped Components**

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**Objective:** This project seeks to isolate and identify enriched noble gas components in sediments and address the fundamental processes that lead to noble gas acquisition and retention, thereby improving the application of noble gas isotope studies to multiphase fluid processes in the Earth's crust.

**Project Description:** Sedimentary rocks and oil field gases typically are enriched in heavy noble gases: Xe/Ar ratios of ~10-10,000 times the ratio in air have been observed. Although abundance patterns suggest an adsorption hypothesis, three observations argue against adsorption as the only mechanism: (1) The difference between Xe and Ar adsorption coefficients (Xe ~30x Ar) is too small to account for the observed large relative Xe enrichments; (2) heating experiments suggests the enriched component is tightly bound, counterintuitive to a simple adsorption history; (3) many sedimentary rocks (~half) and some oil field gases contain excess Ne in conjunction with excess Xe.

**Results:** We have found large Xe enrichments in the organic silica of diatomites and sponge needles extracted from live sponges (*Calyxniccaensis*) that can not be accounted for by the entrapment of water saturated with air at one atmosphere. Step-wise degassing releases He, Ne, and Ar from these samples at low temperatures (T~400 °C), whereas Kr and Xe are retained up to temperatures in excess of ~1400 °C. We have yet to find excess noble gases in inorganic silica phases, such as diagenetic euhedral quartz and petrified wood. We are in the process of analyzing diatoms (*Thalassionira weissflorii*) grown in the laboratory under controlled conditions to determine if the excess heavy noble gas enrichment reflects biotic processes or a post-mortem/depositional effect. Possible post-depositional effects are being investigated in sediment samples from sapropels of the Black Sea and the Mediterranean as well as oceanic sediments from the Peru Trench (organic rich) and the Antarctic (Si-rich). We have also initiated a study of lab aggregated nanoparticles. In preliminary analyses, we found that aggregated  $\alpha$ FeOOH (goethite) to be enriched in He and Ne up to 1000 and 40 times that expected for an equal mass of air saturated water, respectively. Step-wise degassing suggests that processes other than adsorption or diffusive acquisition of air-derived He and Ne are responsible for the excesses. These observations are being verified with re-analyses of  $\alpha$ FeOOH samples agglomerated in solutions of different pH.

## UNIVERSITY OF FLORIDA

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**Grant:** DE-FG02-98ER14853

### **Pore-Scale Simulations of Dissolution Breakthrough in Rough Fractures**

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**Objectives:** To use numerical simulations to gain a better understanding of the role of roughness in controlling the time for dissolution breakthrough in fractured rocks.

**Project Description:** A fundamental understanding of the role of fractures, and the effects they have on fluid flow, solute transport and mechanical properties, is an essential component of theoretical models of geological systems. In particular, CO<sub>2</sub> sequestration will require predictive models for the effects of fracture on the overall permeability of rock-fluid systems, and more importantly, how this fracture permeability evolves with time. In fractured rocks, naturally occurring variations in aperture can, under the right flow conditions, cause highly localized erosion. There is a feedback mechanism, which tends to amplify initially small variations in permeability leading to the formation of channels through which almost all the fluid flows. We have confirmed that such mechanisms exist independent of order of the erosion kinetics. The goal of this work is to better understand how aperture variation can promote dissolution breakthrough via flow focusing. To accomplish this we are developing pore-scale numerical simulations of chemical erosion in fractured rocks and validating the methods by comparison with laboratory experiments on model fracture systems.

**Results:** A three-dimensional numerical model was constructed, in which the fluid velocity field was calculated with an implicit lattice-Boltzmann method, and the transport of dissolved species was modeled by an innovative random walk algorithm that incorporates the chemical kinetics at the solid surfaces. The model contains no free parameters or semi-empirical mass-transfer coefficients. The simulated morphological changes in a complex fracture were compared with laboratory experiments with the same initial topography. A simple network model of the evolution of dissolving channels was developed and its properties studied. The results were compared with pore-scale simulations of fracture dissolution using the full three-dimensional numerical model. Despite its simplicity, the network model was found to retain the essential features of the nonlinear interaction between the channels.

We are engaged in extending these studies to model the aftermath of dissolution breakthrough. Here the flow becomes much more rapid and inertial effects in the fluid can no longer be ignored. We are therefore developing new numerical tools to study this regime. We use parallelized solvers for the flow and transport to enable us to study larger systems and at greater resolution than was possible with our previous serial code. A simple 2<sup>nd</sup>-order boundary condition has been developed specifically for situations where there is only a narrow gap between the solid surfaces.

Current code development is aimed at incorporating non-linear kinetics models into the simulations. This will enable us to compare the effects of fracture roughness with the “kinetic trigger” mechanism to

make better predictions of dissolution breakthrough. Our major accomplishment this year has been a new method to map a rough surface onto the lattice-Boltzmann grid. Test calculations show a sphere erodes extremely smoothly and we expect a substantial improvement in the accuracy of the fracture simulations.

## GEORGE WASHINGTON UNIVERSITY

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**Grant:** DE-FG02-02ER15366

### **Crystal Defects, Etch Pits, and Rough Surfaces: A More Complete Picture of Mineral-Water Interactions during Dissolution and Growth**

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**Objectives:** To test (1) the predictability of classic transitional state theory (TST) on carbonate dissolution kinetics; (2) the effect of dislocation density on dissolution kinetics; (3) the effect of atmospheric pCO<sub>2</sub> on carbonate dissolution.

**Project Description:** Bulk dissolution experiments were performed in a mixed-flow reactor and continued until steady state was attained. Calcite fragmental and powdered samples were prepared from single crystals of optical-quality Iceland spar. The fragments were in 1-2 mm size fraction and powder (milled for 5 and 60 min., respectively) in 0.18-0.125 mm size fraction. For closed-system experiments, dissolution was carried out in a 250 ml Nalgene® heavy-duty polypropylene vacuum bottle in a temperature-adjustable (accuracy ± 0.1 °C) water bath with a magnetic stir plate. The reaction vessel was filled with N<sub>2</sub> and sealed by a polypropylene caps combined with Araldite® rapid multi-purpose adhesive. Continuous stirring at 600-800 rpm was achieved through a magnetic stirring bar. Reactive solutions were injected into the reactor using a Manostat® peristaltic pump that allows flow rates ranging from 0.16 to 9.1 ml/min with micro-bore tubing that has a 0.89 mm internal diameter. Dissolution experiments were initiated by placing 2 to 6 g of powdered or fragmental calcite sample (Chihuahua, Mexico) into the reactor. The input and output solution flow rates were maintained at 0.91 ml/min for all runs. In addition, the output solutions were pumped out the reactor through a filter and sampled to measure Ca concentration of the solutions. Steady-state Ca concentrations were used to calculate dissolution rates. The calcium concentrations were determined using a Perkin Elmer Optima™ 4300 DV ICP Optical Emission Spectrometry or an Orion 97-20 ionplus® calcium ion selective electrode. Open-system experiments were carried out using the similar setting except that the reaction chamber was in direct contact with the atmosphere (pCO<sub>2</sub> = 10<sup>-3.5</sup> atm).

*In situ* fluid cell Atomic Force Microscope imaging was further conducted using a DI Nanoscope IIIa Scanning Probe Microscope to confirm the formation of etch pits on dissolving surfaces. All images were captured in Contact Mode® at least 30 minutes after experimental solutions were introduced into the fluid cell. All AFM experiments were conducted at room temperature.

**Results:** Experimental observations show a highly nonlinear dependence of the dissolution rates on the Gibbs free energy. In the region of  $\Delta G < -12$  KJ mol<sup>-1</sup>, all data suggest that the dissolution rates of calcite are constant and independent of solution saturation. At closer to equilibrium ( $-1.7 \leq \Delta G \leq -12$  KJ mol<sup>-1</sup>), the dissolution rates of calcite sharply decrease with increasing of  $\Delta G$ , indicating a very strong inverse relation between the dissolution rate of calcite and the Gibbs free energy. At near equilibrium

when  $0 > \Delta G > -1.7 \text{ KJ mol}^{-1}$ , the dissolution rates show a weak dependence on the Gibbs free energy. Furthermore, the dissolution kinetics does not seem to be affected by dislocation density near or far from equilibrium, as shown by the similar dissolution rate for samples milled for 5 and 60 min. Finally, the dissolution rates measured at same saturation conditions are similar regardless the experimental settings, closed or open, indicating the insignificant effect of atmospheric  $p\text{CO}_2$  at the experimental solution compositions.

These results suggest that: (i) The classic TST model may not be sufficient to depict the relation between dissolution rate and Gibbs free energy for calcite in all saturation conditions. The demonstrated sigmoidal trend in the  $R$ - $\Delta G$  relationship indicates that, though the TST rate equation is sufficient to describe calcite dissolution kinetics when  $\Delta G < -12 \text{ KJ mol}^{-1}$ , it clearly overestimates the dissolution rate when the system approaches equilibrium. (ii) The effect of high-energy surface sites associated with crystal imperfections may be overwhelmed by that of preexisting steps and those generated by dissolution at corners and edges, as evidenced by *in situ* AFM observations. (iii) The partial pressure of  $\text{CO}_2$  in ambient environment bears little importance to calcite dissolution once the saturation conditions of the solutions are fixed.

## GEORGIA INSTITUTE OF TECHNOLOGY

School of Earth and Atmospheric Sciences

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**Grant:** DE-FG02-07ER15901

### **Barite Growth and Dissolution at the Molecular Scale**

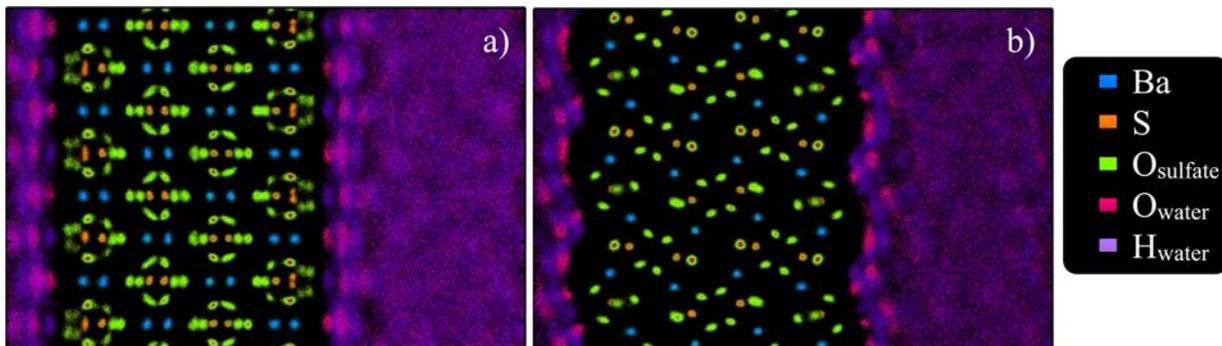
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**Objectives:** The main objective of this research is to test proposed reaction mechanisms for barite dissolution and growth by directly comparing rates of step movement measured experimentally to reactions simulated using atomistic computational methods.

**Project Description:** The desire to understand and control barite growth and dissolution is motivated by the mineral's precipitation as scale in oil pipelines and reservoirs, in oceans and its use as a biomineral. At intermediate saturations, the rate of growth or dissolution of a crystal surface is limited by the rate of movement of monomolecular steps whose net velocity is controlled in part by two reactions: kink site formation and propagation. Many growth modification agents such as biomineralization proteins are thought to act by inhibiting these reactions. In this project, rates of step movement will be measured during growth and dissolution as a function of saturation and temperature using the Atomic Force Microscope (AFM). Step velocities will be used to estimate the formation and activation energies of kink sites. The rates of these reactions will be compared to estimates made using molecular dynamics (MD) simulations after validation of the model.

**Results:** In FY2007, the MD force field for the barite-water system was validated by comparison of predicted vs. experimental estimates of aqueous ion and bulk structure and energies. The calculated structure of the {001} barite-water interface (Figure) was compared to an estimate made by X-ray reflectivity (XRR) measurements. The MD and XRR structures reveal consistent water density and interatomic distances, but MD predicts a more intricate water structure than what can be statistically justified in the XRR. As a precursor to modeling crystal growth reactions, estimates of the kinetics of water exchange have been made using the reactive flux method. The predicted rate constant for exchange on aqueous barium ion is  $4.8 \times 10^9 \text{ s}^{-1}$ , within the experimental estimate range of  $10^9$ - $10^{10} \text{ s}^{-1}$ . The same method applied to a barium ion at the {001} barite-water interface yields an exchange rate 3.5 times faster, yet bond lengths are similar. This contrasts with previous computational estimates made on calcite showing a significant decrease in exchange rate for surface sites relative to the aqueous calcium ion. The differing behavior between two relatively similar materials implies that solvent structure at the interface affects interface reaction kinetics in ways that are not immediately obvious or predictable.



**Figure:** 2-D histograms of MD simulated {001} barite-water interface structure, viewed along the a) [100] and b) [010] directions. The simulation predicts an intricate water structure at the interface, where some oxygens on water are coordinated to surface bariums and some hydrogens are coordinated to surface sulfates.

## HARVARD UNIVERSITY

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**Grant:** DE-FG02-03ER15384

### Growth and Dissolution of Iron and Manganese Oxide Films

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**Objectives:** The first objective is to understand the growth and dissolution of Fe and Mn oxide films on mineral surfaces, especially as influenced by the adsorption of other ions. The second objective is to establish how adsorption affects surface charge distribution and how, in turn, surface charge affects the growth of the Fe and Mn oxide nanostructures that make up the film.

**Project Description:** Nanostructure oxide films are grown on substrates by the *in situ* oxidation of  $\text{Mn}^{2+}(\text{aq})$  and  $\text{Fe}^{2+}(\text{aq})$  ions by dissolved oxygen. The nanostructures are characterized by their morphology and height using atomic force microscopy. Their electrostatic properties, including surface potential, ion mobility, and interfacial adhesive forces, are characterized using Kelvin probe force microscopy, scanning polarization force microscopy, and force-volume microscopy. Surface potential and ion mobility are studied for variable relative humidity to examine the effects of surface dissolution.

**Results:** Over the past year, we have characterized the surface charge heterogeneities that Mn-oxide ( $\text{MnO}_x$ ) nanostructures induce on the parent substrate. The observations of interfacial forces in 1 mM  $\text{NaNO}_3$  solution from pH 5 to 9.7, highlighted in Figure 1, show that the oxide nanostructures have different surface charges from the rhodochrosite substrate. This surface-charge heterogeneity is probed by force-volume microscopy using a charged silicon-nitride probe. Unlike the rhodochrosite substrate, which has only a modest interaction with the probe across the entire pH range, the oxide nanostructures exert significant repulsive interfacial forces with respect to the probe. The maximum interfacial repulsion between the nanostructure and the probe occurs when they are  $2.4(\pm 1.1)$  nm apart. The magnitude of the interfacial repulsion increases from pH 5 to 6.5, reaches its minimum, and increases with further increase of pH. This pH dependence can be described by a simple linear model:  $f_{rep}^{max}(\text{pN}) = 23(\pm 4)[6.8(\pm 2.1) - \text{pH}]$  (for  $\text{pH} < 6.5$ ) and  $19(\pm 2)[\text{pH} - 6.1(\pm 1.0)]$  (for  $\text{pH} \geq 6.5$ ). The results suggest that the oxide nanostructures have a point of zero charge around pH 6.5. The surface-charge heterogeneity of reacted rhodochrosite is further explained by separate mechanisms that regulate the surface charges of oxide nanostructures compared to the rhodochrosite substrate. Quantifying surface-charge heterogeneity is the first step in accounting for its effects on contaminant (im-)mobilization and bacterial attachment on surfaces present in aquifers.

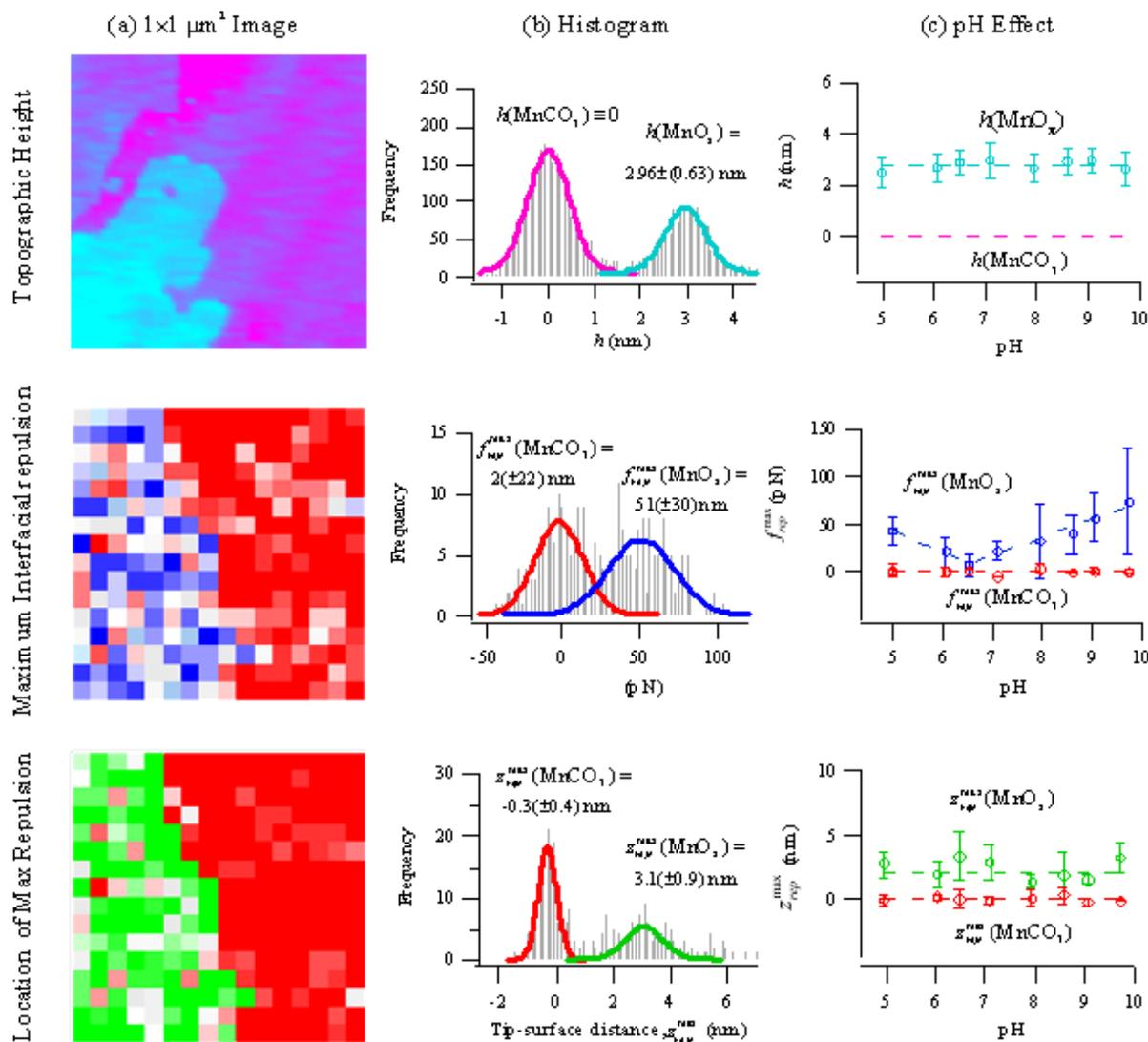


Figure 1. Topographic height  $h$ , maximum interfacial repulsion  $f_{rep}^{max}$ , and its location  $z_{\phi}^{max}$  of oxide nanostructures ( $MnO_x$ ) and the substrate ( $MnCO_3$ ) on reacted rhodochrosite. The three quantities are presented by the three rows, respectively, in terms of (a)  $1 \times 1 \mu m^2$  images, (b) histograms, and (c) pH Effect. The measurements were conducted in 1 mM  $NaNO_3$  solution at  $25^\circ C$  by in-situ force volume microscopy.

## UNIVERSITY OF HOUSTON

Department of Physics

University of Houston

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**Grant:** DE-FG02-05ER15697

### **Seismic Imaging Beneath an Unknown Overburden: Method Development and Evaluation on Synthetic and Real Data**

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**Objectives:** We identify two main branches of research necessary to develop and extend existing inverse scattering series algorithms to more completely accommodate measured seismic reflection data measured over a complex subsurface structure. First, we must carry out the basic research into the formalism itself, to extract and compute terms that locate and invert for structure at depth in situations of rapidly-varying media and corrugated/rugose boundaries. Second, and equally important, we must develop and refine forward modeling methods such that the very wave field complexity required by the inverse scattering series can be provided synthetically, and under controlled circumstances, as a tool to validate and test our derived algorithms.

**Project Description:** The inverse scattering series (ISS) is a comprehensive theory for processing primaries and multiples without the traditional need for a subsurface velocity. Several task-specific subseries of the ISS corresponding to classical objectives of seismic data processing have been identified: subseries for (1) free-surface multiple elimination, (2) internal multiple attenuation and elimination, (3) imaging reflectors at depth, and (4) determining the parameter changes at reflectors. In addressing the first branch of our research objectives, in this project our team has specifically developed and refined algorithms which address task (3) above, that is, imaging reflectors at depth. The deliverables in this case are formulas for determining the location of reflectors in 2D from measurements of reflected primary data. Further, we continue to progress the use of non-linear inverse scattering series methods (specifically, internal multiple attenuation methods) to not only provide new highly capable algorithms, but to provide necessary input for current imaging methods. In addressing the second branch of our research objectives, we have (1) defined and made preparations to enter into a collaborative project with Huang and Fehler at Los Alamos National Laboratory, to identify and address outstanding issues of modeling wave fields in complex media, and (2) progressed the use of the forward scattering series in modeling of post-critical wave phenomena and developed a scattering series based calculation of selected wave field events in complex media.

**Results:** In the imaging branch of our research, progress has been achieved (subsequent to our last report) on several fronts. In the last report we mentioned that the imaging capability within the 2D inverse scattering series had been identified and collected that address multi-dimensional imaging objectives that have a 1D analog. That subset of the full ISS capability produced a closed form imaging algorithm that tested with encouraging results on synthetic data from a salt model provided by Exxon-Mobil. This past year the latter imaging algorithm was also tested on a fault shadow zone imaging

challenge and once again produced positive results. Although each of these tests produced very encouraging results, there were remaining imaging challenges that had no analog in 1D that as expected were not satisfactorily addressed. Among the latter imaging challenges that have no one dimensional analog are collapsing of diffractions (since diffractions don't exist in a 1D subsurface) and imaging beneath a rapid lateral velocity varying overburden. The capture of distinct imaging terms that address the latter uniquely multidimensional problems has progressed this past year. The result is a new imaging algorithm that while no longer allowing a closed form, is never-the-less computable with both increased capability and a commensurate increased run-time. Coding of that new algorithm is soon to be completed with further tests to determine the efficacy in addressing imaging challenges beyond our earlier algorithm. The previous imaging algorithm and the latest more complete and advanced version, all derive from different levels of capture of imaging terms within the inverse series. Neither requires knowledge of the subsurface velocity in principle and practice. The first field data tests of the earlier and faster algorithm are underway and synthetic tests of the newer and more effective imaging algorithm are planned for this coming year.

In forward modeling, the traditional methods of ray methods and wave modeling (e.g. finite difference or finite element) each have different strengths and limitations. Ray methods are less complete than wave theory algorithms, and cannot model diffractions or rapid lateral varying media and boundaries. They have problems with caustics which represent a singularity and/or a breakdown in ray methods and do not accurately represent what transpires when a wave actually experiences that type of complex medium.

However, ray methods are faster than wave methods and have the advantage over wave methods of being able to select and model certain desired events without having to model all events. The latter event selectivity property of ray theory can have certain important practical advantages. During this past year a new modeling method was developed based on the forward scattering series that combines the completeness and accuracy of wave theory predication, with the event selectivity of ray methods. We anticipate that this could mitigate some of the modeling challenges in large scale wave theory modeling using complex and realistic elastic models.

**IDAHO STATE UNIVERSITY**  
Department of Biological Sciences  
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**Grant:** DE-FG02-06ER15824

**Redox Interaction of Cytochromes and Bacteria with Oxide Surfaces: Probing Redox-Linked Conformation Change**

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**Objectives:** The objective of this research is to better understand the role of conformation change in electron transfer from cytochromes to minerals, a process that underpins respiratory metal reduction by bacteria in nature and in bioremediation strategies, including reductive immobilization of radioactive contaminants.

**Project Description:** The biochemistry of bacterial proteins involved in redox transformations of metals and minerals is, without dispute, an important area of research. Nevertheless, most studies on bacterial metal transformation have focused not on biochemistry but on genetics and genomics. Our DOE-funded work is specifically focused on answering long-standing questions about the biochemical behavior of these very interesting proteins, and our findings in FY07 have continued to support our basic idea of conformational gating and control of electron transfer to mineral and other electrochemically active surfaces.

**Results:** Progress highlights in FY 07 include:

- 1) Sabbatical leave travel for Magnuson to the University of Wyoming, to work with collaborators Carrick Eggleston and Patricia Colberg. Magnuson gave a seminar for the UW Physiology and Zoology Department in Fall 2007, and performed experiments on c-type cytochromes using the newly-acquired Optical Waveguide Lightmode Spectrometer (OWLS).
- 2) Studies with OWLS and with Quartz Crystal Microbalance: We examined two cytochromes, PpcA and OmcB (from *Geobacter sulfurreducens*) for their comparative adsorption properties to glass waveguide surfaces. Essentially, OWLS and QCM help to determine how quickly and how strongly proteins adsorb to surfaces, and how the degree of protein hydration changes during this process. PpcA, a small periplasmic cytochromes, was found to be compact, and showed slower adsorption kinetics than OmcB (Cell surface cytochrome), which appears to be more 'floppy' and adsorbs and desorbs faster from surfaces (Fig. 1). This suggests that the protein is tailored for quick electron discharge to a mineral surface, followed by rapid desorption and 'reloading' with more electrons.
- 3) Fluorescence spectroscopy: We have continued characterization of the cytochromes c purified from *Geobacter* and *Acidiphilium*, and are now using Fluorescence Spectroscopy to examine conformational change and redox state. Studies on ApcA (10.1 kDa cytochromes c from *A. cryptum*) show a distinct shift in the Tyrosine adsorption band, suggesting that conformation is different depending on whether the protein is oxidized or reduced. Studies are ongoing with the other representative cytochromes.
- 4) Homology Modeling using PHYRE: Using genome sequence data for *Acidiphilium* and *Geobacter*, we have constructed homology models of cytochromes c using PHYRE. These models are extremely useful in understanding protein structure, and thus far correlate with other laboratory observations. For

example, ApcA (*A. cryptum*) is a relative compact protein with a well-defined heme binding site, and easily identifiable His and Met heme coordinating residues.

5) Training of undergraduate researchers (Andy Fielding, Sean Clark), and support of a Research Associate (Mike Swenson).

6) Development of a new collaboration with the Pacific Northwest National Laboratory-Environmental Molecular Science Laboratory (EMSL). We will examine cytochrome structure using high-field NMR instruments (400 and 700MHz).

7) Arrangement of additional Sabbatical Leave for Spring Semester 2008 for the PI to travel to the University of Wyoming for conducting experiments and working directly with collaborators.

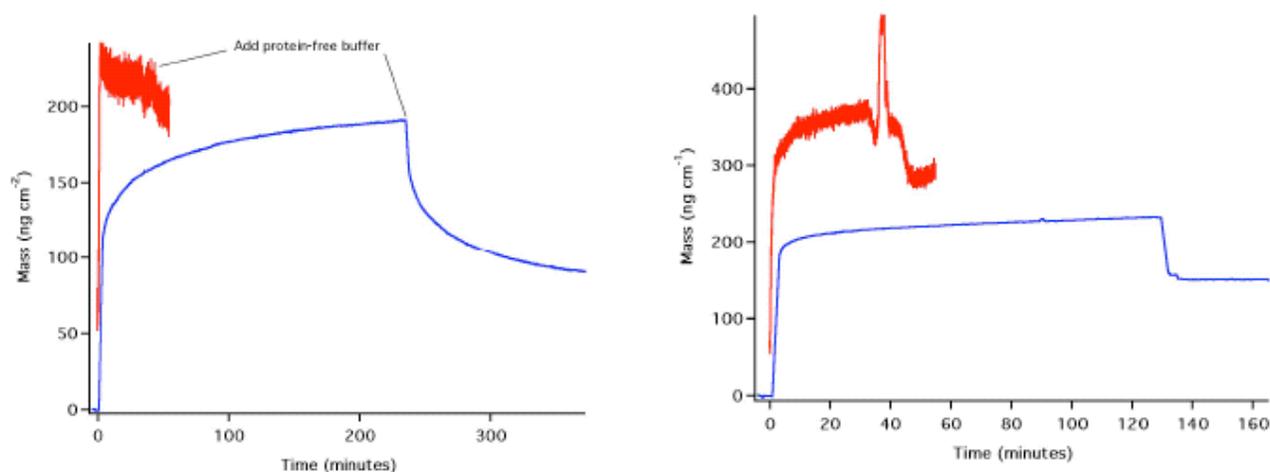


Figure 1. OWLS (Blue trace) and QCM (Red trace) data for PpcA (left) and OmcB (right). Not rapid adsorption and desorption kinetics of OmcB compared to ApcA.

## UNIVERSITY OF ILLINOIS

Department of Geology  
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**Grant:** DE-FG02-00ER15028

### Computational and Spectroscopic Investigations of the Molecular Scale Structure and Dynamics of Geologically Important Fluids and Mineral-Fluid Interfaces

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<http://www.msu.edu/~kalinich/research.html>

**Objectives:** Research supported by this grant focuses on development of molecular scale understanding of a range of central issues related to the structure and dynamics of geochemically important fluids, fluid-mineral interfaces, and confined fluids using computational modeling and experimental methods.

**Project Description:** Molecular scale knowledge of the structure and dynamics of aqueous fluids, how these fluids are affected by mineral surfaces and molecular-scale (nano-) confinement, and how water molecules and dissolved species interact with surfaces is essential to understanding the fundamental chemistry of a wide range of geochemical processes relevant to energy geoscience. These processes include mineral reactivity, dissolution and precipitation, sorption and geochemical transport. Our principal efforts are devoted to continued development of advanced computational approaches to address these problems, application of these approaches to important geochemical questions, relevant experimental studies, and application of the computational methods to understanding the experimental results. The combination of computational modeling and experimental approaches is proving highly effective in addressing otherwise intractable problems.

**Results:** 2007 saw significant advancement in new, highly promising research directions along with completion of on-going projects and final publication of work completed in previous years.

New computational directions focused on modeling proton exchange reactions in aqueous solutions using *ab initio* molecular dynamics (AIMD), metadynamics (MTD), and empirical valence bond (EVB) approaches. Proton exchange is critical to understanding the structure, dynamics, and reactivity at mineral-water interfaces and for oxy-ions in solution, but has traditionally been difficult to model with molecular dynamics (MD). Our ultimate objective is to develop methods to do this in classical MD calculations, because these methods are much less computationally demanding than quantum-chemical approaches. We also extended our previous MD simulations of metal binding to natural organic matter (NOM) to a much longer time scale (up to 10 ns) for significantly larger systems. These calculations have allowed us, for the first time, to study the effects of metal cations with different charges and charge density on the NOM aggregation in aqueous solutions. Other computational work investigated the long-time-scale dynamical behavior of aqueous species at the quartz-water interface, which we investigated simultaneously by NMR spectroscopy.

Our experimental NMR studies in 2007 focused on understanding the structure and dynamics of water and dissolved species at mineral-water interfaces and in two-dimensional nano-confinement within clay interlayers. Combined NMR and MD study of H<sub>2</sub>O, Na<sup>+</sup>, and Cl<sup>-</sup> interactions with the surface of quartz provided new interpretations of sum frequency vibrational spectroscopic experiments for this interface and will be an important reference for future studies. We also used NMR to examine the behavior of <sup>39</sup>K<sup>+</sup> and H<sub>2</sub>O in the interlayer and at the surfaces of the clay minerals hectorite and illite-rich illite-smectite. <sup>39</sup>K NMR is quite challenging, and this is the first time K<sup>+</sup> dynamics has been characterized spectroscopically on the molecular-scale in geochemical systems. Using the high-field instrumentation at Pacific Northwest National Laboratory, we developed a new NMR approach to study ultra-wide-line nuclei, such as <sup>75</sup>As or <sup>131</sup>I. This resulted in the first ever <sup>75</sup>As NMR study of arsenic oxysalts, provided the first evidence of a strong relationship between the chemical shift and structural parameters for this experimentally challenging nucleus, and highlighted the potential of <sup>75</sup>As NMR as a probe of arsenic geochemical behavior.

In 2007 we also initiated a series of inelastic and quasi-elastic neutron scattering measurements of the dynamics of interlayer and interfacial H<sub>2</sub>O molecules in layered double hydroxides and clays with the objective to probe the correlations of H<sub>2</sub>O librational and diffusional motions in confined spaces over the scale of times and distances most directly comparable to our MD simulations and on a time scale different than that probed by NMR. The first experiments were performed at the IPNS facility of the Argonne National Lab and at the NIST Center for Neutron Research with the dehydrated and hydrated samples of hydrocalumite across the temperature range covering the order-disorder phase transition in the interlayer of this material.



Cover of the October 2007 issue of the *Journal of Magnetic Resonance*, featuring the results of our <sup>75</sup>As NMR study.

## UNIVERSITY OF ILLINOIS

Department of Geology

243 NHB

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**Grant:** DE-FG02-02ER15317

### **Field-Constrained Quantitative Model of the Origin of Microbial and Geochemical Zoning in a Confined Fresh-Water Aquifer**

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**Objective:** The goal of this project is to demonstrate the role of the subsurface microbial community in controlling the chemistry of groundwater, especially the content of metals and semi-metals. We are (1) extending our sampling of the Mahomet to a regional scale, to consider how microbial life affects the concentrations of a suite of heavy metals and semi-metals, (2) performing downhole experiments to directly observe microbial activity and measure its rate, and (3) using numerical modeling techniques to interpret those results quantitatively, and to extract parameters for kinetic models of microbial metabolism.

**Project Description:** The regional Mahomet Aquifer System is a widespread Pleistocene deposit that supplies drinking water to much of central Illinois. The aquifer system is composed of glacial sediments that infill a bedrock river valley that extends from West Virginia to the Illinois River Valley in western Illinois. Our study combines field, lab and numerical modeling tasks to obtain an integrative synthesis of aquifer biogeochemistry. This has led us to focus on relationships between microbial community composition, microbial activity and water geochemistry.

For field and lab studies we have developed a close working relationship with scientists at the Illinois State Water Survey, who allowed us unlimited access to dozens of their monitoring wells across the Mahomet Aquifer. We focused our study on 21 wells, located mainly in the eastern part of the aquifer. From these wells we obtained water samples for chemical and microbiological analysis. We use modern molecular microbiological tools for these analyses and this represents the first time such an extensive study has been done on a large regional aquifer. To investigate the attached microbial community we have developed an *in situ* microbial sampler using natural Mahomet sediments. Unattached microbes are obtained by filtering the groundwater. This allows us to evaluate the relative importance of attached versus unattached bacteria in the aquifer setting and is of fundamental importance to reactive transport modeling.

Our modeling focuses on developing the first theoretical analysis of the relationship between thermodynamic drive and the rate of microbial metabolism, and demonstrating the usefulness of these results in understanding natural systems. We are also using reactive transport modeling combined with the theoretical results just mentioned to develop a dynamic understanding of the origin of zoned microbial communities.

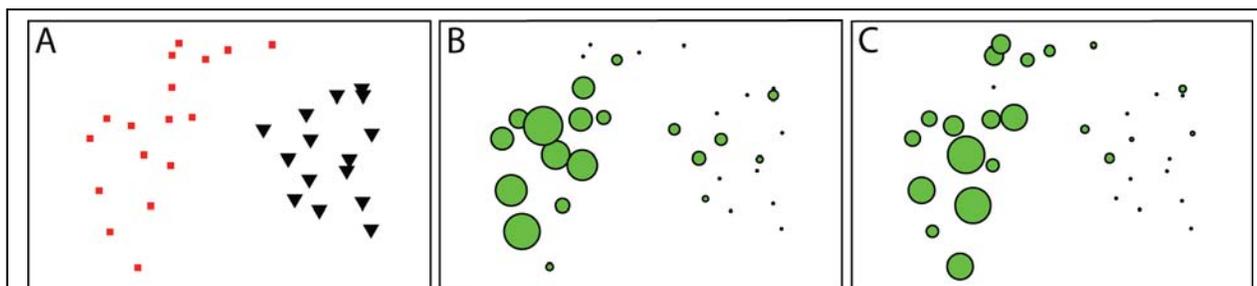
**Results:** In the last year we have developed a new DNA extraction protocol that is considerably more efficient than the method most people use, allowing us to extract high quality genomic DNA from only two liters of water.

We performed the first comprehensive comparison of the attached and unattached microbial

communities in an aquifer. We analyzed the bacterial communities of all samples using the PCR-based method, terminal restriction fragment length polymorphism (T-RFLP) analysis, which yields a fingerprint diagnostic of the community composition. A statistical comparison of these community profiles show systematic similarities and differences between attached and unattached bacterial communities (Figure 1). Both groups share populations, but some communities are exclusively unattached or attached to aquifer sediments. For example known iron reducing bacterial populations were predominant in the attached community and nearly non-detectable amongst the unattached populations. Our data suggest that there are benefits to sampling both types of communities when investigating aquifer biogeochemistry.

To test if any geochemical parameter measured was associated with community changes based on TRFLP analysis, we looked for correlations between the geochemical data and the similarity between microbial communities in different wells. We observed an apparent relationship between the community profiles and the sulfate concentration. Our statistical analysis showed that microbial communities in areas with high (>100 mg/L) sulfate are distinctly different from those with low (0.9-20 mg/L) or no detectable sulfate. This result may indicate a switch from communities dominated by active sulfate reduction to a community where methanogenesis is most important.

We have made significant progress developing a quantitative understanding of the factors that influence the distribution of microbial populations in the subsurface, and the origin of microbial zoning in pristine aquifers. The numerical models show that current theories of the origin of zoning based on thermodynamics or simple kinetics do not explain the mechanism by which some microbial populations exclude others from a zone. Instead, populations appear capable of excluding others by maintained conditions at which growth is insufficient to replace cell decay and predation. The models also show that communities long assumed to be dominated by one functional group may in fact be areas of mixed metabolism, and that zones containing iron-rich groundwater may be dominated by sulfate reducing bacteria, rather than iron reducers.



**Figure 1.** (A) MDS ordination of Bray-Curtis similarity coefficient rankings for attached (squares) and suspended (triangles) microbial communities. Stress, the amount of strain imposed on the figure by fitting a multidimensional ordination into two dimensions, is equal to 0.15. (B) and (C) are the MDS plot (A), overlain with circles representing the predominance of a T-RF of the same size as the *in silico* digest of a clone belonging to the genus *Geobacter* (B) and *Geothrix* (C). The size of the circle is proportional to the relative proportion of the T-RF in that sample. Small dark circles represent samples in which the *Geobacter* or *Geothrix* T-RF was not present.

## UNIVERSITY OF ILLINOIS AT CHICAGO

Department of Earth and Environmental Sciences  
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**Grant:** DE-FG02-03ER15381

### **Mineral-Fluid Interactions: Synchrotron Radiation Studies at the Advanced Photon Source**

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**Objectives:** The objective of this program is to advance the basic understanding of rock-fluid and soil-fluid interactions through experimental studies on atomic-scale processes at mineral-fluid interfaces. This is crucial to establishing the relation between atomic-scale processes and macroscopic geochemical transport in natural systems.

**Project Description:** The principal approach is to observe single-crystal mineral surfaces *in situ* during chemically controlled reactions with fluids using high-brilliance synchrotron radiation. Experimental techniques include high-resolution X-ray scattering (X-ray reflectivity, x-ray standing waves, resonant anomalous X-ray reflectivity) as well as X-ray absorption spectroscopy. Phenomena of interest include mineral-water interface structure, adsorption/desorption of ions and organic molecules, dissolution, precipitation and growth. Experiments are performed on common rock- and soil-forming minerals under conditions representative of geochemical environments near Earth's surface. A fundamental understanding of the molecular-scale processes are obtained through direct observations of interfaces before, during and after reaction.

**Results:** Recent research focused on understanding dynamic processes of adsorption, growth and dissolution at mineral-water interfaces using advanced synchrotron X-ray scattering techniques. This work is collaborative with P. Fenter at Argonne National Laboratory and others. Observations of dolomite surfaces in contact with saturated and supersaturated solutions led to new insights into the “dolomite problem” (i.e., the apparent inability of dolomite to precipitate). The results showed that dolomite readily reacted with supersaturated solutions, but that the reaction was self-limiting and partially irreversible. The surface was terminated by a two-layer thick compositionally altered layer,  $\text{Ca}_x\text{Mg}_{1-x}(\text{CO}_3)_2$  film with  $x \sim 3/4$  when in contact with a dolomite-supersaturated solution. In addition, new results were obtained that reveal important differences in the adsorption geometry of Rb and Sr at the orthoclase-water interface, with implications for the relative energetics of dehydration and adsorption at this interface.

## UNIVERSITY OF ILLINOIS AT CHICAGO

Department of Earth and Environmental Sciences

845 W. Taylor St., MC-186

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**Grant:** DE-FG02-06ER15364

### Nanoscale Reactivity of Clays, Clay Analogues (Micas), and Clay Minerals

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**Objectives:** Our objectives are to determine the nanoscale/molecular scale structure of the interface between mica and aqueous solutions containing various sorbates and to explore systematics that control the incorporation of inorganic and organic chemical components during aging of nanoparticles of iron-oxides and aluminosilicate clays.

**Project Description:** The basal surface of phyllosilicates is a primary sorbent of environmental contaminants, natural organic matter, and nutrients. Micas are also superb atomically-flat substrates used in materials science and surface physics applications. We are applying X-ray scattering techniques using high brilliance synchrotron radiation coupled with atomic force microscopy (AFM) to investigate molecular-scale details of mica's interface structure in solutions containing common and toxic cations, anions, and natural organic molecules. Nanoparticles are ubiquitous in the environment and have a high capacity for sorbing contaminants through the combined effects of their high surface areas and pH-dependent surface charge. Aging of nanoparticles from metastable to stable phases can be inhibited by sorption of nonstructural components, but exact mechanisms are unknown. We are precipitating Fe-oxides and phyllosilicate clays in the presence of selected anions, and organic molecules, and quantifying uptake of these additives during aging.

**Results:** X-ray reflectivity and resonant anomalous X-ray reflectivity were used to determine the mica-solution interface structure in fulvic acid solutions as a function of pH and time, and in the presence of Ba, Sr, Pb, Cu, Zn, and Hg at selected pHs. Positions of cations in the absence and presence of fulvic acid films are determined with sub-Ångström-scale resolution and are correlated with pH, binding strength to functional groups on the fulvic acid, competition with the fulvic acid for mica sorption sites, and order of addition of cations to the fulvic acid (before or after addition of the mica). Some results are highlighted here. We observed that Ba<sup>2+</sup> is adsorbed dominantly as an inner-sphere cation in the absence of fulvic acid, and acts as a bridging cation in the presence of fulvic acid at pH 3.7 and 5.5, in both cases in amounts that fully satisfy the charge on the surface. In contrast, Hg<sup>2+</sup> adsorbs as both an inner-sphere and outer-sphere cation in the absence of fulvic acid and is broadly distributed and in comparatively higher concentration within an adsorbed fulvic acid layer at pH 2 (Figure 1). The extent of cation uptake within sorbed fulvic acid films on muscovite depends on pH, binding strength to functional groups in the fulvic acid, and cation hydration enthalpy, size, and charge.

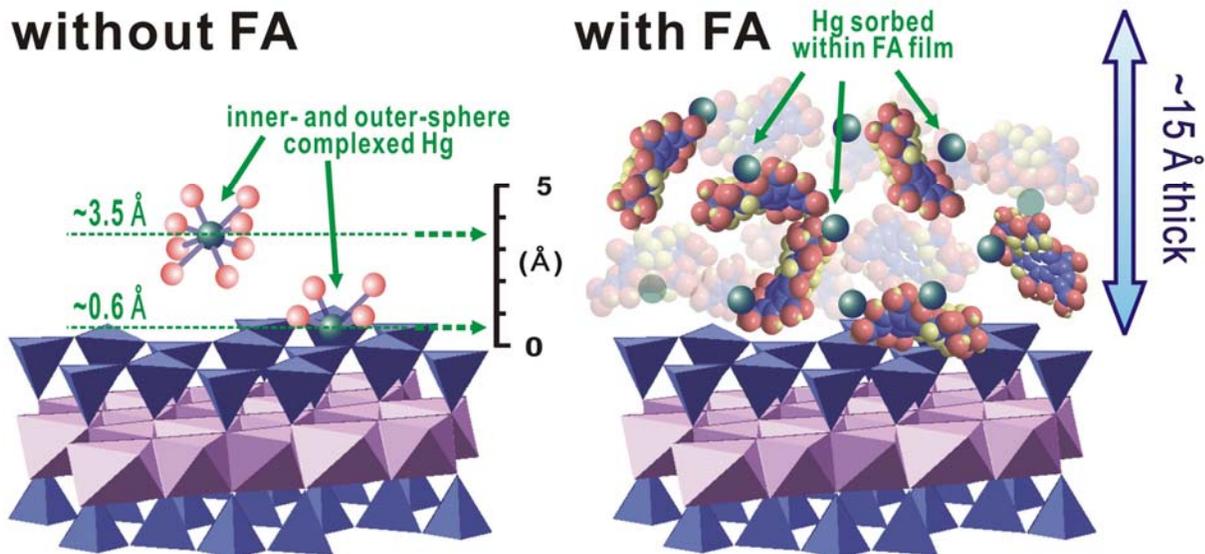


Figure 1. Schematic diagram showing  $\text{Hg}^{2+}$  uptake at the muscovite (001) surface from an aqueous solution of 0.001 m  $\text{Hg}(\text{NO}_3)_2$  at pH 2 (left) and a solution of 0.001 m  $\text{Hg}(\text{NO}_3)_2$  and 100 ppm Elliott Soil Fulvic Acid II from the International Humic Substances Society (right).  $\text{Hg}^{2+}$  is distributed at two well-defined distances from the surface in the absence of fulvic acid, and in greater amounts throughout the organic layer in the presence of sorbed fulvic acid.

## INDIANA UNIVERSITY

Department of Geological Sciences  
Bloomington IN 47405

**Grant:** DE-FG02-00ER15032

### Significance of Isotopically Labile Organic Hydrogen in the Thermal Maturation of Source Rocks

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**Website:** <http://mypage.iu.edu/~aschimme/hydranit.html>

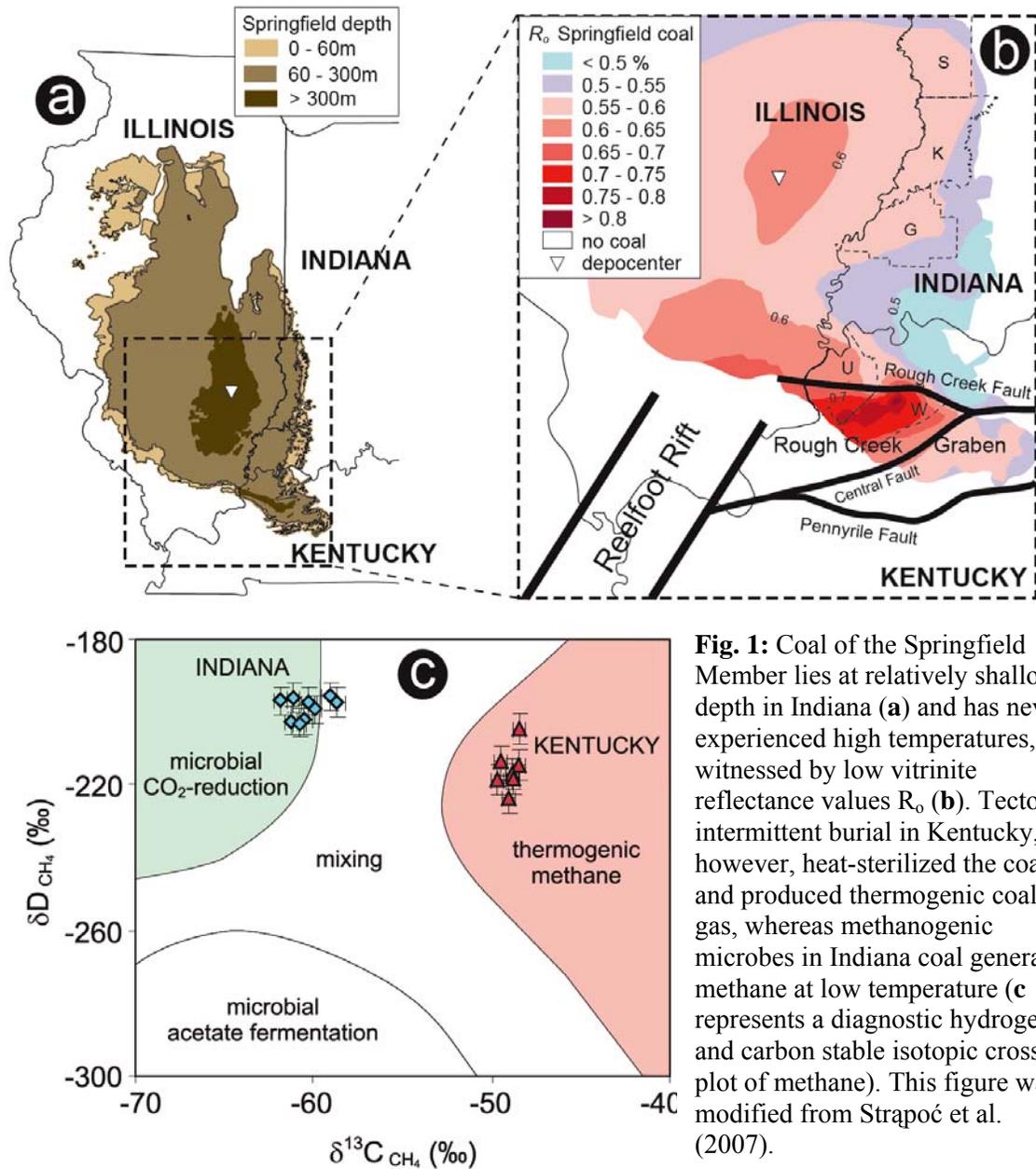
**Objectives:** Explore the geochemical conditions and mechanisms that contribute to changes in the D/H stable isotope ratio of organic hydrogen in sedimentary organic matter during thermal maturation. Evaluate the diagenetic and/or paleoenvironmental significance of D/H ratios in different types of kerogen, specific macerals and isolates, oils, fractions of oil, and gas.

**Project Description:** Isotopically labile organic hydrogen in fossil fuels occupies chemical positions that participate in isotopic exchange and in chemical reactions during thermal maturation from kerogen to bitumen, oil and gas. The chemical interaction between hydrogen-limited but carbon-rich kerogen and abundant inorganic hydrogen in formation water may in fact extend the generation of hydrocarbon fluids beyond the limitations of pre-existing organic hydrogen in immature kerogen. Controlled isotopic equilibration of isotopically labile organic hydrogen with isotopically distinct water vapor hydrogen is used to quantify the amount of exchangeable organic hydrogen. Hydrogen isotope ratios in natural gas species are diagnostic for the origin of gas.

**Results:** We developed a versatile analytical “GASIS” interface to measure the compound-specific hydrogen (and carbon) stable isotope ratios in hydrocarbon gas mixtures, for example in natural gases. Two of our Ph.D. students (Strapoć and Lis) spearheaded this effort.

The analytical GASIS method was used to expand the utility of hydrogen stable isotopes in exploration for coalbed gases. Indiana’s coalbed gases in the southeastern Illinois Basin were characterized using compound-specific hydrogen and carbon stable isotope ratios (among other geochemical and microbiological data). Figure 1 highlights some results, shown below.

Thermally immature stratigraphic sequences of source rocks display a correlation between the abundance of isotopically exchangeable hydrogen and nitrogen stable isotope ratios, whereas more mature source rocks do not. The reason had not been clarified until 2007 when we collaborated with Jean-Paul Boudou at CNRS Paris/France in a study of organic nitrogen chemistry during low-grade metamorphism. Our new data show that some organic nitrogen in lower-grade rocks is linked to organic hydrogen that is isotopically exchangeable. However, with increasing maturity, the shrinking pool of organic nitrogen becomes almost exclusively linked to carbon and thus loses its relationship with hydrogen exchangeability.



**Fig. 1:** Coal of the Springfield Member lies at relatively shallow depth in Indiana (a) and has never experienced high temperatures, as witnessed by low vitrinite reflectance values  $R_0$  (b). Tectonic intermittent burial in Kentucky, however, heat-sterilized the coal and produced thermogenic coalbed gas, whereas methanogenic microbes in Indiana coal generated methane at low temperature (c represents a diagnostic hydrogen and carbon stable isotopic cross-plot of methane). This figure was modified from Strapóć et al. (2007).

## JOHNS HOPKINS UNIVERSITY

Department of Earth and Planetary Sciences  
Baltimore MD 21218

**Grant:** DE-FG02-96ER14619

### **Physiochemical Evidence of Faulting Processes and Modeling of Fluid Flow in Evolving Fault Systems in Southern California**

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**Objectives:** This is a collaborative study to quantify basal fluid flow, submarine methane migration and diagenetic effects within deforming faults in a transpressional setting that is seismically active. Most of the work deals with faulted basins of California, most recently in the Santa Barbara Basin (SBB) and the Los Angeles Basin (LAB).

**Project Description:** We have mainly targeted active faults and young petroleum fields in southern California for study including the Refugio and Elwood faults in the SBB, and the Newport-Inglewood fault (NIF) in the LAB. Subsurface core samples, outcrop samples, well logs, reservoir properties, pore pressures, fluid compositions and published structural-seismic sections are being studied to characterize the tectonic/diagenetic history and degree of compartmentalization for these known fault networks. We are also investigating the geochemical signatures in carbonate that characterize rapid CO<sub>2</sub> degassing. These data provide constraints for finite element models that are being developed to predict fluid pressures, multiphase CH<sub>4</sub>/CO<sub>2</sub> flow patterns, rates and patterns of deformation, subsurface temperatures and heat flow, and geochemistry associated with large transpressive-related fault systems.

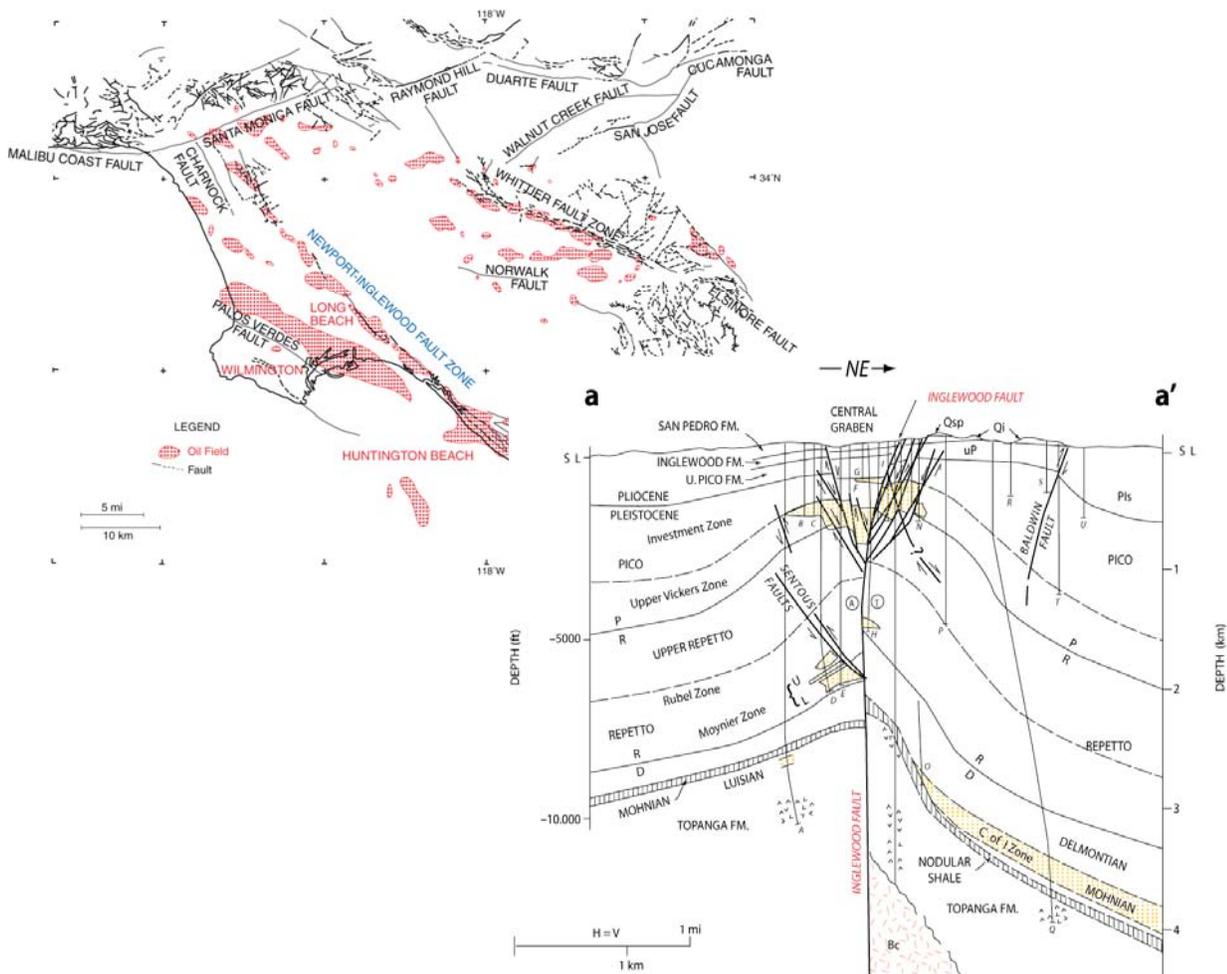
**Results:** Boles has recently been completing studies of disequilibrium effects during calcite crystallization as a result of CO<sub>2</sub> degassing and fluid mixing. His goal has been to develop a quantitative understanding of this phenomenon in order to interpret geochemical signatures (including both isotopic and trace element compositions) of fault zone cements. Boles also continues to study faults and wells in the South Elwood field where fault permeability was calculated from the rate of seawater influx into an underpressured reservoir. In the LAB, a Boles-UCSB student is analyzing formation water samples, core samples, and geophysical logs from deep zones along the NIF in the LAB that will allow us to explore the hydrology of this important transpressional fault zone. Igneous rock is associated with the termination of the NIF and appears to have caused significant diagenetic and thermal effects on the reservoir sands. It is anticipated new exploration wells will be drilled and cored in 2008, and Boles hopes to garner and analyze new data for further study.

Garven's flow modeling in 2007 was based on fully-coupled, 2-D numerical applications with the RST2D finite element software (JHU). With collaboration of Boles and a former JHU student Martin Appold (Univ. Missouri), we simulated reactions associated with deep migration of aqueous CH<sub>4</sub> and CO<sub>2</sub> and mixing with meteoric groundwater in faulted, submarine reservoirs, which are partially uplifted along coastal SBB. The idea here was to further test and evaluate the geochemical model based on the petrologic studies of fault mineralization and reactive flow by Boles. Numerical reactive transport

models of a structurally complex and geologically heterogeneous 2-D profile across the SBB support this hypothesis, although the source of the overpressures (long-term basin compaction disequilibrium vs. episodic fault compression) remains strongly debated among ourselves. This work on the Refugio fault system provided a springboard for Garven's 2007 studies of faulted reservoirs of similar age in the LAB, as shown below. Garven's JHU/Tufts graduate students has recently built and tested a hybrid finite element/finite volume numerical model for characterizing petroleum migration, trapping, and leakage at the field scale and we are now running simulations to verify and validate the mathematical attributes of the numerical code.

The collaboration between UCSB and JHU/Tufts continues to be strong and successful, and we are incorporating new collaborators when opportunities appear. For example, Juli Morgan (Rice Univ.) conducted a series of discrete-element simulations for our project, with the goal of rendering possible scenarios of fault deformation. She is sharing with us her expertise and numerical experience on using particle-dynamics simulation PDM methods to explore strike-slip fault deformation processes. For this fault-modeling PDM study, Morgan carried out preliminary 3-D simulations driven by right-lateral basal-boundary displacements, analogous to a small segment of a long-lived strike-slip fault, (e.g., NIF). With the geomechanical model, we will be better prepared to characterize the transient geohydrologic properties and multiphase fluid dynamics and relate it to the Boles petrologic observations.

Figure 1: Map and cross section of faults and oil fields in the Los Angeles Basin.



## JOHNS HOPKINS UNIVERSITY

Department of Earth and Planetary Sciences  
Baltimore MD 21218

**Grant:** DE-FG02-89ER14074

### Crystal Chemistry of Toxic Metal Sequestration

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**Objectives:** For FY07, specific objectives center on development of focused ion-beam milling (FIB) techniques, initiation of monochromated electron energy-loss spectroscopy (EELS) studies, and applications of these techniques to U contaminated soils.

**Project Description:** The project centers on the crystal chemistry of mineral hosts and their interactions with toxic metal-bearing aqueous fluids. The current focus is investigation of uranium sequestration by adsorption on surfaces and incorporation within mineral hosts using TEM, FIB, and synchrotron-based techniques.

**Results:** During this first year of the project cycle, we have successfully developed focused ion-beam (FIB) milling for the sensitive uranyl-phosphate minerals of the autunite group. This work is a critical step in fully utilizing the TEM's spatial resolution to establish the uranium budget of contaminated sites. Our work includes museum samples as well as natural samples from contaminated soils at Hanford and Oak Ridge. Our protocol allows production of electron transparent, crystalline samples of the phosphates with nanometer scale precision. Specifically, we have established that we can maintain the basal spacing of metatorbernite despite ion- and electron-bombardment during milling and imaging and exposure to the high-vacuum environments of the FIB and TEM. Meta-autunite is more beam sensitive and shows some reduction in basal spacing in the TEM. This reduction is, however, reproducible and less than that shown by earlier workers. Aspects of the work were presented at the Frontiers in Mineral Sciences meeting in Cambridge, UK, in June.

We have begun applying these new, high-resolution techniques to supplement our microprobe-based investigations of contaminated soils at Oak Ridge and Hanford. Our results include demonstration that the uranium-phosphorous association that we reported in Oak Ridge soils (Stubbs et al, 2005) truly includes a discrete phase and that it is an aluminous uranyl phosphate. We have also discovered a Zr-rich component in the Hanford soils and have begun characterizing it.

Our work with museum specimens of meta-autunite group minerals has revealed extraordinarily rapid and extensive depletion of interlayer Cu in metatorbernite  $[\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$  during electron microprobe analysis. Understanding this phenomenon is critical to obtaining accurate chemical analyses of this important uranium sequestering phase and for interpreting previously published microprobe results. In addition, this work should enhance our understanding of the bonding environment of Cu in metatorbernite. Aspects of this work were presented at the American Geophysical Union meeting in San Francisco in December.

We have also begun TEM based electron energy-loss spectroscopy (EELS) using the uranium  $\text{O}_{4,5}$ ,  $\text{N}_{4,5}$ ,

$N_{6,7}$ , and  $M_{4,5}$  and oxygen K absorption edges to probe details of bonding and valence states of uranium. This work includes EELS with the monochromated instruments at Lawrence Livermore National Laboratory. To date, we have spectra on uranyl phosphates and  $UO_2$  with  $\sim 0.4$  eV resolution. We anticipate  $\sim 0.1$  eV resolution with the improved instrumentation that will soon be available to us.

## JOHNS HOPKINS UNIVERSITY

Department of Earth and Planetary Sciences  
Baltimore MD 21218

**Grant:** DE-FG02-96ER14616

### **Predictive Single-Site Protonation and Cation Adsorption Modeling**

*Dimitri A. Sverjensky, 410-516-8568, [sver@jhu.edu](mailto:sver@jhu.edu)*

**Objectives:** The overall goal of this research is to develop a predictive model of adsorption processes at the mineral-water interface that can advance a fundamental understanding of the role of mineral-surface chemistry in the chemical evolution of shallow and deep groundwaters, the fate of contaminants in groundwaters, and the storage of carbon dioxide in the subsurface.

**Project Description:** The research is aimed at generating a comprehensive, internally consistent, quantitative description of the interactions of natural waters with mineral surfaces for both well crystallized and poorly crystalline materials and both inorganic and organic species. The model is being developed to integrate all the available experimental information on adsorption with spectroscopic results for the nature of surface species. By so doing, it will facilitate the comparison of experimental data from different investigators and enable interpolation and extrapolation to conditions not yet studied experimentally. This provides a basis for analysing the role of surface complexation in natural and contaminated environments. It will help lead to predictive models of the behavior of nuclear waste in the subsurface, the migration of subsurface carbon dioxide, and the behavior of nanoparticles interacting with contaminants.

**Results:** Building on our published work quantifying the attachment of alkalis and alkaline earths to minerals, our work has now focussed on describing the attachment of sulfate, carbonate and organic acid anions to mineral surfaces. We have increased our emphasis on the role of water dipoles during attachment. Water dipoles play critical roles in two processes: the desolvation of adsorbing species near an interface, and the removal of chemisorbed water dipoles from the surface. Taking account of these processes enables us to integrate experimental uptake data and experimental spectroscopic results with a predictive theoretical model. Testable predictions of surface speciation as a function of environmental variables in systems of geochemical relevance can now be made. We have applied this approach to help understand exactly how toxic species such as arsenate and selenate are mobilized in mineral-water systems as functions of environmental conditions. Our results emphasize that on polycrystalline materials, species such as arsenate and sulfate attach as multiple surface complexes. The proportions of these vary with environmental conditions. This reinforces the need for predictive models that can be applied in concert with laboratory and field studies.

## JOHNS HOPKINS UNIVERSITY

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**Grant:** DE-FG02-06ER15831

### Development of New Biomarkers for Surficial Earth Processes

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**Objectives:** **I.)** An examination of isolated DNA as both an isotopic substrate and a source of genetic information, and **II.)** an emphasis on fungal microorganisms, with isotopic characterization of fractionation due to different carbon metabolic pathways.

**Project Description:** The first project includes an examination of isolated DNA as both an isotopic substrate, and a source of genetic information. DNA ligation, plasmid introduction, and cloning techniques will be employed to resolve the phylogeny of soil microorganisms, and to test assumptions about community make-up. Specific PCR primers may be engineered to use for this approach, using a trial and error approach in order to focus primers on particular regions of DNA.

The second project places emphasis on fungal microorganisms, and will isotopically characterize fractionation due to different carbon metabolic pathways (also as found within lipid biomarkers), while simultaneously monitoring the biochemistry of the substrate. Plans to pursue the isolation and analysis of PFLA 18:2 $\omega$ 6,9 are included, following the method of Klamer and Baath (2004). These analyses will be complemented with  $^{14}\text{C}$  studies on organic matter in particularly organic rich soils to confirm preservation. The lipid content (relative to other components of the cells) will be assessed for each species studied. The oxygen fugacity and ethanol concentration,  $\text{CO}_2$  concentration, and  $\delta^{13}\text{C}$  value will be monitored to quantify the variability of each microbial growth environment.

**Results:** Towards these goals, the following data has been obtained: **Goal I.)** I compared the  $\delta^{13}\text{C}$  value of whole tissues with that of DNA for five organisms for which the entire genome has been sequenced and the map and function of an exhaustive set of genes are understood: *Homo sapiens* (human), *Mus musculus* (mouse), *Drosophila melanogaster* (fruit fly), *Caenorhabditis elegans* (nematode) and the bacterium *Escherichia coli*. In every case, isolated DNA was found to be isotopically enriched relative to bulk organism tissue. The isotopic enrichment of animal DNA relative to bulk tissue ( $\Delta = 1.19\text{‰}$ ) is similar to the enrichment we have established for Plantae ( $\Delta = 1.30\text{‰}$ ). The isotopic offset we observed for humans is more than sufficiently consistent to allow for the interpretation of shift in diet from C3 to C4 (or *vice versa*) using DNA extracted from ancient materials. **Goal II.)** I reported the  $\delta^{13}\text{C}$  of fungal microorganism biomass resulting from common soil respiration pathways: glucose oxidation (GO) and ethanol-intermediate glucose oxidation (EIGO). Results showed that isotopic differentiation between GO and EIGO occurs during stationary growth when substrate is limiting. The average isotopic enrichment of fungal microorganisms relative to their substrates was +2.32‰ for GO and +1.73‰ for EIGO; this offset was much less variable than those reported for prokaryotes (including bacteria) in comparable environments.

## UNIVERSITY OF MARYLAND

Department of Chemistry and Biochemistry  
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**Grant:** DE-FG02-94ER14467

### Theoretical Studies on Heavy Metal Species in Solution

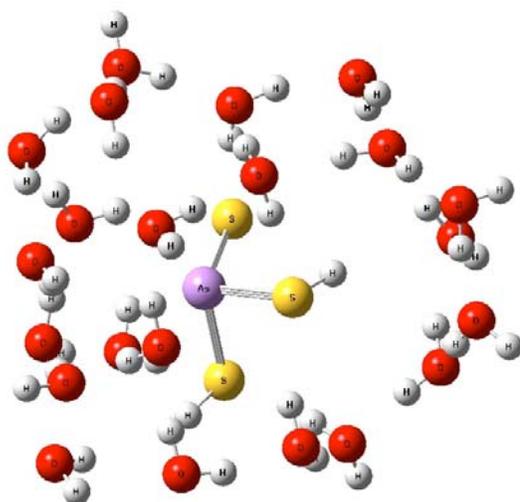
*J. A. Tossell, 301-405-1868; Fax 301-314-9121; [tossell@chem.umd.edu](mailto:tossell@chem.umd.edu)*

**Objectives:** This study utilizes the techniques of computational quantum chemistry to determine the structures, energetics and properties of various metal species in both gas-phase and aqueous solution, as components of mineral glasses, or absorbed on mineral surfaces. One focus has been on calculating accurate free energies in aqueous solution for reactions of borates, carbonates and As oxides and sulfides.

**Project Description:** To understand the mechanisms of dissolution and formation of minerals one must understand the structures and properties of precursor species in aqueous solution. We are developing quantum methodologies which will allow us to accurately calculate the energetics for the formation of both light element and heavy metal complexes in solution and evaluate species properties, such as IR/Raman spectra and UV-vis spectra which will help in their identification. On several of the topics under study we have collaborated with Prof. George Helz (UMCP), who either made the initial experimental observations suggesting the theoretical study or is engaged in experimental work in response to our calculations. Much of the work involves the speciation of metalloids such as As and Sb or metals such as Mo and Re in both oxic and sulfidic solutions.

**Results:** Our research during most of FY2007 was covered by a no-cost extension. Recently we have calculated pKa's for several carbonate species, including the dimer of carbonic acid, which is essentially a "supramolecular" compound held together by H-bonding. It is important to recognize that pKa's are strongly influenced by hydrogen bonding; for example, the pKa's of the inner (H-bonded) and outer (not H-bonded) protons of  $(\text{H}_2\text{CO}_3)_2$  are calculated to differ by about 3 pK units in aqueous solution. In general, pKa's become more positive if the environment of the product ions becomes less stabilizing, such as by substituting a nonpolar organic solvent for water.

We have also looked at the stabilities, Raman and UV spectra and acidities of As sulfides in aqueous solution. By employing state-of-the-art quantum chemical techniques to determine gas-phase harmonic and anharmonic frequencies and solution phase corrections, we can accurately match features observed in experimental spectra. We have calculated the equilibrium structure and the harmonic vibrational frequencies of the  $\text{AsS}(\text{SH})_2^- \dots 22\text{H}_2\text{O}$  nanocluster (Figure 1) at the CBSB7 B3LYP level. For this nanocluster, an isolated vibrational feature at  $425 \text{ cm}^{-1}$  is attributed to an As=S stretch, close to the value determined by Wood et al. (2002). We have also calculated harmonic and anharmonic vibrational frequencies for the free solute species  $\text{AsS}(\text{SH})_2^-$  at a number of different quantum mechanical levels. Our calculations suggest that the features around  $700\text{-}800 \text{ cm}^{-1}$  are related to As-O stretches and those around  $350\text{-}450 \text{ cm}^{-1}$  to As-S stretches.



**Figure 1:**  $\text{AsS(SH)}_2 \dots 22\text{H}_2\text{O}$  nanocluster.

**MASSACHUSETTS INSTITUTE OF TECHNOLOGY**  
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**Grant:** DE-FG02-97ER14760

**Collaborative Research: Evolution of Pore Structure and Permeability of Rocks under Hydrothermal Conditions**

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**Objectives:** The broad objective of this proposal is to study the interrelationships among permeability, mechanical properties, and the pore structure of rocks under hydrothermal conditions, with and without metamorphic reactions.

**Project Description:** Each experimental study or calculation was designed to isolate a particular aspect of a natural process, rather than to conduct more complex experiments in which several processes act simultaneously, as often occurs in nature. Our recent work falls into four general categories: A.) the effect of mechanical deformation on transport properties, B.) the effect of thermal loading on permeability, C.) the effect of structural heterogeneity on fluid transport, and D.) some aspects of the methods of measuring permeability in the laboratory.

**Results:** 1) Pressure solution closure of rough joints.

We are investigating changes in surface roughness of microcrystalline quartz (Novaculite) joints at 400-500°C under normal loading. Novaculite disks were cut and rectified with a surface grinder. For each disk, one side was left rough while the other was wet-polished with a 0.1  $\mu\text{m}$   $\text{Al}_2\text{O}_3$ . The joints were prepared by stacking the disks together with rough and polished sides facing each other. Before starting the experiment, we let the pore water equilibrate with quartz at run temperature so pressure solution would be the most likely mechanism activated by compression. 3D imaging of polished disk surfaces pre- and post-experiment shows changes in surface topography that might be interpreted as dissolution features (see Figure 1). In future experiments, we will quantify joint closure and joint permeability as functions of time. We aim to make the image analysis easier and more quantitative by increasing the magnitude of the initial topography variations on the rough disk sides and by using structured topographic patterns rather than random roughness.

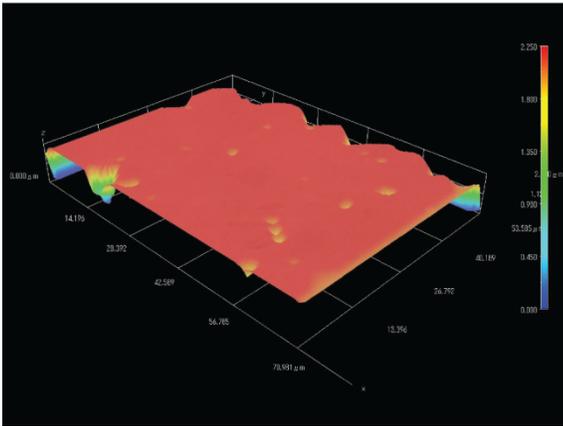
2) Oscillating flow through porous rocks: wave propagation phenomena.

When the compressibility of the fluid or the compliance of the solid framework are not negligible, flow in a fluid-saturated porous media, subjected to an oscillating pressure head may become wave-like. A biologic example is the pulsing propagation of blood in the human artery system. We analyzed propagation of such flow waves in a single, semi-infinite pipe generated by harmonic pressure oscillations at the pipe entrance. The dispersion equation was derived, allowing determination of the phase velocity and quality factor as functions of frequency. Wave reflections at the end of a finite-length pipe and ensuing interferences between forward and backward traveling waves were then examined. Because of fluid storage in the pipe, the amplitude of the AC volumetric fluxes entering and exiting the pipe at its upstream and downstream ends are not equal. Thus, two different, AC, hydraulic conductivities must be introduced, one upstream and one downstream, both of which are frequency-

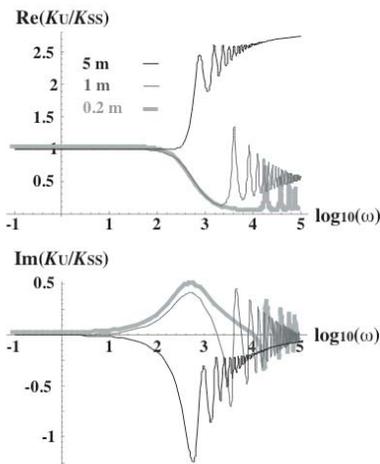
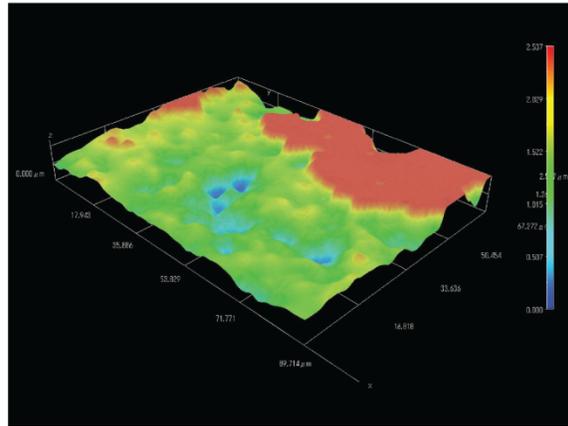
dependent. Superposed on the classic viscous-inertial flow transition (controlled by the pipe radius), these complex-valued parameters show another transition between an interference-free regime at low frequencies and a strong interference regime above a critical frequency that roughly scales as the pipe length (see Figure 2). The single pipe model was used to investigate fluid flow waves through pipe networks with results very similar to those described above. This suggests that flow wave propagation, reflections and interferences could be seismically observed in geologic formations, provided the distance between flow wave reflectors is not too small compared to the wavelength.

**Figure 1:** Surface Topography of polished Novaculite samples.

a) Pre-experimental sample with 'smooth' texture and few pores/indentations



b) Post-experimental sample with significantly increased numbers of indentations.



**Figure 2:** Real and imaginary parts of the normalized apparent conductivity  $Ku/K_{ss}$  for pipes with different lengths  $L$  (thick grey line,  $L = 0.2$  m; thin grey line,  $L = 1$  m; thin black line,  $L = 5$  m; the pipe radius is equal to  $100 \mu\text{m}$ ). The frequencies are given in Hertz.

**MASSACHUSETTS INSTITUTE OF TECHNOLOGY**  
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**Grant:** DE-FG02-99ER15004

**Physics of Channelization: Theory, Experiment, and Observation**

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**Objectives:** We seek a fundamental understanding of the physical processes that erode channels and create drainage networks, by integrating theoretical models, laboratory experiments, and field observations.

**Project Description:** We address two aspects of the erosion problem: the “two-phase phenomenon” of water-driven granular flow, and the growth and interactions of channels. We study the former problem in the laboratory and the latter problem in both the laboratory and the field. In both cases we combine our empirical studies with theoretical analysis.

We specifically address the problem of erosion driven by subsurface “seepage” flows. As in the more commonly studied problem of erosion by overland flow, an understanding of the two-phase flow of water and grains is required to predict the conditions under which material is eroded and subsequently transported by rivers and streams. Compared to the case of overland flow, however, the growth of seepage channels is relatively decoupled from topographic roughness. Channel networks driven by groundwater flow instead reflect more purely their competition for water. We seek to better understand the conditions necessary for the initiation of erosion, the mechanisms that govern the growth of seepage-driven channels, and the processes that determine the geometry of seepage networks.

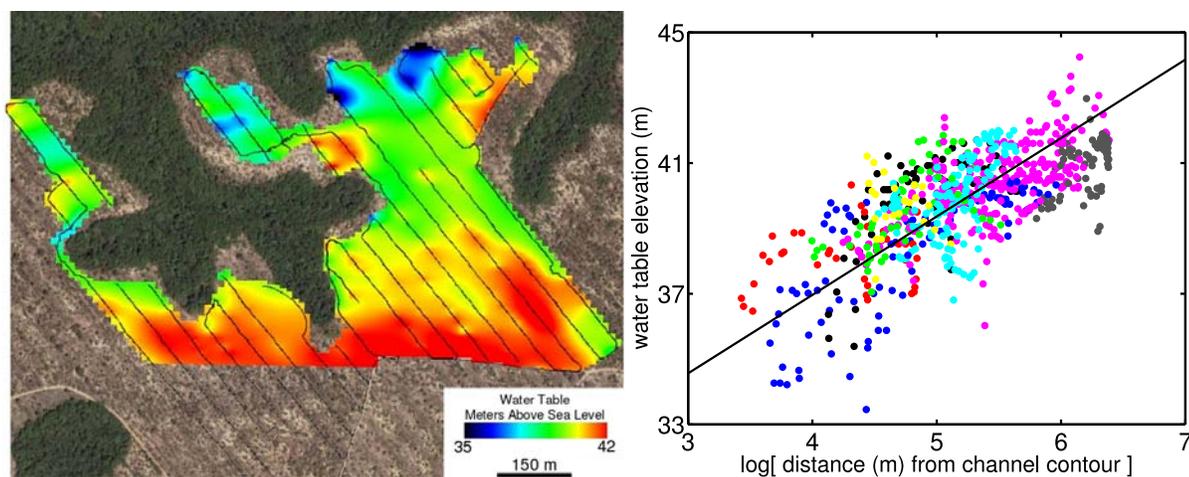
**Results:**

**Field study.** We have studied how the flow of subsurface water shapes the “steephead channels” that drain into the Apalachicola River near Bristol, Florida, on the Florida Panhandle (Figure 1). The channels are cut through 65-m thick surface deposits of sand, and are about 100 m wide and up to 4 km long. Groundwater emerges at the base of each conical channel head. The channel network is characterized by regularly spaced channels with a rough orthogonal structure. To determine how the flow of groundwater interacts with the growing channel network, we collected three-dimensional ground-penetrating radar (GPR) data in the vicinity of highly bifurcated channels. Our results suggest that the subsurface sands through which the channels are cut are effectively homogeneous at length scales comparable to or greater than a typical channel width. We conclude that the ordered, regular structure of this channel network derives from dynamics rather than subsurface heterogeneity.

**Theory.** Numerical simulations of fully three-dimensional subsurface flow into a side branch show that the vertically integrated flux into a channel's tip is roughly proportional to the planar surface area that is closer to the channel tip than to any other point on the main channel or the side branch. This *geometric area* can therefore be used to approximate the true, hydrodynamic, drainage areas and drainage

densities. We use this approximation to construct a model in which channel tips grow at a velocity proportional to the water flux they attract, and new channel tips nucleate at a rate proportional to the local drainage density. A characteristic length scale is then the typical distance  $l$  traversed by growing channels between nucleation events. The structure of the resulting network is then determined by the dimensionless ratio  $l/H$ , where  $H$  is the distance to the groundwater divide. Results show that as  $l/H$  becomes large, channels “screen” each others’ growth and the typical dimensionless distance  $d/H$  channels decreases to a constant, thus providing a tentative explanation of the ordered structure of seepage networks.

**Experiments.** The large-scale interactions between channels ultimately derive from the microscopic mechanisms that drive erosion within a single channel. A fundamental problem is to predict the granular flux for a known fluid flow. To explore this problem in the laboratory, we have constructed a new apparatus that provides visualization of the grain-scale and fluid motions that occur near the critical Shields number, i.e., when the shear stresses on a granular bed are just sufficient to mobilize grains. Our flow geometry, in which the depth of the fluid gap gradually increases as the grains are eroded, results in the cessation of granular flow and thus allows for an unambiguous definition of the Shields threshold condition. By varying the fluid flux through the cell, we have verified the hypothesis that the boundary viscous shear stress is sufficient to predict cessation of granular flow.



**Figure 1:** *Left:* Three-dimensional reconstruction of the water table geometry superimposed on an aerial photo of a bifurcated channel. The relatively flat terrain through which the channels are cut is roughly 55 m above sea level, or 13-20 m above the depicted water table. Black lines show transects of the GPR survey. *Right:* Elevation of the water table as function of the natural logarithm of the distance from the 40-m elevation contour that contains the channels. Different colors correspond to discrete segments of the 40-m contour.

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**Grant:** DE-FG02-07ER15839

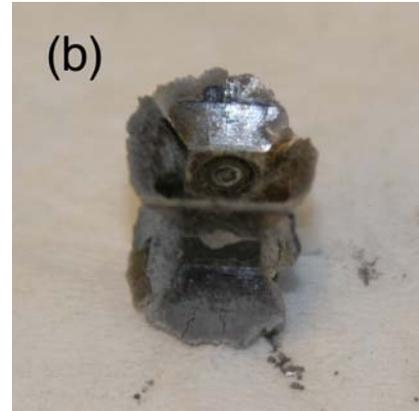
**Rheological Properties of Earth's Lithosphere: Experimental Constraints on Low-Temperature Plasticity of Olivine-Rich Rocks at High Pressures**

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**Objectives:** The objective of this work is to measure the flow properties of olivine-bearing rocks under lithospheric conditions, which have been heretofore unachievable in deformation experiments, and to understand deformation processes sufficiently to extrapolate measurements to the geologic setting.

**Project Description:** This project owes its existence to the recent development of the Deformation-DIA (D-DIA), a solid-medium, multi-anvil type of apparatus. It differs from conventional deformation instruments in that synchrotron x-rays are used to measure stress and plastic strain directly within the material of the test sample. Experiments are carried out at temperatures in the range 773 to 1173 K and pressures from 6 to 12 GPa. First, we have focused on quantifying low-temperature plasticity of olivine under anhydrous conditions. Second, we are extending this research to hydrous conditions. Our primary goal is to produce low-temperature flow laws (i.e., to quantify the dependence of creep rate (viscosity) on differential stress, pressure, temperature, and water fugacity) for olivine-rich rocks. The results of this study then provide the basis for modeling geodynamic processes occurring in the mantle.

**Results:** In close collaboration with David L. Kohlstedt and Shenghua Mei at the University of Minnesota, we conduct deformation experiments at synchrotron radiation facilities, most often at the National Synchrotron Light Source, Brookhaven National Laboratory, to explore the rheological properties of olivine at pressures up to ~12 GPa and temperatures ranging from 773 to 1173 K. An important technological advance during the past year turned out to be critical for reaching a new level of measurement resolution. We designed, built, tested, and finally put to use a new high-pressure cell with a two-material composite design, the inner material being a bone-dry substance (mullite) and the outer being a ductile, gasket-forming material (pyrophyllite). The rheological behavior of olivine is notoriously water-dependent and highly variable when water content is uncontrolled. We showed that olivine samples remain very dry throughout testing in the new assembly, and the resultant behavior was very reproducible, allowing us to quantify a high-pressure olivine flow law under anhydrous conditions. The first olivine experiments began in the middle of the past fiscal year, and the preliminary results already constrain temperature- and stress-dependence of strain rate.



Shown above is the new hybrid D-DIA cell. (a) Cell parts. A 6-mm diameter mullite sphere is cradled and lightly cemented between two pieces of unfired pyrophyllite to form a solid cube of 6-mm edge length. The pyrophyllite has excellent pressure-sealing properties but its water content is undesirably high for the experiments; the mullite is bone dry, but too friable to hold a pressure seal. (b) Appearance of cell following testing in the D-DIA. Gasketing “fins” (some are broken off) of pyrophyllite have been extruded at the edges the cubic cell, now approximately 5 mm in edge length. A spot of mullite is visible on the front face, but no mullite has extruded into the gaskets. The top of the deformation column is visible at the center of the top face.

## UNIVERSITY OF MASSACHUSETTS, AMHERST

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**Grant:** DE-FG02-05ER15740

### Quantifying the Micromechanical Effects of Variable Cement in Granular Porous Media

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**Objectives:** (1) To quantify grain-scale physical effects of variable cement quantity, composition, and location on the elastic and inelastic deformation of granular porous media.

(2) To use the resulting understanding of the fundamental micromechanical processes that govern macroscopic deformation to accurately capture meaningful grain-grain interactions in Discrete Element Model (DEM) simulations.

**Project Description:** The project scope requires us to develop methods of appropriately small-scale experimental deformation and structural characterization of granular porous media. We chose to work with both natural and synthetic grain-cement systems using novel approaches that provide insight into grain-scale mechanics. We will:

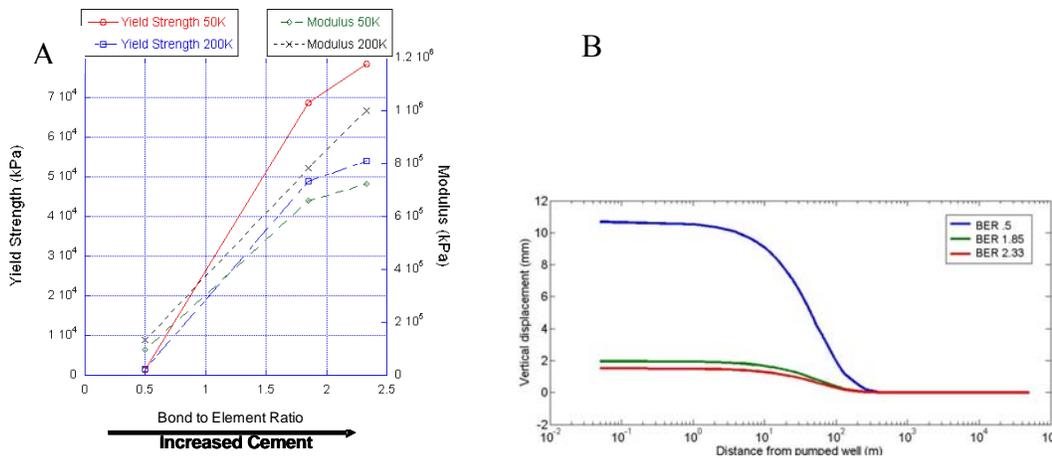
- Develop methods for fabrication of synthetic assemblages of soda-lime silicate beads and both sodium silicate and calcium carbonate cements.
- Design apparatus to test mechanical properties of synthetic grain-cement assemblages.
- Use nanoindentation to probe properties such as elastic modulus, hardness, and plasticity of grains and cements in both natural and synthetic systems. Use ultrasonic velocity and uniaxial deformation experiments to characterize variably cemented natural sandstone.
- Integrate microstructural and experimental analyses to relate physical elements of progressively cemented natural and synthetic systems to their structural response to stress.
- Develop quantitative relationships describing the stress-strain response of cemented granular systems and incorporate microscale material response into a DEM.

**Results:** Current understanding of the impact of cement on the mechanical response of granular porous media is largely based on a widely accepted conceptual model of a circular cement “bridge” between two grains. Our observations and literature review indicate, however, that this meniscus-type cement geometry is uncommon in natural materials. The UW group has therefore focused on designing an approach to quantitatively characterize, and determine the mechanical impact of, natural cement morphologies. Because quartz is the most common cement in siliciclastic sediments, our work has focused on the St. Peter Sandstone, a well sorted, quartz-cemented quartz arenite. The St. Peter exhibits considerable variation in cement abundance, with typical quartz overgrowth geometries. Quartz cement morphology changes with progressive cementation. Grains in low-cement samples exhibit thin, encrusting layers of quartz with isolated crystal facets. Pore spaces are relatively equant and

interconnected. In contrast, high-cement samples have an interconnected network of cement with well defined facets, more angular and crack-shaped pores, and diminished pore connectivity.

The Sandia team has begun to use these morphological observations to construct physically based finite element models to explore cement-grain mechanical behavior. Perhaps not surprisingly, the stress distribution at our modeled grain-cement boundaries is distinctly different from that of the previously studied meniscus-type cement morphologies.

At a larger spatial scale, the UMass team's DEM modeling provides quantitative insight into the effects of changing grain size and percent cement on bulk material properties (e.g., Young's modulus, Poisson's ratio). To investigate the effects of progressive cementation, a bond length is assigned to a DEM model domain. The assigned length specifies the maximum distance between elements that can be 'cemented', leaving 'grains' that are further apart 'uncemented'. Thus, increasing the bond length increases the number of bonds between elements in the domain. The number of bonds, or 'cement' links between elements, divided by the number of elements, is termed the Bond to Element Ratio (BER). BER is a proxy for percent cement; increasing BER increases yield strength (Figure 1A). To evaluate the effects of cementation on large-scale fluid removal and resulting reservoir deformation, the theoretical bulk modulus properties from the DEMs were input into 2D, axially symmetric, poroelastic continuum models. Poroelastic model results indicate that the bulk moduli calculated from DEMs with BER= .5 and BER=2.33 resulted in 10.5 mm and 1.8 mm of deformation, respectively (Figure 1B). These values are consistent with sample derived BERs of the St. Peter sandstone.



**Figure 1.** (A) Yield strength and modulus (stiffness calculated from the DEM) as a function of bond to element ratio. (B) Simulated vertical displacement as a function of distance from a pumped well. The bulk moduli for these models were calculated using DEMs with variable cement content.

The UMass team has continued to work on producing cements between glass beads, focusing on creating a more natural precipitation process. They have designed a system to precipitate calcite at the contacts of two or more touching glass beads or sand grains. Powdered calcium carbonate is dissolved in water in a CO<sub>2</sub>-rich atmosphere, effectively lowering the solution pH. The solution is then pumped into a secondary container, mixed with air, and pumped through a specially designed specimen holder. As the pH of the solution is raised, the calcium carbonate begins to precipitate at nucleation sites in contact with the fluid. We have produced micro-crystalline calcite using this technique at the contacts of the glass beads, and are working to produce a larger volume of cement.

## MINERALOGICAL SOCIETY OF AMERICA

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**Grant:** DE-FG02-01ER15127

### Support of MSA and GS Short Courses and the Companion Reviews Volumes

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**Objectives:** Support of short courses and the companion *Reviews in Mineralogy and Geochemistry* volumes proposed to and accepted by the Mineralogical Society of America (MSA) and Geochemical Society (GS) held in 2004-2008.

**Project Description:** The support has two purposes: (1) keeping student registration fees affordable; and (2) producing the Reviews volumes. Speaker travel costs have become the most significant MSA and GS short course expense. Student fees were kept low indirectly through support of that speaker travel.

**Results:** There were four short courses during FY2007, each with a companion *Reviews in Mineralogy and Geochemistry* volume:

[1] **Water in Nominally Anhydrous Minerals**, 1-4 October 2006, Verbania, northern Italy. Convenor was Hans Keppler, Bayerisches Geoinstitut. The course had 65 participants (31 students and 34 professionals + speakers). Volume 62: **Water in Nominally Anhydrous Minerals**, Hans Keppler and Joseph R. Smyth, editors i-viii and 478 pp. ISBN 0939950-74-X

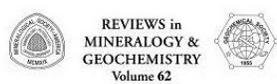
[2] **Neutron Scattering in Earth Sciences**, 7-8 December 2006, Holiday Inn-Bay Bridge, 1800 Powell Street, Emeryville, California. Convenors were *Hans-Rudolf Wenk* (University of California-Berkeley) and *Nancy Ross* (Virginia Tech). Registrations were taken by the Mineralogical Society of America and the course had 60 participants (17 students and 32 professionals, 11 speakers). Volume 63: **Neutron Scattering in Earth Sciences**, Hans-Rudolf Wenk, editor, i-xx and 471 pp. ISBN 978-0939950-75-1.

[3] **Medical Mineralogy and Geochemistry**, 9-10 December 2006, United States Geological Survey (USGS), 345 Middlefield Rd, Menlo Park, California. Convenors were Nita Sahai (University of Wisconsin-Madison) and Martin A. A. Schoonen (Stony Brook University). Registrations were taken by the Mineralogical Society of America and the course had 76 participants (27 students and 38 professionals, 11 speakers). Volume 64: **Medical Mineralogy and Geochemistry**, Nita Sahai and Martin A. A. Schoonen, editors, i-xi and 332 pp. ISBN 978-0939950-76-8.

[4] **Fluid-fluid Equilibria in the Crust: Petrology - Geochemistry - Economic potential**. August 16-17, 2007 (preceding the Goldschmidt Conference 2007 in Cologne, Germany). Convenors are *Axel H. Liebscher* and *Christoph A. Heinrich*. The course had 43 participants (16 students and 16 professionals + 11 speakers). Volume 65: **Fluid-Fluid Interactions**, Axel Liebscher and Christoph A. Heinrich, editors, i-xii and 430 pp. ISBN 978-0-939950-77-5.

Copies were distributed to all short course participants, 648-777 copies to library subscribers to *American Mineralogist* (who include library subscribers to *Geochemica et Cosmochimica Acta*), book

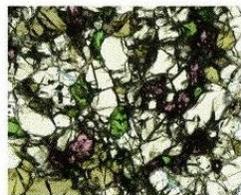
reviewers, and by mail and meeting sales. Volumes 62, 63, 64, 65 are also posted on *GeoScienceWorld* (GSW) that as of September 2007 had 242 subscribers.



REVIEWS in  
MINERALOGY &  
GEOCHEMISTRY  
Volume 62

**WATER IN NOMINALLY  
ANHYDROUS MINERALS**

EDITORS  
Hans Keppler and Joseph R. Smyth



GEOCHEMICAL SOCIETY  
MINERALOGICAL SOCIETY OF AMERICA

Series Editor: Jodi J. Rosso

206

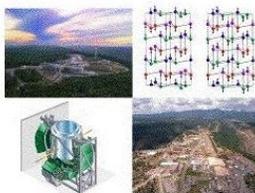
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REVIEWS in  
MINERALOGY &  
GEOCHEMISTRY  
Volume 63

**NEUTRON SCATTERING  
IN EARTH SCIENCES**

EDITOR: Hans-Rudolf Wenk



GEOCHEMICAL SOCIETY  
MINERALOGICAL SOCIETY OF AMERICA

Series Editor: Jodi J. Rosso

206

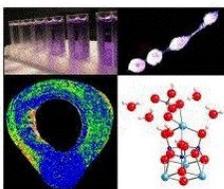
ISSN 1529-4466



REVIEWS in  
MINERALOGY &  
GEOCHEMISTRY  
Volume 64

**MEDICAL MINERALOGY  
AND GEOCHEMISTRY**

EDITORS:  
Nita Sahai and Martin A.A. Schoonen



GEOCHEMICAL SOCIETY  
MINERALOGICAL SOCIETY OF AMERICA

Series Editor: Jodi J. Rosso

206

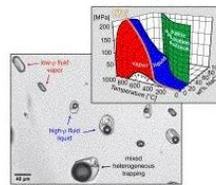
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REVIEWS in  
MINERALOGY &  
GEOCHEMISTRY  
Volume 65

**FLUID-FLUID  
INTERACTIONS**

EDITORS:  
Axel Liescher and Christoph A. Heinrich



MINERALOGICAL SOCIETY OF AMERICA  
GEOCHEMICAL SOCIETY

Series Editor: Jodi J. Rosso

207

ISSN 1529-4466

## UNIVERSITY OF MINNESOTA

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**Grant:** DE-FG02-04ER15500

### **Rheological Properties of Earth's Lithosphere: Experimental Constraints on Low-Temperature Plasticity of Olivine-Rich Rocks at High Pressures**

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**Objectives:** To provide a better understanding of rheological properties of mantle rocks under lithospheric conditions, we have undertaken deformation experiments on olivine, the most abundant mineral in the upper mantle, under both anhydrous and hydrous conditions in a high-pressure deformation testing apparatus at low temperatures and high differential stresses. This study builds on our experience in carrying out high-pressure, high-temperature experiments under controlled thermodynamic conditions and takes advantage of our experience with large-volume, high-pressure deformation experiments at synchrotron x-ray beam lines. The objective of this study is to determine constitutive equations appropriate to low-temperature plastic flow in order to permit modeling of properties and processes in Earth's interior. Additionally, we perform microstructural and spectral analyses to improve the physical basis for those constitutive relationships.

**Project Description:** This project owes its existence to the recent development of the deformation-DIA (D-DIA), a solid-medium, multi-anvil type of apparatus. It differs from conventional deformation instruments in that synchrotron x-rays are used to measure stress and plastic strain directly within the material of the test sample.

Experiments were carried out at temperatures in the range 773 to 1173 K and pressures from 6 to 12 GPa. First, we have focused on quantifying low-temperature plasticity of olivine under anhydrous conditions. Second, we are extending this research to hydrous conditions. Our primary goal is to produce low-temperature flow laws (i.e., to quantify the dependence of creep rate (viscosity) on differential stress, pressure, temperature, and water fugacity) for olivine-rich rocks. The results of this study then provide the basis for modeling geodynamic processes occurring in the mantle.

**Results:** In close collaboration with Dr. William B. Durham at Massachusetts Institute of Technology, we conduct deformation experiments at synchrotron radiation facilities, most often at the National Synchrotron Light Source, Brookhaven National Laboratory, to explore the rheological properties of olivine at pressures up to ~12 GPa and temperatures ranging from 773 to 1173 K under anhydrous conditions. In these experiments, we determine pressure (i.e., mean stress) and differential stress, based on x-ray diffraction patterns, from the elastic strain of various lattice planes measured as a function of orientation with respect to the stress field. Sample strain is computed from the length change of deforming samples measured from a series of x-radiographic images. Temperature is determined either

directly with a thermocouple or indirectly from furnace power based on the results of calibration tests, carried out under identical conditions at the University of Minnesota.

In the past year we completed experiments to reach our goal of characterizing with good resolution the rheological behavior of olivine. Over the past year, several important technological advances, including cell development and temperature calibration, turned out to be critical for reaching this new level of measurement resolution. Although some more experiments conducted recently are still in the process of data reduction and analysis, the results from our previous runs are very promising. Plots of stress versus deformation rate for the runs conducted at different temperatures are shown in Figure 1. As illustrated in the figure, at a given stress, deformation rate increases substantially with increasing temperature while, at a given strain rate, differential stress decreases with increasing temperature. Our latest efforts are focused on conducting experiments with satisfactory resolution to further delineate the rheological behavior of olivine at low temperatures and high differential stresses in establishing a robust flow law at these important lithospheric conditions.

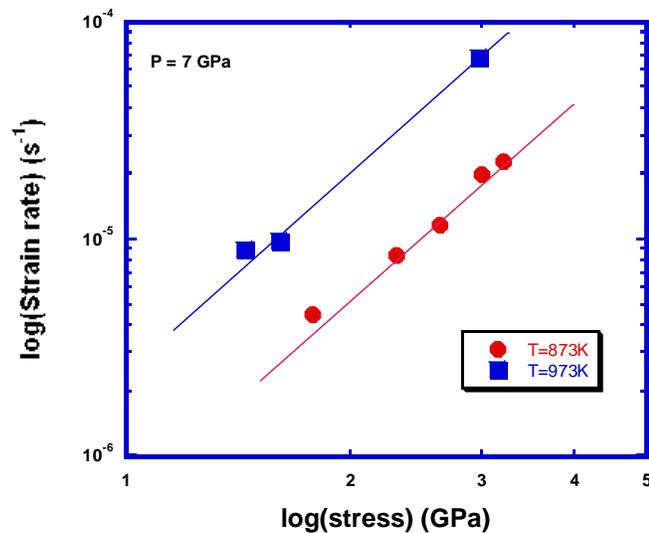


Figure 1. Log-log plot of stress versus strain rate for experiments conducted at  $P = 7$  GPa for two different temperatures. Differential stress in the sample is computed from the (122) reflection in x-ray diffraction patterns taken during the deformation experiment. Strain is calculated from radiographs taken periodically during the run.

## **NATIONAL ACADEMY OF SCIENCES**

Board on Earth Sciences and Resources

500 5th Street, N.W.

Washington, DC 20001

**Grant:** DE-FG02-07ER15915

### **Board on Earth Sciences and Resources and Its Activities**

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**Website:** <http://dels.nas.edu/besr/>

**Objectives:** The Board on Earth Sciences and Resources (BESR) provides a focal point for National Research Council activities related to the earth sciences. Under the aegis of the Board, *ad hoc* committees provide independent advice to the federal government on a wide range of earth science issues, including research, the environment, natural hazards, resources, data, and education. It also provides guidance related to U.S. participation in international earth science programs.

**Project Description:** The Board and its five standing committees (Committee on Earth Resources; Geographical Sciences Committee; Committee on Geological and Geotechnical Engineering; Committee on Seismology and Geodynamics; and Mapping Science Committee) hold approximately two meetings each year. At these meetings, potential studies are discussed and developed. Many of these activities are in response to requests from agencies of the federal government for advice on specific technical or policy issues. Other activities are federally mandated, or initiated by the Board in accordance with its efforts to support the continued health of the earth sciences. The Board responds by establishing an *ad hoc* committee or panel to address the specific issue. The Board continually seeks to provide accurate and timely input to support wise decision-making in government, academia, and industry.

**Results:** In FY 2007, the Board oversaw 14 studies. Examples of studies underway in FY 2007 are Grand Research Questions in Solid-Earth Sciences, and Coal Research, Technology, and Resource Assessments to Inform Energy Policy. BESR completed 9 studies in FY 2007. The results of BESR's studies are published in its peer-reviewed reports. Examples of completed studies include **Assessment of the Performance of Engineered Waste Containment Barriers**, and **Tools and Methods for Estimating Populations at Risk from Natural Disasters and Complex Humanitarian Crises**.

During this reporting period, the Board held two meetings. The October 2006 meeting was held at the Beckman Center in Irvine, California. At this meeting, two BESR standing committees, the Committee on Geological and Geotechnical Engineering and the Committee on the Geophysical and Environmental Data, were reviewed. The board discussed recent reports published by its *ad hoc* committees: Contributions of Land Remote Sensing for Decisions About Food Security and Human Health--Workshop Report; and Successful Response Starts with a Map--Improving Geospatial Support for Disaster Management. Most of the meeting was devoted to a roundtable on 'Discarding America: Status, Trends, and Future of Waste Disposal within a Sustainable Earth System.' To this end, the speakers:

(1) assisted in developing an outline/description/definition of the immense challenges related to waste disposal and environmental management, focusing on differences and similarities related to local, national, and global perspectives. Or, how do we develop a rational or approach to the problem of waste disposal when the challenge spans such diverse scales related to aspect such as production rate, chemical composition, geographic coverage, and geologic setting.

(2) discussed how the existing waste production, transport, and disposal systems (in their areas of specialty) impact processes/systems/reservoirs/fluxes within the earth system. Or, how is the sustainability of the Earth system services impacted by changes in the quantities and composition of waste and byproducts of the lifestyle of our Nation's citizens?

(3) identified approaches and methods that might be used to address the challenge of capturing not only the changes in the total volume of wastes but also significant changes in the composition of wastes. At the broadest scale, would assessment enhance our understanding of the emergence of non-natural substances as a component of waste streams and the appearance of new categories of materials within that new mega-category. Sub-classes of interest, although probably too tough to capture right now, would be toxic/radioactive/etc. wastes and waste types that are not biodegradable.

(4) discussed waste disposal in the context of the future global economy in which many developing countries (notably China and India) continue to strive to emulate the growth in the economy and the affluence of the United States (and of other developed countries/regions such as Japan, western Europe, Canada, and Australia) while at the same time endorsing the commitments made by these developed countries toward a sustainable Earth System. Or, how can we better understand and predict changes in the geographical distribution of waste generation as immense populations in areas such as Asia, representing half of the population of the world, pursue sustained rates of economic growth of 6-8% per year?

The May 2007 meeting was held in Washington, DC. At that meeting the new Earth science directors of the U.S. Geological Survey, the NSF Earth Sciences Division, and NASA's Earth Science Division presented current and future directions of their respective agencies. A major portion of the meeting's open session was devoted to a roundtable on 'Carbon Capture and Sequestration in Geologic Formations.' This roundtable was deemed by all present to be highly successful and has led to a federally mandated study on geologic and terrestrial sequestration and a mandated study on carbon capture and sequestration for tertiary education (undergraduate and graduate).

## **NATIONAL ACADEMY OF SCIENCES**

Board on Earth Sciences and Resources

500 5th Street, N.W.

Washington, DC 20001

**Grant:** DE-FG02-05ER15664

### **Grand Research Questions in Solid-Earth Sciences**

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**Website:** <http://www8.nationalacademies.org/cp/projectview.aspx?key=BESR-U-05-03-A>

**Objectives:** A National Academies committee will formulate a short list of grand research questions driving progress in the Earth sciences. The questions will cover a variety of spatial and temporal scales, from sub-atomic to planetary, and from the past (billions of years) to the present and beyond. The questions will be written in a clear, compelling way and will be supported by text and figures that summarize research progress to date and outline future challenges.

**Project Description:** Over the past three decades, Earth scientists have made great strides in understanding our planet's workings and history. We understand as never before how plate tectonics shapes our planet's surface, how life can be sustained over billions of years, and how geological, biological, atmospheric, and oceanic processes interact to produce climate-and climatic change. Yet, at the most basic level, this progress has served principally to lay bare more fundamental questions about the Earth. Expanding knowledge is generating new questions, while innovative technologies and new partnerships with other sciences provide new paths toward answers.

The committee was established to frame some of the great intellectual challenges inherent in the study of the Earth and planets. Although many reports have identified research priorities in Earth science, few have cast them as fundamental science questions. Such "big picture" questions may require decades to answer and research support from many agencies and organizations.

**Results:** The committee submitted the report, which covers the topics below, to external review.

1. Formation of the Earth and other planets. While it is generally agreed that the Sun and planets all coalesced out of the same nebular cloud, we still do not know how Earth obtained its particular chemical composition in enough detail to understand its subsequent evolution, or why the other planets ended up so different from ours and from each other.
2. Evolution of the early (the first 500 million years) Earth. Collision of a Mars-sized planet added so much heat to Earth that the entire planet melted. Little is known about how this magma soup differentiated into the core, mantle, and lithosphere of today, or how Earth developed its atmosphere and oceans, in part because almost no rocks of this age are preserved.
3. Origin of life. When life first arose the conditions at Earth's surface may have been much different than today's, and one critical challenge is to develop an accurate picture of the physical environments

and the chemical building blocks available to early life.

4. Earth's internal processes. Convection in Earth's interior produces the magnetic field and drives volcanism, seafloor generation, and the exchange of water and carbon dioxide between the surface and deep interior. But we can neither precisely describe these convective motions today, nor determine with confidence what they were like in the past and how differences might have affected Earth's surface environment.

5. Plate tectonics and continents. Plate tectonics operates today, but we still do not know why it started and how closely it is related to other unique aspects of Earth, such as abundant water, the existence of life, and the formation and persistence of continental crust for billions of years.

6. Earth material properties. The keys to understanding geologic processes are the basic physics and chemistry of planetary materials, but it is a challenge to study them at the extreme temperatures, pressures, and temporal and spatial scales of planets.

7. Climate change. Geological evidence shows momentous changes in climate, but we do not understand how Earth's surface temperature has remained habitable for most of the last 4 billion years, or the special conditions that led to extremely hot, cold, or rapidly changing climates.

8. Earth-life interactions. For example, we do not fully understand the links between biological and inorganic processes that oxygenated the atmosphere and allowed other forms of life to flourish, or the exact ties between geology and evolution that caused massive extinctions in the past and influenced the course of evolution.

9. Prediction of earthquakes and volcanic eruptions. Predictions of volcanic eruptions are improving, but a clear picture of magma movement, from sources in the upper mantle to the surface where it erupts, has not yet been developed. It may never be possible to predict the exact time and place an earthquake will strike, but understanding more about crustal stresses and fault behavior may help improve long-term forecasts.

10. Fluid flow and transport. Good management of natural resources and the environment requires knowledge of the behavior of fluids, but we have not yet developed models that can predict stream flow, or determined the distribution, flow, and thermal and chemical exchange of subsurface fluids with their host formations.

## UNIVERSITY OF NEW MEXICO

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**Grant:** DE-FG02-08ER15930

### **Investigation into the Relationship between Heterogeneity and Heavy-Tailed Solute Transport**

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**Objectives:** The objective of this project is to characterize the influence that naturally complex geologic media has on anomalous dispersion and to determine if the nature of dispersion can be estimated from the underlying heterogeneous media.

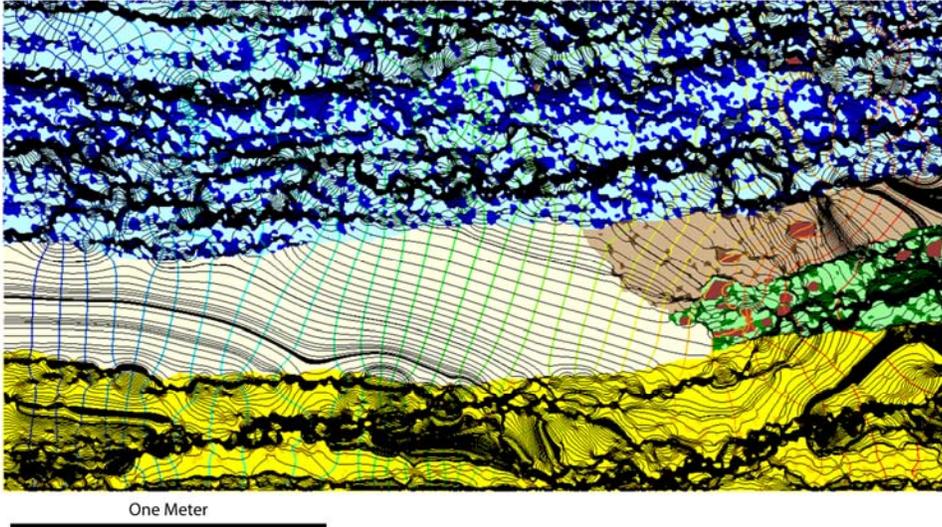
**Project Description:** This project combines outcrop-scale heterogeneity characterization, laboratory experiments, and numerical simulations. The study is designed to test whether established dispersion theory accurately predicts the behavior of solute transport through heterogeneous media and to investigate the relationship between heterogeneity and the parameters that populate these models. The dispersion theory tested by this work is based upon the fractional advection-dispersion equation (fADE) model. Unlike most dispersion studies that develop a solute transport model by fitting the solute transport breakthrough curve, this project will explore the nature of the heterogeneous media to better understand the connection between the model parameters and the aquifer heterogeneity.

**Results:** In the first year of this study, we collected lidar scans from numerous outcrop exposures in the Albuquerque, New Mexico, area. We successfully applied segmentation to the scan images using live-wire and threshold segmentation algorithms in order to distinguish various lithologic types (e.g., sand vs. gravel) from the high-resolution (2 mm) outcrop scans. By applying reasonable hydraulic conductivity (K) values for sand or gravel and populating a groundwater model with conductivities based on the lidar scan, we produce steady-state velocity fields that capture the influence of this fine-scale heterogeneity (Fig. 1A). Because some uncertainty exists with our K estimates, we developed models using different K contrasts, including differences in K of  $\frac{1}{2}$ -, 1-, 2-, and 3-orders of magnitude while holding the geometric mean of K constant. Numerical simulations using pathline analysis (MODPATH) show the strong influence of gravel interbeds, where most of the groundwater flow is focused through relatively high conductivity gravels. This focusing occurs in all realizations with K contrast  $>$  1-order of magnitude. The focusing caused by gravels and the variable velocity field that result from heterogeneity in these simulations produces non-Fickian breakthrough of particles (Fig. 1B). Though these models offer an indication of the influence of heterogeneity at small scales, assumptions behind these models must be evaluated more fully.

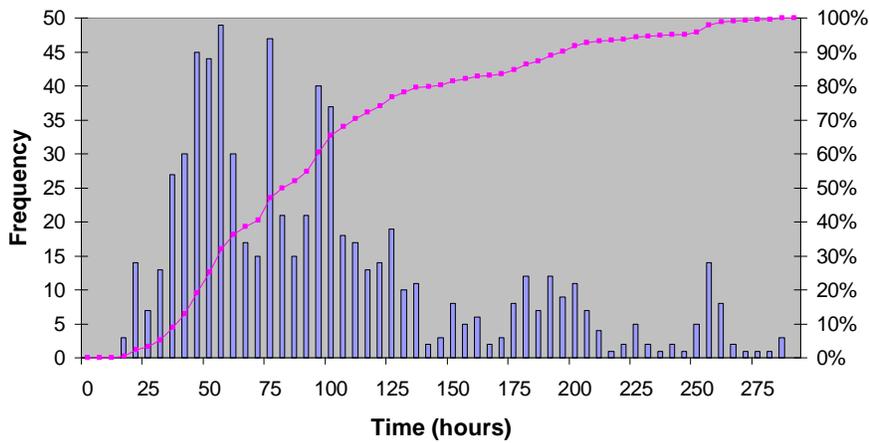
For the evaluation of sedimentary texture on non-Fickian transport, we constructed a specialized permeameter to induce an instantaneous tracer pulse (deuterated water). By collecting samples at the downgradient end of the permeameter, we measured breakthrough characteristics for different

sedimentary textures (varying mean grain size and sorting). We are still evaluating the results from this experiment.

**A.**



**B.**



**Figure 1: A.** Groundwater and advective pathline simulation results from the high-resolution lidar-based outcrop image. Darker colors indicate gravels within each of the stratigraphic units. Note the strong focusing of particles into well connected gravel units. We used a 2-order of magnitude contrast in K for this example. **B.** Resulting breakthrough times for particles showing non-Fickian behavior.

## THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK

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**Grant:** DE-FG02-06ER15817

### Complex Fluids in Self-Affine Fractures

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**Objectives:** To understand the dynamics of non-Newtonian liquids and particulate suspensions in self-affine fractures, and in particular how the correlated surface roughness affects permeability, tracer dispersion and sedimentation.

**Project Description:** Naturally fractured rocks have “self-affine fractal” surfaces which exhibit power-law correlations giving rise to distinctive velocity fluctuations and transport inhomogeneities when fluids or tracers pass through the fracture. The goal of this research is to understand the interplay of diffusion and convection in the hydrodynamic dispersion of non-Newtonian liquids, and the evolution of the fracture surface when (non-colloidal) particulates carried by the fluid deposit on the walls. Both problems are characterized by nonlinear feedback mechanisms, which render their analysis difficult. In the first case, the velocity variation within a heterogeneous fracture leads to an inhomogeneous shear stress pattern, which in a shear-thinning liquid causes spatial variations in viscosity, which enhances the velocity variation. In the second problem, deposition processes alter the fracture geometry which in turn alters the velocity and stress fields, which can then promote or discourage deposition in different regions of the fracture. We will employ numerical simulations based on the lattice-Boltzmann method, based on our newly developed codes for shear-thinning liquids and solid particle transport, complemented by effective medium and other averaging techniques. The proposed analytical and numerical work at CCNY will be complemented by a continuing collaboration with an experimental group led by J.-P. Hulin at the Université de Paris - Orsay.

**Results:** Two computational tools were developed and used to obtain initial results on particulate motion and non-Newtonian fluid behavior. A lattice Boltzmann code which simulates the motion of particle-laden fluids in fractures at finite Reynolds number was prepared and tested on one and two-particle systems. The single particle computations were in agreement with previous results in the literature for migration and rotational behavior, while in the two-particle case we observed novel interaction dynamics with regions of fixed point behavior as well as open and closed limit cycles. Independently, we developed a slightly novel algorithm for power-law (shear thinning or thickening) fluid flow computations in channels. As applied to self-affinely rough fractures, we first studied local aspects of power-law fluid flows, such as velocity, pressure and stress distributions and the drag and thrust exerted by the fluid on the fracture walls. We then considered the fracture permeability as a function of flow rate, and showed first that the familiar sequence of transitions in the pressure drop vs. flow rate relation for Newtonian fluids in porous media - linear then cubic, then quadratic - is also present for power-law fluids in rough fractures. Secondly, we showed that by use of an appropriate definition of Reynolds number the permeability variation of the various fluids could be all collapsed into

a single friction factor vs. Reynolds number curve, resembling the classical friction factor relationship for flow in pipes.

## THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK

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**Contract:** DE-FG02-03ER15458

### Study of Damping Granular Materials

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(Schlumberger-Doll Research), (617) 768-2348, fax (617) 768-2385*

**Website:** <http://www.jamlab.org>

**Objectives:** The goal of this project is to combine experimental characterization, continuum and micromechanical modeling and computer simulations to understand the elastic properties and the mechanisms of dissipation of acoustic modes in granular materials.

**Project Description:** This project is motivated by a desire to understand acoustic propagation and dissipation in earth formations. A distinct feature of granular materials is the ability to dissipate acoustic energy through the network of interparticle contacts or viscous dissipation through the surrounding medium. Indeed, loose grains damp acoustic modes very efficiently and they are routinely used as an effective method to optimize the damping of unwanted structure-borne acoustic signals. Despite its fundamental importance and practical applications, the microscopic origins of the mechanisms of dissipation in jammed granular materials are still unknown. To this end, we pursue the concept of the effective mass of a loose granular aggregate contained within a rigid cavity which is vibrated at different frequencies as well as the flexural modes in a resonance bar with a cavity filled with grains. Apart from the fundamental aspects of this research we are motivated by the practical need to develop an effective method for optimizing the damping of waves in structure borne sound.

**Results:** We have performed a series of experiments, simulations and theoretical studies done in parallel at Schlumberger and CCNY. In order to unravel the origins of dissipation in earth materials from a fundamental point of view, we have developed the concept of a frequency dependent effective mass of a loose granular aggregate contained within a rigid cavity. The effective mass is complex valued; its real part reflects the elastic properties while its imaginary part the dissipative properties of the granular medium. We demonstrate how the distinct features of the effective mass allow the study of some of the mechanisms of damping of acoustic modes, aging and elasticity in granular matter.

Generally speaking, the effective mass exhibits a sharp resonance which we interpret in terms of an effective sound speed describing the elasticity of the material. The imaginary part of the effective mass of shows a broad resonance peak which quantifies the attenuation of acoustic waves in the system. We observe remarkable changes in a humidity controlled environment in the stiffness and attenuation in the medium. By monitoring the effective mass in time, we find a logarithmic aging effect in the resonance frequency as well as an increase of the damping upon humidification and its subsequent drastic decrease upon drying. We interpret these effects as manifestations of capillary condensation occurring between the asperities at the contact surfaces between the grains during humidity-dry cycles. We conclude that,

in loosely jammed granular materials, dissipation of acoustic energy is dominated by the asperities at the interparticle contact surfaces. Therefore humidity drastically affects the attenuation of the material through the capillary condensation of liquid bridges. The large variations in dissipation found in this study demonstrate the conditions for effective particle damping and are relevant to a variety of applications for optimizing attenuation of structure-borne acoustic waves.

## STATE UNIVERSITY OF NEW YORK, STONY BROOK

Department of Geosciences  
Stony Brook NY 11794

**Grant:** DE-FG02-96ER14633

### Complexities Affecting the Rate and Mechanism of Pyrite Oxidation: An Interdisciplinary Approach

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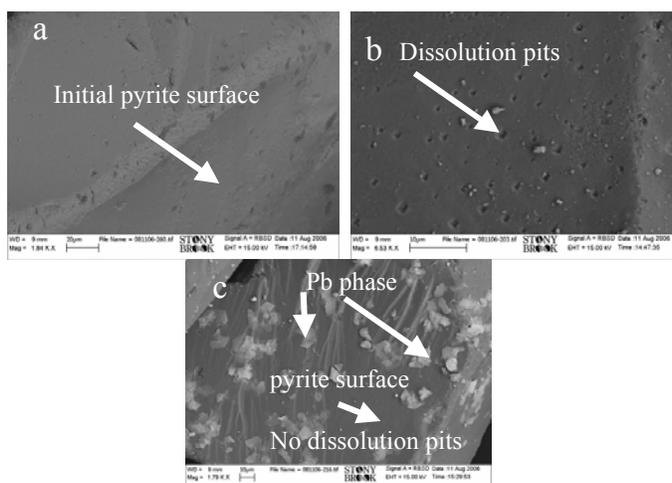
**Objectives:** The primary goal of this research program is to understand the microscopic aspects of pyrite oxidation. Our continuing research strategy is to understand macroscopic observations of pyrite reactivity with an atomic/molecular level view. The results of this research will lead to a better understanding how pyrite reacts in a range of chemical environments.

**Project Description:** The reactivity of pyrite in anoxic and oxic environments is being investigated by integrating aqueous geochemical and modern surface science techniques. An emphasis of the research is to develop *in-situ* techniques to study the mineral surface on a microscopic level in the presence of an aqueous or gaseous phase. The work at Stony Brook focuses on the effect of commingling of sulfides to evaluate if dissolution rates measured on monomineralic systems can be used to predict rates of dissolution in multi-mineral systems.

**Results:** Research progress in FY2007 at Stony Brook focused on pyrite oxidation when commingled with other common sulfides.

#### *Results of Commingling Experiments*

Mine waste and natural occurrences of pyrite often contain an assemblage of sulfide minerals, non-sulfide minerals, and organic material (e.g., coal). To address the influence of the complexity of the waste or natural material, we are investigating the interaction between coexisting sulfide minerals. Few studies have addressed the interaction and possible synergistic interplay that may occur as two or more sulfides are present in the same system. Our working hypothesis is twofold. (1) Hydrogen peroxide and hydroxyl radical formed in the oxidation of pyrite may accelerate the oxidation of other sulfides. (2) Electron transfer between pyrite and other metal sulfides (i.e., galvanic contact) will alter the oxidation rate of the two phases, when compared to the individual and electrically separated phases. Recent column flow-through experiments have shown that having galena (PbS) in contact with pyrite in



**Figure:** (a) initial pyrite surface; (b) pyrite after exposure to aqueous oxidizing conditions; (c) pyrite exposed to oxidizing conditions in the presence of galena. The presence of galena suppresses the oxidation of the pyrite surface.

an oxidizing aqueous environment, there is a significant reduction in the pyrite oxidation rate. Scanning electron microscopy (SEM) images show that when galena is present, the dissolution pits that characterize pyrite oxidization are reduced. The amount of Fe released into solution also is reduced under these same conditions consistent with the SEM observation. The galena, however, oxidizes readily (Pb secondary phases resulting from this process appear on the pyrite). Galena does not oxidize readily under these conditions if it appears alone. Hence, there is a synergistic effect when pyrite and galena are present together. Experiments with a range of pyrite-galena mixtures with and without an inert insulator material are underway to evaluate the necessity of electronic contact for this synergistic effect to occur. Understanding this process will have great implications on understanding the oxidation of sulfides in important environmental processes, such as acid mine drainage.

## STATE UNIVERSITY OF NEW YORK, STONY BROOK

Department of Geosciences  
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**Grant:** DE-FG02-99ER14996

### **Microscale Processes and Macroscopic Behavior of Porous Geomaterials**

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**Objectives:** This This project aims to provide a fundamental understanding of microscale basis for the macroscopic deformation and transport properties of porous geomaterials, using an integrated approach consisting of experimental rock mechanics testing, quantitative microscopy and statistical microgeometric characterization, and theoretical and numerical analyses.

**Project Description:** The microstructure of natural earth materials is extremely heterogeneous and complex. The underlying microscale characteristics that control deformation and transport processes are not understood quantitatively for natural earth materials such as soils, sandstones and chinks, and low-porosity crystalline rocks. Increased fundamental understanding of the microscale basis for the macroscopic response such as deformation behavior (and stability) under changing loading conditions (such as may be experienced in a subsurface geologic reservoir during CO<sub>2</sub> sequestration, or during production of hydrocarbons) is necessary. Likewise, an increased understanding of how the pore structure and its evolution with deformation affect fluid transport processes (during underground injection of greenhouses gases to mitigate climate change, or during primary and enhanced oil recovery) is required. Systematic experimental investigation provides a detailed understanding of the microstructure of porous earth materials and how those microscale characteristics affect the deformation and fluid transport properties at the macroscale. The laboratory data together with quantitative microscopy will be used to formulate and evaluate theoretical and numerical models of rock deformation and fluid flow.

**Results:** (1) Constitutive modeling of mechanical compaction and strain localization. In geomechanics the phenomenon of mechanical compaction is conventionally simulated using either the critical state or cap model, which have been incorporated into various numerical codes even though there have been limited constraints from a paucity of high-quality data. Synthesizing laboratory data we have mapped out the conditions under which some of the conventional models are valid and clarified the predictions on the inception of strain localization. We have also developed a new experimental methodology for mapping out the compactive yield envelope under undrained conditions, that allows one to characterize the initial yield envelope and its evolution with strain hardening, which otherwise would require numerous conventional triaxial tests to acquire. These results have now appeared in publication. In parallel we continue our comprehensive investigation of compaction in porous carbonate rock.

(2) Development of new experimental methodology and 3-D imaging technique to characterize the evolution of compaction and localization. Digital image correlation is a technique that is widely used in experimental mechanics to map out the spatial distribution of strain, but seldom in geomaterials. We have developed a technique whereby X-ray radiographs of undeformed and deformed samples can be used to delineate the spatial distribution of relatively small inelastic strain and to characterize the

influence of bedding on the development of strain localization. In principle imaging techniques we have developed can be implemented for computed synchrotron tomography. We have initiated the design of a rig for this purpose.

(3) Discrete element and probabilistic modeling of compactive failure and permeability evolution. We have used the discrete element modeling for analyzing the complex micromechanics of brittle failure and compaction localization in clastic rocks. In particular we focus on the influence of grain-scale pore heterogeneity. Our simulations highlight how discrete compaction bands are promoted by grain-scale homogeneity. These two studies have now appeared in publication.

## STATE UNIVERSITY OF NEW YORK, STONY BROOK

Department of Applied Mathematics and Statistics  
Stony Brook NY 11794

**Grant:** DE-FG02-05ER15635

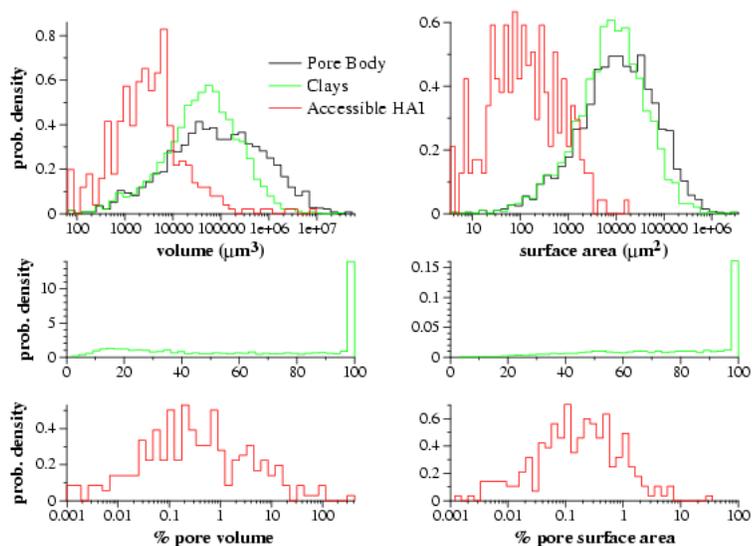
### Up-Scaling Geochemical Reaction Rates for CO<sub>2</sub> in Deep Saline Aquifers

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**Objective:** The goal of the project is to use a combination of experimentation and simulation to bridge the gap between our knowledge of small-scale geochemical reaction rates and reaction rates meaningful for modeling reactive transport at core scales. The focus is on CO<sub>2</sub>-water-rock interactions in the context of geological sequestration of carbon dioxide.

**Project Description:** This study focuses on reaction rate laws describing acid-driven mineral dissolution. The work combines (i) spectroscopic imaging and innovative image processing to characterize sedimentary rocks, (ii) development of new pore-scale network models of reactive transport in porous media, and (iii) simulations to examine reaction rate upscaling. Rock specimens come from the Viking Formation in the Alberta Sedimentary Basin, provided by the Alberta Geological Survey. Imaging methods include X-ray computed microtomography and subsequent analysis for 3D void space characterization. We also employ a combination of backscatter electron microscopy (BSE) and energy dispersive X-ray (EDX) spectroscopy for statistical characterization of reactive mineral patterns. One important goal of the spectroscopic imaging and interpretation is to characterize pore contact with individual minerals thereby quantifying meaningful surface areas for use in reactive transport models.

**Results:** Analysis (year one) of the void space of nine rock specimens provided a wealth of data on connectivity of pore networks as well as distributions of pore volumes, surface areas, and throat areas. All the specimens are sandstones of comparable porosity, and yet order of magnitude variation is found in pore properties across them. Furthermore, there is order of magnitude variation of pore properties within specimens. To characterize the mineralogy and its relation to pore space, we developed (year two) an innovative procedure which combines EDX spectroscopy and BSE imagery of 2D thin sections (see figure in 2006 Summary) to generate a single mineral map. The BSE/EDX method is accurate, but restrictive in that it generates only 2D maps. This year we explored using the CT images to extract a (coarser) 3D map which, when used in combination with the mineral identification from BSE/EDX, provides more rapid 3D information on mineral distribution.



**Fig. 1** CT-based analysis of 3D mineral distribution. Mineral identification was divided into sandstone, minerals having attenuation coefficient smaller than sandstone (Clays: largely kaolinite based on BSE/EDX studies) and minerals having attenuation coefficient larger than sandstone (HAI: apatite, plagioclase and pyrite). Left-hand plots measure accessible clays and HAI in comparison to pore volumes; right-hand plots indicate percentage of pore surface that is actually clay or HAI.

This year has been devoted to the development of reactive flow simulations in pore-network models based on the void-space and mineralogical characterizations of the Viking formation sandstones. Simulation conditions represent inflow of acidic CO<sub>2</sub>-rich brine under high-pressure conditions relevant to carbon geosequestration. These simulations are designed to examine pore-to-core up-scaling of reaction rates. Two unique features of these simulations are: flows within a sample of cores of formation sandstone whose pore network geometry has been accurately characterized; incorporation of accurate characterization of reactive mineral distribution in the network – in particular, characterization of reactive surface areas that are accessible and in-accessible for reactions.

The accurate characterization of the network geometry has enabled lattice Boltzmann (LB) modeling of single phase flow in individual pore-pore connections. Our work is also investigating the development of network flow models which replace the classic simplified geometry-based computations of pore-pore conductivities with more accurate conductivities based on LB computations.

We are also begun the development of a (two phase) network flow model which allows for the local formation and movement of CO<sub>2</sub> gas bubbles when pressures fall below critical values. Our immediate interest is in the modification of effective reaction rates with degree of bubble formation.

## UNIVERSITY OF NORTH TEXAS

Department of Chemistry

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**Contract:** DE-FG02-04ER15508

### **The Influence of Mineral Surfaces on Multi-electron Reduction Mechanisms for Polyvalent Metals**

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**Objectives:** To better understand electron transfer reactions between Fe(II) in silicates and sorbed polyvalent metals such as U(VI). To develop *ab initio* models for the XPS and XANES of transition metals and uranium in order to help elucidate information on oxidation states and bonding environments.

**Project Description:** This project concerns reactions between minerals and toxic metal-bearing aqueous fluids. Specifically, we are exploring the mechanisms of oxidation-reduction reactions at the mineral-fluid interface involving reductants structurally bound in minerals. Key techniques used are electron microscopy, x-ray photoemission spectroscopy, (XPS) and x-ray adsorption near edge structure (XANES). The project includes major theoretical efforts on the interpretation and prediction of XPS and XANES; the *ab initio* theoretical work is coupled to the experimental efforts.

**Results:** For the theoretical 4f XPS results for an embedded cluster model of  $\text{UO}_2$ , where the XPS is related to the materials chemistry, see the PNNL report by Eugene Ilton.

We have investigated the dependence of the multiplet splitting of the U 4f XPS on the occupation of the 5f shell. As shown in the figure that gives the 4f XPS for isolated U cations, the energy spacing of the multiplets is largest for U(V), where there are doublets for both main 4f peaks, and smallest for U(III). This result is counter intuitive since, using the usual models for ionic actinide systems, one expects the exchange splitting to increase with the number of unpaired 5f electrons; the opposite result is a due to the 5f spin-orbit splitting. It is possible that multiplet splitting may provide another way to distinguish different oxidation states of U. Further calculations, for embedded clusters, and higher resolution XPS, using synchrotron radiation, are planned to test this possibility.

The branching ratios of spin-orbit split X-Ray absorption peaks at core-level edges have been analyzed in terms of Russell-Saunders, RS, multiplets. This is a powerful method for understanding these ratios because there are strong selection rules for transitions between multiplets. Applications have been made for the  $\text{N}_{\text{IV,V}}$  XANES edge of  $\text{U}^{+6}$ , where j-j coupling dominates, for the  $\text{O}_{\text{IV,V}}$  edge of  $\text{U}^{+6}$ , where RS coupling dominates, and for the  $\text{L}_{\text{II,II}}$  edge of  $\text{V}^{+5}$ , where the coupling is mixed. The analysis predicts and explains the general features of the structure for these different couplings.

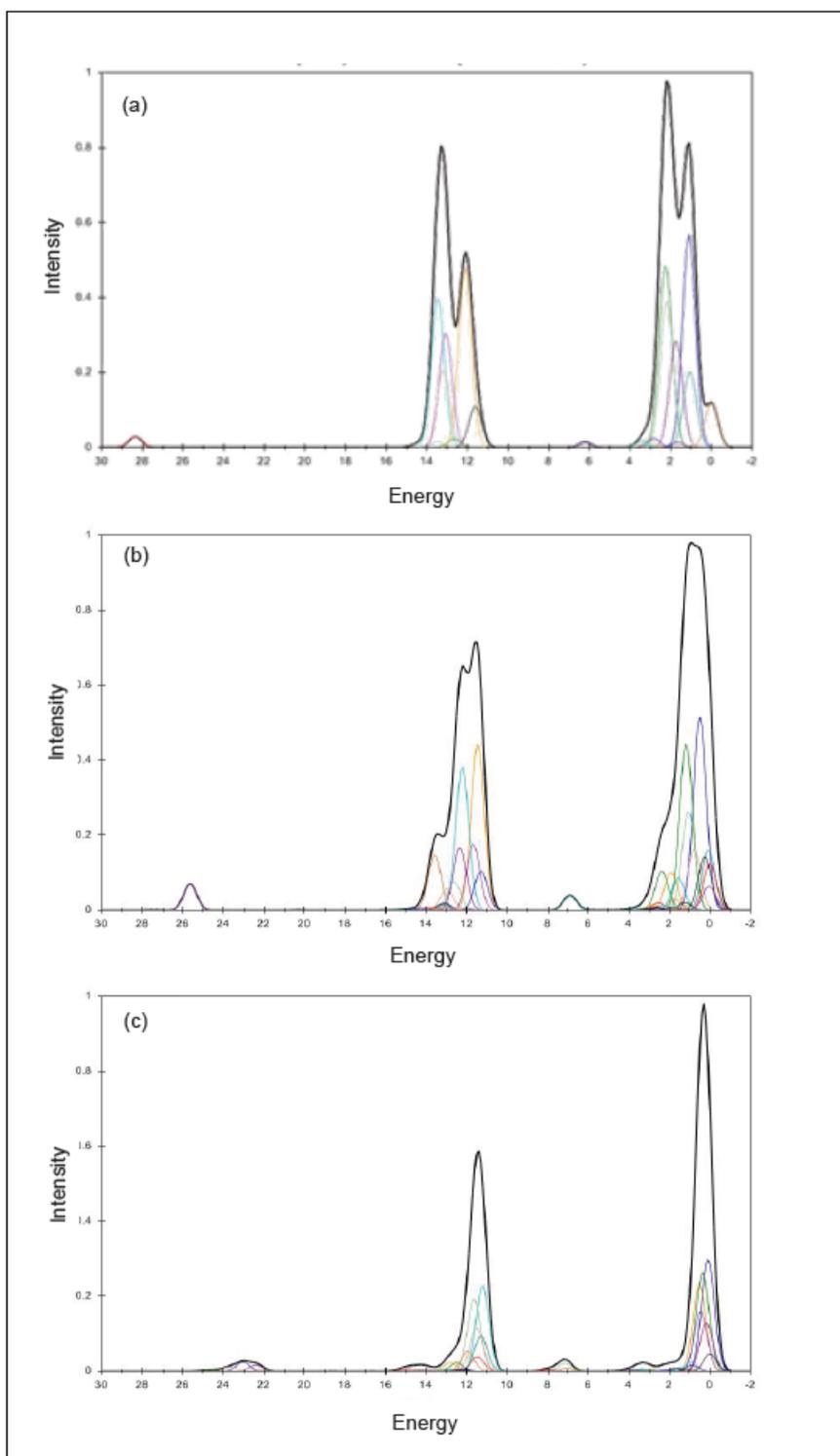


Figure. The theoretical 4f XPS of (a)  $U^{5+}$ , (b)  $U^{4+}$ , and (c)  $U^{5+}$  where the calculated XPS transitions are broadened by a Gaussian of 0.75 eV FWHM; broadening with smaller FWHM increases the differences between the various 5f occupations. Based on studies with embedded clusters, we expect the atomic differences to be present in condensed systems.

## **NORTHWESTERN UNIVERSITY**

Department of Civil and Environmental Engineering  
Evanston IL 60208

**Grant:** DE-FG02-93ER14344

### **Approaches to Some of the Outstanding Problems in the Heterogeneous Compactive Deformation of Geomaterials**

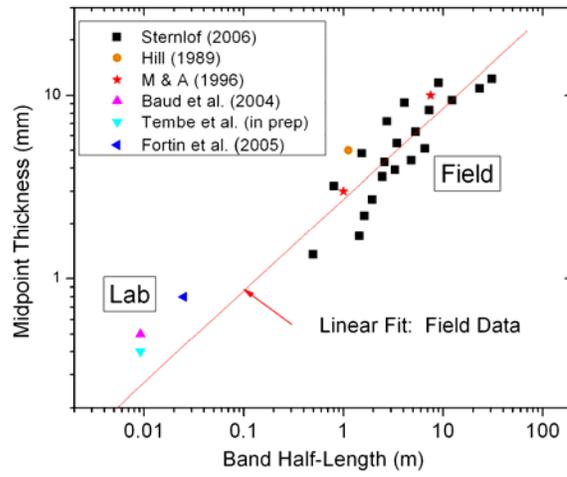
*J.W.Rudnicki, 847-491-3411; FAX 847-491-4011; [jwrudn@northwestern.edu](mailto:jwrudn@northwestern.edu)*

**Objectives:** To obtain an improved understanding of the factors governing the formation and extension of bands of localized compaction and their effect on subsurface fluid flow with applications to the technologically common problem of storing or recovering fluids from the earth's crust.

**Project Description:** Evidence from laboratory experiments and field observations on porous rocks (and other materials) has indicated that compaction does not necessarily occur homogeneously, but, instead, is localized in narrow planar zones that are perpendicular to the maximum compressive stress. Because the permeability of these zones is reduced by several orders of magnitude, they present barriers to fluid flow across them. Consequently, their formation in reservoirs or aquifers can adversely affect attempts to inject or withdraw fluids, such as carbon dioxide. Because the zones are narrow, they will be difficult to detect from the surface and, as a result, it is important to understand the conditions for their formation and extension.

**Results:** Recent work has focused on modeling extension of compaction bands to the tens meters observed in the field. A log-log plot of the field data (Figure 1) indicates that the midpoint width of the band scales as the half-length of the band to a power very nearly one-half. This dependence is consistent with that of a very thin elliptical inclusion subjected to uniform compactive displacement over the central portion of the band. If it is assumed that propagation of the band requires a critical value of energy released per unit area of advance then the compactive displacement is proportional to the square root of the length and the value of the constant of proportionality provides an estimate of the critical energy release rate. For values of Poisson's ratio and shear modulus representative of the field site, the energy release rate is about 30 kJ/m<sup>2</sup>, comparable to other estimates from the field (10 to 60 kJ/m<sup>2</sup>) and notched laboratory specimens (40 to 60 kJ/m<sup>2</sup>). The decrease of energy release rate with band length in this model suggests that the bands form with a release rate initially greater than the critical value and then grow until the release rate falls below that value.

Figure 1: Compaction Band Data



Linear Fit:  $y = A + Bx$

	$A$	$B$
Field Data	0.43240	0.49891

## NORTHWESTERN UNIVERSITY

Department of Chemistry  
2145 Sheridan Road  
Evanston IL 60208

**Grant:** DE-FG02-06ER15787

### **Surface Charge Densities and Acidities of Biogeochemically Important Organic Adlayers at Mineral/Water Interfaces Studied by Nonlinear Optics**

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**Website:** [http://chemgroups.northwestern.edu/geiger/new\\_page/GEIGER\\_LABS/Welcome.html](http://chemgroups.northwestern.edu/geiger/new_page/GEIGER_LABS/Welcome.html)

**Objectives:** We apply nonlinear optics to determine, with an unprecedented sensitivity and dynamic range, the interfacial pKa values, interfacial potentials and charge densities, and the energy densities of tailor-made biogeochemically important aqueous/solid interfaces in order to test and expand existing surface complexation models that are useful for assessing contaminant transport by computer-based pollutant transport modeling calculations.

**Project Description:** We are generating chemically diverse and geochemically important tailor-made organic adlayers at various mineral/water interfaces and spectroscopically characterize them using nonlinear optics. We determine their interfacial charge densities, interfacial potentials and energy densities with the goal of assessing their affinity towards ionic and neutral aqueous pollutants using second harmonic generation (SHG). Furthermore, we track changes in the molecular structure of the organic adlayers and in the absolute orientation of the interfacial water molecules both with SHG and broadband vibrational sum frequency generation while working at environmentally relevant pH, ionic strength and temperature. Our results improve surface complexation models and chemical transport models by incorporating heterogeneous parameters derived from interface-specific kinetic, thermodynamic, spectroscopic, and structural data.

**Results:** This year, we have shown that the interfacial acid-base chemistry of silica/water, alpha-alumina/water, and silica/amino acid/water interfaces tracks the bulk pH at low salt concentrations. However, ten to 100 mM salt concentrations however jam the interfacial acid-base chemistry for hours until the system finally cascades into a steady state within minutes. Given the environmentally and biologically relevant electrolyte concentrations and flow rates that promote this effect, the long time scales during which the systems stay jammed have direct implications for interfacial acid-base chemistry wherever surfaces and interfaces are routinely subjected to changing bulk solution pH conditions. The discovery of jammed acid-base chemistry at interfaces impacts many critical scientific areas, especially acid-base chemistry involving weathering, acid-base cycling, and heterogeneous contaminant transport processing in heterogeneous geochemical environments. We also used SHG to track the interaction of the environmentally important contaminants barium, strontium, and cadmium, chromate, oxytetracycline, and the nitrate anion with fused quartz/water and the (11bar02) alpha-Al<sub>2</sub>O<sub>3</sub>-water interfaces at various bulk pH values. Using a dynamic flow system, we assessed the extent of reversibility in the binding process and report the absolute number density of adsorbed cations, their charge densities, and their free energies of adsorption. We also present resonantly enhanced SHG

experiments that show that nitrate, oxytetracycline, and chromate are surface active and report the free energies and binding constants for the adsorption processes. The SHG spectrum of surface-bound nitrate shows a new adsorption band that cuts further into the solar spectrum than nitrate in the aqueous or solid state. The results that we obtain for all the ions and the implications for geochemistry are discussed in the context of fundamental science as well as pollutant transport models. Results from measurements regarding the charge state of the alpha-Al<sub>2</sub>O<sub>3</sub>-water interface as well as the chromium(VI) saturation surface coverages and the pH-dependence of the chromium(VI) equilibrium binding constants are also used to develop a thermodynamic and mass-balanced model that describes the interfacial interactions on the molecular level. Special attention is paid to the interfacial speciation state of chromium(VI) as a function of bulk solution pH. Scaling up, we estimate the mobility of chromium(VI) in alumina-rich soils by using the K<sub>d</sub> model. This work presents a significant advancement in our understanding of the molecular-level interactions between chromium(VI) and alpha-Al<sub>2</sub>O<sub>3</sub> and improves our ability to predict the environmental mobility, speciation, and ultimate fate of chromium(VI). Finally, we studied how organic adlayers control the binding of a more complex contaminant, namely the veterinary antibiotic oxytetracycline (OTC). Specifically, four environmentally relevant chemical moieties were covalently tethered to fused quartz surfaces using silane and amide coupling chemistry to survey how amides, polyfunctional binding sites, and phenyl rings that are common in humic acids control OTC binding at pH 8. The model geochemical surfaces prepared for this study were the following: methylamide-terminated fused quartz as well as amide-linked carboxylic acid-, benzoic acid-, and benzyl-terminated fused quartz. We found that amide-linked benzoic acid-terminated silanes display the highest equilibrium binding constant ( $1.1 \times 10^6 \text{ M}^{-1}$ ) among the systems surveyed. A straightforward predictive method of using contact angle measurements and the corresponding interfacial energy densities to predict OTC mobility across humic acid-containing mineral/water interfaces is discussed in the context of the emerging bacterial antibiotic resistance development threat.

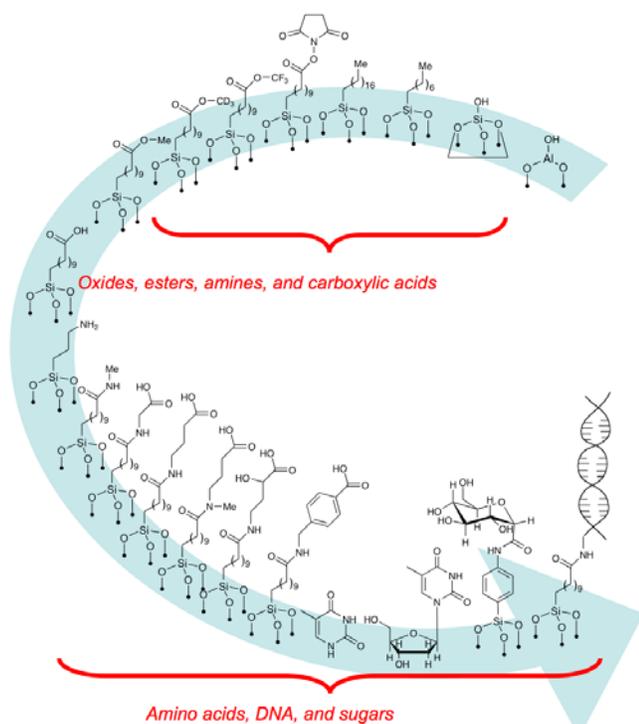


Figure 1. Geochemically important functional groups prepared, characterized, and studied under DOE-BES Grant #DE-FG02-06ER15787

## THE OHIO STATE UNIVERSITY

Department of Chemistry  
100 W. 18<sup>th</sup> Ave.  
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**Grant:** DE-FG02-04ER15495

### **Metal-Anion Pairing at Oxide/Water Interfaces: Theoretical and Experimental Investigations from the Nanoscale to the Macroscale**

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**Objectives:** The objectives of this research are to develop an approach for predicting the types of metal surface complexes that form on mineral surfaces by focusing on the role of metal-anion complexes, and to incorporate these surface complexes into thermodynamic surface complexation models to predict adsorption behavior.

**Project Description:** We combine the use of several techniques including bulk adsorption experiments, X-ray absorption, infra-red, and vibrational sum frequency spectroscopies (XAS, IR, VSFG), and molecular modeling to investigate ion-pairing in solution and at mineral surfaces. XAS provides data on how the metal binds to the surface (e.g., monodentate, bidentate), IR provides data on ion-pairing in aqueous solution, and VSFG provides data on the impact of adsorbed metal-anion pairs on water structure at the mineral surface. Molecular modeling will be used to guide spectroscopic data interpretation by providing information on water structure around ions in solution and the structure of metal-anion complexes in aqueous solution. In addition, molecular modeling can be used to provide insight into water structure at mineral surfaces, the surface sites involved in ion adsorption, and the distribution of ion pairs between aqueous solution and the mineral surface. Our studies have focused on systems involving alkaline earth metal ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ) and heavy metal ( $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ ) cations. The anions we have selected for study include  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{SeO}_3^{2-}$ . Ion adsorption and the potential formation of ternary complexes on silica (quartz, amorphous silica), alumina (corundum and gibbsite), and ferric iron (goethite) oxides are under investigation.

**Results (Allen Lab):** We have focused on investigations of nitrate systems in aqueous solutions and within the air-water interface using Raman and VSFG. Ion pairing in the bulk aqueous solution and at interfaces of aqueous  $\text{Mg}(\text{NO}_3)_2$  has been particularly interesting. Its bulk ion pairing properties are distinctly different from its interfacial properties. We have evidence of solvent-separated ion pairing in the interfacial region based on frequency shifts of the nitrate symmetric stretch mode. Below (Figure 1) we show VSFG spectra of aqueous  $\text{Mg}(\text{NO}_3)_2$  solutions with polarization ssp indicating the dramatic spectral change for two different concentrations of aqueous  $\text{Mg}(\text{NO}_3)_2$  within the air-water interface. This is indicative of an increase of forced ion pairing as the concentration is increased. This spectral change is not observed in bulk ion pairing studies and is unique to magnesium nitrate. Magnesium is forced to the interface, a region that  $\text{Mg}^{2+}$  does not prefer to be due to issues of solvation, more specifically, lack of solvation.

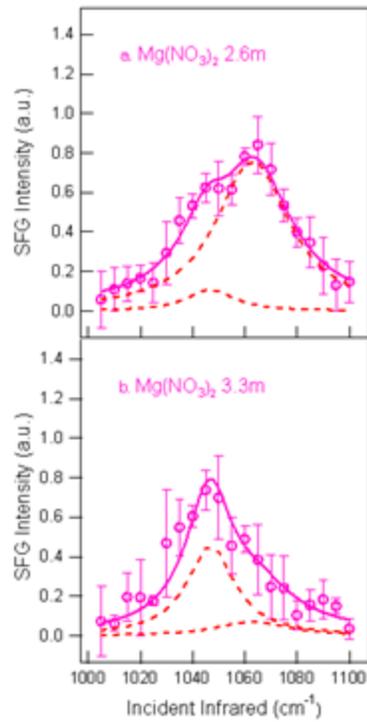


Figure 1: VSG spectra of aqueous Mg(NO<sub>3</sub>)<sub>2</sub> solutions with polarization ssp: a) 2.6 m Mg(NO<sub>3</sub>)<sub>2</sub>; b) 3.3 m Mg(NO<sub>3</sub>)<sub>2</sub>. Circles: experimental data with error bars; Solid lines: overall fits; dashed lines: Lorentzian component peaks.

## OREGON STATE UNIVERSITY

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**Grant:** DE-FG02-02ER15318

### **Efficient Inversion of Multi-Frequency and Multi-Source Electromagnetic Data**

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**Objectives:** The primary project objective is to develop more efficient inversion algorithms for electromagnetic (EM) geophysical data, taking advantage of some special features of inverse problems in which data are collected at multiple frequencies, or with multiple sources. A secondary objective is to develop a modular system for EM inversion, in order to (1) provide a test-bed for experimentation with new inversion algorithms; (2) to allow inversion schemes to be readily adapted for testing with different source/receiver configurations; and (3) to allow advances/modifications in other aspects of modeling or inversion methodology to be more rapidly incorporated.

**Project Description:** Electromagnetic (EM) geophysical data used for imaging the subsurface are commonly collected at multiple frequencies, or with multiple source geometries. As a result, inversion methods based on gradient based minimization of a penalty functional can be very costly in terms of computation. In particular, each forward solution (to evaluate data misfit) and each gradient calculation (to derive the next search direction) requires solution of one forward problem for each frequency/source (transmitter). We have been exploring hybrid schemes which combine features of an iterative conjugate gradients (CG) search scheme with a Gauss-Newton (GN) scheme, which traditionally requires computation of the full data sensitivity matrix. The key idea underlying our approach is that each search step in a CG type scheme implicitly generates data sensitivities (essentially columns of the Jacobian) for a series of linear data contrasts, one for each transmitter. If the coefficients of the data contrasts, and the corresponding data sensitivities are saved, a GN type scheme can then be used to solve the regularized inverse problem in a data subspace. This data subspace is always at least as large as the subspace implicit in a CG type search scheme, and potentially much larger, making the hybrid schemes potentially more efficient.

To more effectively explore these ideas we have developed a modular system for EM inversion. Our approach has been to focus first on a simple (two-dimensional magnetotelluric; MT) problem as a specific example, but to develop the code using an object oriented approach, independent of details of this specific problem. The top level of modules implements gradient calculations, and the specific inversion algorithms we are testing. These are implemented in an abstract way, to allow generalization to other problems. In parallel, modules have been developed for a general class of 3D EM inverse problems, with initial focus again on MT. One specific feature of the system is that the model parameter is treated as a purely abstract data type—i.e., objects which represent the unknown model parameter have only private attributes, which are not referenced by any of the modeling or inversion modules except through methods that are within the module. This programming approach greatly simplifies support of multiple model parameterizations, since we can guarantee that no modules depend on details of the model parameter representation, or its implementation. In particular, this will be useful

for implementing constraints, physically based model parameters (e.g., making resistivity a function of other physical parameters and inverting for these), and decoupling the solution grid from the model parameterization.

**Results:** During FY2007 we have made significant progress on developing the modular system for 3D EM inversion. Principal accomplishments during the project period include: (1) Development and refinement of Matlab inversion drivers, for prototyping and initial testing of new algorithms. These call F95 routines from the modular system for forward modeling and gradient computations. (2) Testing and comparison of a range of inversion algorithms including standard (NLCG, Occam, and DCG) and hybrid schemes on 2D MT problems. Results were presented at the IUGG meeting in Perugia, Italy (July, 2007). (3) More extensive tests of hybrid schemes were conducted. The scheme initially suggested, (Lanczos bi-diagonalization of the Jacobian, separately for each frequency, to generate (and save) a series of linear data contrasts and corresponding data sensitivities, followed by an Occam inversion in the data subspace) is very efficient for the early stages of the inversion. However, as data fit is pushed to actual error level, we have found the scheme to be overly sensitive to outliers in the data. Overcoming this shortcoming will be a focus of future work. (4) Development of the first 3D application has been nearly completed. This effort has required some refinement of the modular system, which now works with both 2D and 3D applications. (5) A first draft of a manuscript describing the modular system has been completed.

## PENNSYLVANIA STATE UNIVERSITY

Department of Geosciences  
University Park PA 16802

**Grant:** DE-FG02-05ER15675

### **Rate and Mechanism of Transformation of Bedrock into Saprolite During Spheroidal Weathering**

*Susan L. Brantley, [brantley@essc.psu.edu](mailto:brantley@essc.psu.edu), 814-865-1619; Mary Ann Bruns*

**Objectives:** We hypothesize that the rates and mechanisms describing the reactions that control the transformation of cohesive bedrock to disaggregated saprolite are determined by coupling between chemical, physical, and microbial processes driven by water and reactant fluxes into bedrock.

**Project description:** We are developing a model for water influx and reaction at the bedrock/saprolite interface and testing it on several rock types, including quartz diorite weathering in Puerto Rico. We are using geochemical mass balance methods, microbiological studies, and methods from fracture mechanics to develop a model to predict the rate of spheroidal weathering, and hence the rate of production of saprolite from intact bedrock in this setting. Because spheroidal weathering is a phenomenon that occurs on almost every rock type in almost every climatic regime, our model will be useful for bedrock systems globally.

**Results:** Work has been published on advanced 1-d models of reaction & transport without fracturing. The model captures the emergence of steady-state weathering profiles under a condition of constant rate of erosion. Both numerical and approximate analytical results have been obtained. Regimes of local-equilibrium, transitional, and kinetic-controlled behavior have been characterized.

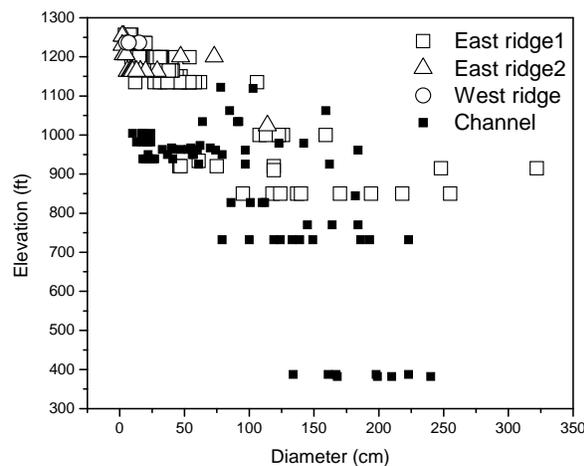
We have also developed and field-tested a weathering conveyor belt model which uses approximate first-order descriptions of weathering rate and chemistry within the weathering profile to study the evolution of a random distribution of initial joint-bound block sizes as these bedrock “particles” move upward through the weathering zone, eventually leaving exposed corestones at the erosional surface. This model is being tested against field data (Fig. 1). We have obtained initial results for the stresses generated due to reaction; these lead to a substantial elastic strain energy that drives cracking that defines spheroidal macro-fractures.

In weathering granite, the first visible reactions deepest within pristine rock are the dissolution of plagioclase and the oxidation of biotite. Microscopic and spectroscopic results reveal that hornblende does not dissolve or oxidize within the ~45-cm thick spheroidally weathered zone, but dissolves completely within the 7 cm spanning the rindlet-saprolite interface. The dissolution of hornblende was found to be the dominant contributor of aqueous iron to overlying saprolite and the source of Fe(II) for deep saprolite microorganisms. Oxidation of Fe(II) within biotite crystals in the rindlets was observed using optical microscopy and inferred from microprobe analysis, which showed a loss of  $K^+$  that increased with distance from the corestone. Biotite loses  $K^+$  ions from the interlayer to maintain charge balance during Fe(II) oxidation. The loss of interlayer  $K^+$  permits adsorption of water expanding the lattice, inferred to cause spheroidal fracturing. X-ray microprobe results documented Fe(III)-rich zones within individual biotite grains. XANES spectral fits demonstrated that the Fe(III)-rich zones are

oxidized biotite and not precipitated Fe(III)-(hydr)oxides or other Fe(III) phases. X-ray microprobe results also document decreased K content.

Biological iron oxidation has been shown to be coupled to the spheroidal weathering. As bedrock weathers, ferrous iron is released from silicate minerals, providing substrate for iron-oxidizing bacteria. In turn, autotrophic iron-oxidizing bacteria fix CO<sub>2</sub>, providing organic carbon substrate for other organisms in the ecosystem. At the base of the soil profile directly above the quartz diorite corestones, direct cell counts revealed that total microorganisms, including iron-oxidizing bacteria, increased in abundance relative to numbers in overlying mineral matrix. Confocal laser scanning microscopy (CLSM) images of saprolite demonstrate physical association between cells and amorphous minerals but not with quartz. Coupled SEM and XRD-microprobe analyses indicate that bacteria are associated with halloysite on grain surfaces. Iron-oxidizing bacteria closely related to *Acidithiobacillus ferrooxidans* have been cultured from the saprolite, and PCR primers have been developed for functional genes in the Fe-oxidation pathway. These primers will be used on DNA extracted from saprolite to indicate the presence of these genes in the community DNA.

To interpret microbial populations within the context of weathering reactions, we developed a model for estimating growth rates of lithoautotrophs and heterotrophs based on measured substrate fluxes. The calculations and observations are consistent with a model wherein electron donor flux driving bacterial growth at the saprolite-bedrock interface is dominated by Fe(II) and where autotrophic iron-oxidizing bacteria support the heterotrophic population and contribute to bedrock disaggregation and saprolite formation.



## PRINCETON UNIVERSITY

Department of Civil and Environmental Engineering  
Princeton NJ 08544

**Grant:** DE-FG02-05ER15636

### Up-Scaling Geochemical Reaction Rates for CO<sub>2</sub> in Deep Saline Aquifers

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**Objectives:** The goal of the project is to use a combination of experimentation and simulation to bridge the gap between our knowledge of small-scale geochemical reaction rates and reaction rates meaningful for modeling reactive transport at core scales. The focus is on CO<sub>2</sub>-water-rock interactions in the context of geological sequestration of carbon dioxide.

**Project Description:** This study focuses on reaction rate laws describing acid-driven mineral dissolution. The work combines (i) spectroscopic imaging and innovative image processing to characterize sedimentary rocks, (ii) development of new pore-scale network models of reactive transport in porous media, and (iii) simulations to examine reaction rate upscaling. Rock specimens come from the Viking Formation in the Alberta Sedimentary Basin, provided by the Alberta Geological Survey. Imaging methods include X-ray computed microtomography and subsequent analysis for 3D void space characterization. We also employ a combination of backscatter electron microscopy (BSE) and energy dispersive X-ray (EDX) spectroscopy for statistical characterization of reactive mineral patterns. One important goal of the spectroscopic imaging and interpretation is to characterize pore contact with individual minerals thereby quantifying meaningful surface areas for use in reactive transport models.

**Results:** The work at Princeton has two thrusts: 2D imaging to quantify accessible surface areas of reactive minerals in sandstones, and pore-scale network modeling of reactive transport related to CO<sub>2</sub> geological sequestration. In both thrust areas, and in the collaborative project as a whole, the sandstones used in imaging and as the basis for modeling come from the Viking Formation in the Alberta sedimentary basin.

During FY2007, we completed a pore-scale reactive transport model that is representative of the pore network structures in one of the selected Viking sandstones (3w4), based on microtomographic images and 3DMA interpretation from our partner, Brent Lindquist at SUNY Stony Brook. This extends our first-generation pore-scale network models which had rectangular lattice structures (Li, et al 2006, 2007, 2008). The model simulates acid-driven dissolution of anorthite with subsequent precipitation of kaolinite.

As with Li's work, the goal is to examine upscaling of kinetic reaction rates from the pore-scale to the core-scale. This is done by comparing reaction rates in the network model, which account for heterogeneity from pore-to-pore, to reaction rates in a continuum model of comparable core-scale properties. Figure 1 shows a sample simulation in which acidity accelerates the dissolution of anorthite, releasing Ca<sup>2+</sup> and Al<sup>3+</sup>. In the continuum model, the reaction rate is over-estimated. This implies that simple linear upscaling of reaction rates may lead to overestimation of the extent of reactions and underestimation of the time frame for important reactions such as carbon mineralization and pH

buffering. However, the extent of overestimation is extremely sensitive to the specified surface areas of reactive minerals.

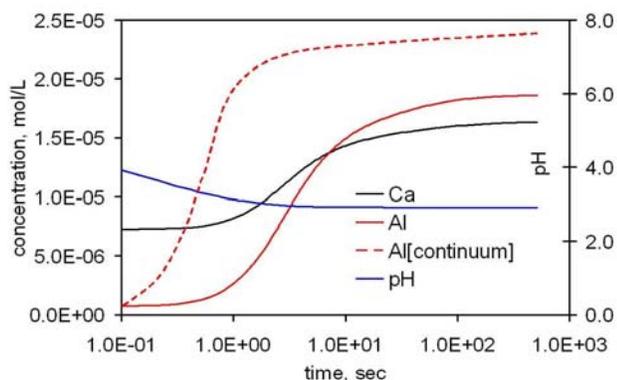
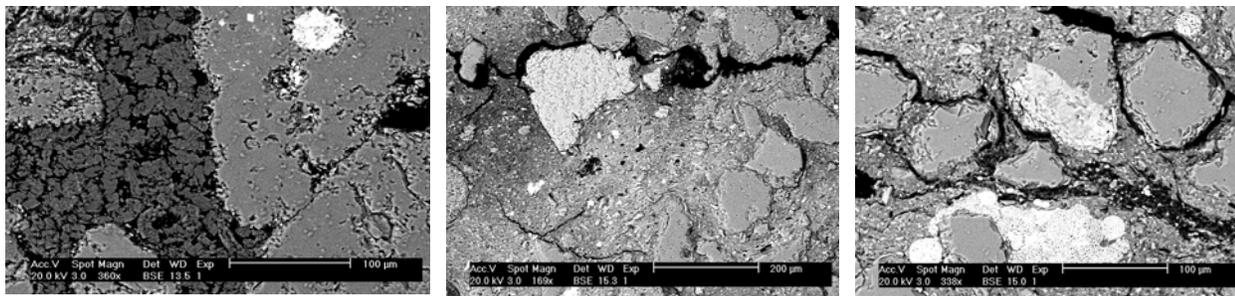


Fig 1: Representative evolution of pH and concentrations of Ca and Al as the network is flooded with CO<sub>2</sub>-rich brine.

The major challenge with reactive transport modeling in consolidated media is accurate characterization of surface area, and the apportionment of this surface area to reactive minerals. This issue now serves as the focus for our remaining work.

During FY2007, we have made substantial progress developing an algorithm for interpreting 2D images

of sandstone thin sections. The algorithm is novel in that it combines interpretation of backscatter electron (BSE) microscopy images and energy dispersive X-ray (EDX) spectroscopic elemental maps. The BSE images have the advantage of clearly resolving kaolinite and quartz, and the EDX images have the advantage of mineral identification. The combined processed image provides valuable information about mineral composition and the accessibility of minerals to pore fluids. A preliminary version of this image processing was shown in the FY 2006 summary. Ongoing collaboration with Brent Lindquist at SUNY Stony Brook is leading to a development of a 3D imaging technique that will lead to similar information.



A) BSE image of conglomerate sandstone showing pore-filling vermicular kaolinite. The large apatite inclusion in the quartz grain is inaccessible to pore fluids. B) BSE image of shaly sandstone. The light colored grain is K-feldspar, which would be reactive with acidic pore fluids. This grain, once inaccessible because of the cemented detrital matrix, is now accessible due to matrix fracturing adjacent to the grain. C) BSE image of shaly sandstone. The white deposit at the bottom of the image is framboidal pyrite, likely authigenic.

## PURDUE UNIVERSITY

Department of Physics  
West Lafayette IN 47907

**Grant:** DE-FG02-97ER14785

### **Self-Assembling Sub-Porosity: The Effect on Fluid Flow and Seismic Wave Propagation**

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**Objectives:** The objective of this proposal is to determine the effects of sub-porosity in a fracture on seismic wave propagation through fractured rock. The principal focus will be on experimentally determining the link between the frequency-dependent seismic properties of fractures and length scales associated with the presence, morphology and spatial distribution of a sub-porosity that affect the hydraulic properties of a fracture.

**Project Description:** To achieve the proposed research objectives we will determine the effect of micro-scale phenomena on macro-scale measurements of fluid-solid phase distribution and seismic wave propagation, and determine the relevant seismic attributes that indicate a sub-porosity within the fracture. Creation or destruction of sub-porosity within a fracture affects length scales associated with the geometry of the fractures. The size of the geometric length scales relative to the seismic wavelength determines the scattering response of the fracture. The spatial correlations in fracture geometry relative to the scale of the field-of-view affect the collection of the energy of scattered waves. An acoustic lens system was used to produce a pseudo-collimated wavefront with a controllable beam diameter to set the field of view to 5mm, 20 mm and 60 mm. This experimental approach was used on two limestone samples, each containing a single induced fracture, and an acrylic control sample. Fluid flow and seismic measurements were made on the fractured samples for the following conditions: water-saturated, after reactive flow and after grain/particle (microsphere) transport.

**Results:** Chemical and transport mechanisms performed on a fracture in rock alter the spatial and probability distributions of fracture specific stiffness through reactive flow, particle deposition and mechanical erosion. Seismic wave transmission across a fracture with probability distributions of fracture stiffness results in a predicted fracture specific stiffness that depends on frequency. The effect of spatial correlations in fracture stiffness on seismic wave transmission depends on the size of the region sampled (field-of-view) relative to the correlation length of the spatial distribution. Within the same region, competing scattering mechanisms are often present that affect interpretation of fracture specific stiffness. For example, Rayleigh scattering causes the stiffness to decrease with increasing frequency because the high frequency components of the signal are scattered out of the collecting field-of-view. But the portions of the fracture that respond as a displacement discontinuity cause the fracture specific stiffness to increase with increasing frequency. The laboratory data indicate that (1) frequency independent stiffness is not sufficient to indicate a homogeneous fracture geometry; (2) competing attenuation mechanisms or scattering effects can be separated by making measurements at different

scales (i.e., field-of-view); and (3) a total of 21 measurements over three scales enabled us to unravel the competing effects of spatial distributions and probability distributions.

## RENSSELAER POLYTECHNIC INSTITUTE

Department of Earth and Environmental Sciences  
Troy, NY 12180

**Grant:** DE-FG02-94ER14432

### **Properties of Interfaces in Fluid-Bearing and Fluid-Absent Rocks**

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**Objective:** To further advance our understanding of mass transport in deep seated regions of the Earth through experimental investigations of diffusion along grain boundaries in polyphase rocks.

**Project Description:** Over the past several years we have examined how interfacial energetics govern the grain-scale distribution of fluids in rocks that affects bulk rock properties such as permeability. Our research showed that the wetting properties of fluids are dependent upon fluid fraction and degree of faceting of the constituent minerals. It was also shown that the anisotropy of grain boundary energies for quartzose rocks is relatively small and does not likely play a major role in controlling long range fluid distribution in equilibrated rocks.

In the final phase of this study we turned our attention to the mobilization and transport of elements along dry grain boundaries. Natural examples of apparent grain boundary control of bulk-rock transport are found in zoning profiles in garnets and other phases, in metamorphic textures, and in size distributions of porphyroblasts and accessory phases. Many crustal and mantle rocks contain minor or accessory minerals that are enriched in components that are incompatible in the minerals that dominate the rock matrix. From a purely geometrical standpoint, it would appear necessary for isolated minor grains to ‘communicate’ with one another by chemical exchange through the grain boundaries in order for their compositions to adjust to changing P-T conditions. In a fluid-absent rock, transport of elements must occur by diffusion along pathways composed of dry grain boundaries and grain edges.

During the past year we developed new experimental and analytical methods that allow us to quantify atomic migrations along dry grain boundaries in rocks. Rock analogs were synthesized so that they contained minor ‘sink’ phases dispersed throughout a matrix dominated by minerals that do not incorporate elements that are compatible in the ‘sink’ phase. After synthesis of the rock analog, a diffusant that is compatible in the ‘sink’ phase was added to the experimental system, and diffusion experiments were conducted at high temperature and pressure conditions. Grain boundary diffusion was monitored by measuring the uptake of the diffusant in the ‘sink’ phases.

**Results:** To address Fe-Mg interdiffusion along dry grain boundaries in crustal rocks, a pre-synthesized quartzite containing ~5% dispersed fayalite ( $\text{Fe}_2\text{SiO}_4$ ) was juxtaposed against an MgO source at 1150°C and 1.4 GPa (Fig. 1a). During the experiments Mg diffused along the dry quartz grain boundaries to the isolated fayalite crystals that acted as the sink phase in this experiment. Substantial Fe-Mg interdiffusion occurred during the experiment as evidenced by Mg uptake in fayalite crystals several hundreds of microns from the MgO/quartzite interface (Fig. 1b), suggesting a very high grain-boundary diffusivity. The importance of this result is that it strongly indicates efficient transport of Fe and Mg through grain boundaries or edges of a mineral (in this case quartz) that is nominally free of these elements. To address grain boundary diffusion in mantle analogs, similar experiments were conducted

in which a Ca-bearing source (diopside + olivine) was juxtaposed against a harzburgite rock analog (olivine + orthopyroxene) at 1350°C and 1.4 GPa, setting up strong calcium chemical potential gradients (Fig. 1c). During the experiment, Ca diffused from the diopside-rich source along the dry olivine grain boundaries and was incorporated into the orthopyroxene sink phase of the harzburgite (Fig. 1d). These results demonstrate that dry grain boundaries can serve as ‘super highways’ for transport of elements that are essentially insoluble in crystal lattices of the dominant minerals that comprise a rock.

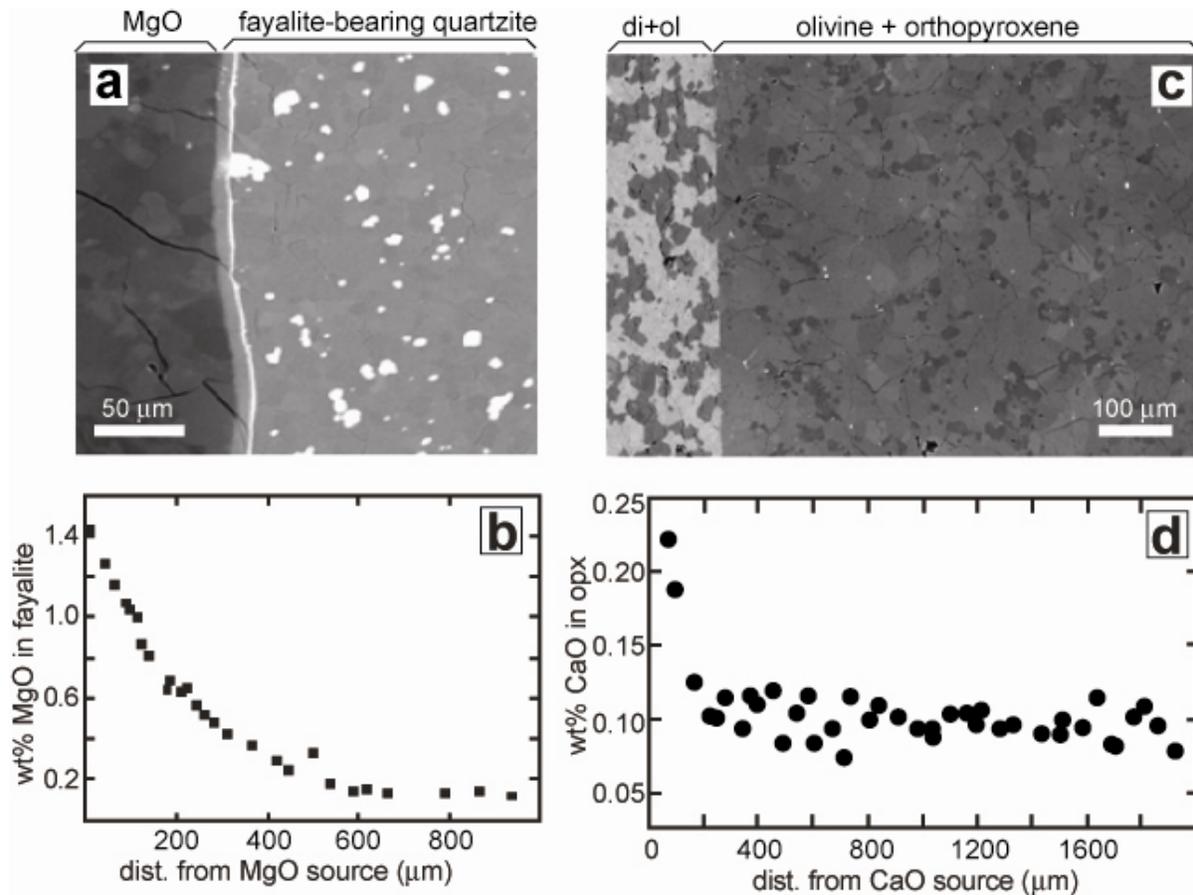


Figure 1. (a) Backscattered electron image of a diffusion couple in which MgO was juxtaposed against a synthetic fayalite-bearing quartzite (bright phase is fayalite). (b) MgO contents of isolated fayalite grains in quartzite as a function of distance from the quartzite/MgO interface. (c) Backscattered electron image of a diffusion couple in which a Ca-rich source (diopside + olivine; bright phase is diopside) was juxtaposed against a synthetic harzburgite sample (olivine + orthopyroxene). (d) CaO contents of orthopyroxene grains plotted against distance from the Ca-rich source. MgO and CaO contents measured with an electron microprobe.

## UNIVERSITY OF SOUTH CAROLINA

Department of Geological Sciences  
Columbia SC 29208

**Grant:** DE-FG02-04ER15515

### **Understanding Long-Term Solute Transport in Sedimentary Basins: Simulating Brine Migration in the Alberta Basin, Canada**

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**Objectives:** This project is designed to determine mass transport rates in a resource-rich sedimentary basin where previous geochemical and hydrogeologic estimates of fluid residence time have contrasted sharply. We hypothesize that previous hydrogeologic studies overestimated the rate of brine flushing by overestimating sediment permeabilities or by neglecting compaction-driven flow.

**Project Description:** Mass transport in deep sedimentary basins strongly affects CO<sub>2</sub> sequestration, ore formation, petroleum migration, and geochemical reactions that affect petroleum reservoir quality, but mass transport in sedimentary basins is not well quantified. This lack of knowledge is highlighted in the resource-rich Alberta Basin, where geochemical studies estimate the residence time of brines in this basin to be hundreds of millions of years, but past hydrogeologic models have predicted that these brines could be flushed out less than 5 My. This project was designed to reconcile these two very different estimates through the use of new hydrogeologic models that account for variable-density fluid flow, heat transport, solute transport, dissolution of salt deposits, and sediment compaction. Including brine migration and such geochemical tracers as oxygen isotopes and Cl/Br ratios will allow these models to be calibrated to a significantly greater body of data than previous models.

**Results:** The computer code COMPACT was modified to account for sediment decompaction during erosion and dissolution of salt deposits. The addition of Br as a tracer was begun, and final code testing and benchmarking was initiated. Preliminary models of Alberta Basin evolution from 100 Ma to the present suggest that sediment compaction can generate a pulse of brines from the deep basin that travels updip along permeable units. Significantly, simulations using permeability values published in previous hydrogeologic modeling studies allowed significant dissolution of evaporites, which contrasts with field observations. Simulations in which permeabilities were reduced below those of previous studies retained more brine, although fluid velocities were then reduced to levels that may not be consistent with geochemical indicators of large-scale mass transport. Additional simulations suggest that compaction-driven flow and compressible beds can affect brine residence time even when permeability remains relatively high.

## STANFORD UNIVERSITY

Department of Civil and Environmental Engineering  
Stanford CA 94305

Grant: DE-FG02-03ER15454

### Framework for Constitutive Branching in Porous Rocks Undergoing Brittle Faulting and Cataclastic Flow

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**Objectives:** This project investigates and develops numerical models to capture two types of instability in rocks, namely, brittle faulting and cataclastic flow. Brittle faulting is a form of strain localization whereas cataclastic flow is associated with pore collapse instability.

**Project Description:** Porous rocks can fail either by shear strain localization or cataclastic flow. Shear localization results from the coalescence of microcracks leading to a tabular deformation band, whereas cataclastic flow is characterized by grain crushing and pore collapse resulting in a severely damaged but macroscopically homogeneous compacted continuum. We view the two types of instability as arising from two distinct bifurcation modes. The first mode, predicted from the singularity of the acoustic tensor, produces a strain rate jump tensor of determinant rank one and defines a deformation band. The second mode, predicted from the singularity of the tangent constitutive operator, is diffuse and produces a full-rank strain rate jump tensor. After identifying the relevant bifurcation mode, we develop a framework for capturing post-failure responses through constitutive branching. The post-collapse constitutive response features a cohesion softening-friction hardening applied either to an emerging fault for brittle faulting or to the bulk constitutive theory for cataclastic flow.

**Results:** Numerical simulations conducted during Year 1 have focused on capturing brittle faulting using two enhanced finite element techniques: the assumed enhanced strain and extended finite element methods. In the first method, slip is interpolated as a piecewise constant function, whereas in the second method, slip is interpolated linearly. The finite element equations for both techniques allow the balance of linear momentum to be written in standard residual form and solved using a full Newton-Raphson iteration. Both methods allow the discontinuity (crack, fault, fracture) to trace its own course, generally passing through the interior of the finite elements and breaking them into two separate pieces. Figure 1 below shows images of a simulated frictional crack generated by the extended finite element method. The crack crosses through the interior of the finite elements and chooses its own propagation direction.

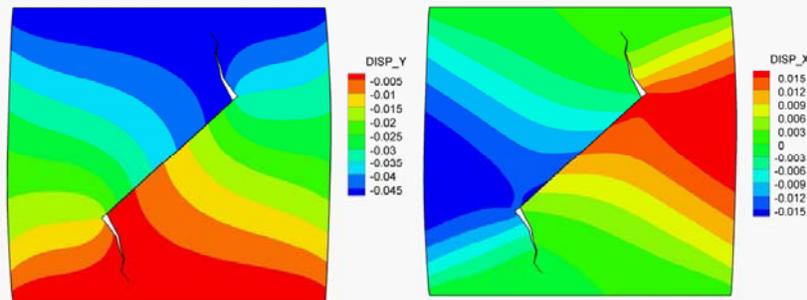


Figure 1. Contours of vertical and horizontal displacements on a frictional body compressed vertically, causing the crack tips to propagate.

## STANFORD UNIVERSITY

Department of Geophysics  
Stanford CA 94305

**Grant:** DE-FG02-03ER15382

### Geochemical Controls on Nuclear Magnetic Resonance Measurements

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**Objectives:** The objective of our research is to advance the fundamental understanding of the link between the nuclear magnetic resonance (NMR) response and geochemical properties of geological materials.

**Project Description:** Proton NMR has the potential to provide a wealth of information about the physical, chemical, and biological properties of geological materials. While it is well established that the presence of iron is a dominant factor in determining the NMR response of rocks and soils, we lack an understanding of how the specific mineralogic form and distribution of iron affects NMR relaxation mechanisms. In addition, the current models of NMR relaxation in porous materials greatly oversimplify both the geometry of the pore system and the related interaction between the water protons and the paramagnetic iron. We are currently conducting a laboratory-based study of NMR relaxation measurements in water-saturated porous materials in which sample composition, pore structure and geochemical conditions are carefully controlled and determined.

**Results:** The NMR parameter of interest in our research is the NMR time constant,  $T_2$ . The NMR time constant is affected by three mechanisms acting in parallel: bulk fluid relaxation, surface relaxation, and diffusion relaxation. In FY 2007 we focused on understanding the effect of the presence of magnetite, an iron mineral, on  $T_2$  and determining the dominant relaxation mechanism by which relaxation occurs in the presence of magnetite. The effect of magnetite was studied by taking NMR measurements of water-saturated magnetite and quartz mixtures. Additionally, numerical simulations were designed to model NMR relaxation in the presence of magnetite.

We measured  $T_2$  of water-saturated magnetite and quartz mixtures with varying magnetite grain sizes and concentrations. Our results show that NMR relaxation times are strongly influenced by both the concentration and grain size of magnetite. The dominant relaxation mechanism in the presence of magnetite appeared to be surface relaxation for all but the highest concentration of the smallest grain; in this sample diffusion relaxation was the dominant relaxation mechanism.

The numerical simulations of NMR relaxation behavior were designed using a random walk algorithm. The simulations will address the relationship between the pore-scale distribution of magnetite and  $T_2$ . By varying parameters affecting relaxation such as grain size, and magnetite concentration, the results from the simulations will help us to gain a theoretical understanding of how the specific mechanisms affect the relaxation measurements allowing for more accurate interpretations of NMR data.

## STANFORD UNIVERSITY

Department of Geophysics  
Stanford CA 94305

**Grant:** DE-FG02-03ER15423

### **Porous Rock with Fluid: Impact of Heterogeneity on Reservoir Transport and Elastic Properties and Application to Unconventional Pore-Filling Materials**

*Amos Nur, (650) 723-9526, [Amos.Nur@stanford.edu](mailto:Amos.Nur@stanford.edu)*

**Objectives:** As the need for much higher accuracy of seismic interpretation, reservoir and aquifer characterization, and reservoir and aquifer simulations massive rock property data sets are becoming much more important than ever before. To achieve such massive data sets we are developing a computational – as opposed to laboratory – rock physics methodology. Ultimately this technology should be able to replace most routine and special core analysis as practiced today. Applications of this methodology is focused on the characterization and simulation of methane hydrate deposits, heavy oil sands, and the sequestration of CO<sub>2</sub> in porous rock system under *in situ* conditions.

**Project Description:** Our methodology consists of (a) obtaining very high resolution and very fast 2D and 3D images of the pore spaces in cores, plugs, or cuttings; (b) use the images to accurately obtain bulk properties very fast using an array of innovative computational codes. *Properties* obtained include porosity, permeability, capillary pressure, relative perm, electrical conductivity, strength, elastic constants, seismic velocities, grain and pore size distributions, and NMR response. Rock types include sands, carbonates, heavy oil/tar sands, tight gas sands, gas hydrates and shales. Samples can be cores, plugs, and cuttings. From the images we also computationally simulate complex pore scale *processes* such as hydrate formation and breakdown, production of heavy oil sands including compaction, sequestration of CO<sub>2</sub> under *in situ* conditions, diagenetic processes, and chemical reactions in the pore space. We also attempt to use this methodology to rigorously link well logs with rock properties, and use well logs to interpret seismic away from the borehole.

**Results:** *Methane hydrates.* We find that in sediments containing methane hydrates seismic or resistivity data, when analyzed separately, cannot provide a unique estimate of the concentration of hydrates in place. However the combination of two rock property models – one that relates elastic-wave velocity to porosity, mineralogy, and pore fluid, and a second that relates electrical resistivity to porosity and saturation – allows us to obtain both porosity and hydrate saturation of the host rock. The results show that the same joint data analysis can also be applied to oil and gas reservoirs. We find also that this concept is amenable to up-scaling so that it can be used to a joint interpretation of seismic and magneto-telluric field measurements. We demonstrate this by jointly analyzing seismic and CSEM data for the Nugget gas field. The approach can be used to include other effects such as diagenetic cementation and dissolution, depositional sorting or the presence of shales.

*Heavy Oil Sands.* The experimental determination of the permeability of oil and tar sands has remained an impossible challenge because of the unconsolidated nature of these materials. With our imaging and computing methodology we were able to obtain remarkably accurate values of permeability as well as porosity, relative permeability, and also simulate the compaction behavior as oil is being removed and

water or steam are introduced under pressure. We show also how permeability, porosity and mechanical properties change upon changes in the amount, temperature and pressure of pore fluids in the pore spaces of these materials.

*CO<sub>2</sub> sequestration.* We have set up the codes needed to simulate the long-term diagenetic changes (e.g., chemical dissolution and precipitation) that would take place in reservoir rocks as a reactive CO<sub>2</sub> phase is introduced in the presence of brine. These codes will help estimate the long-term retention of sequestered CO<sub>2</sub> in the earth's crust.

## STANFORD UNIVERSITY

Department of Geological and Environmental Sciences  
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**Grant:** DE-FG02-04ER15588

### Structural Heterogeneities and Paleo-Fluid Flow in an Analog Sandstone Reservoir

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**Website:** <http://pangea.stanford.edu/geomech/index.html>

**Objectives:** We are developing conceptual and quantitative mechanical models and predictive tools for understanding the spatial distribution of permeability in subsurface sandstone aquifers and reservoirs as determined by structural heterogeneities including faults, joints, sheared joints, shear deformation bands, and compactive deformation bands. Our ultimate objectives are (1) to characterize and analyze the initiation and growth of these structures and (2) to evaluate their impact on fluid flow.

**Project Description:** We are conducting a broad-based research project to map and characterize structural heterogeneities in the Jurassic Aztec Sandstone exposed at the Valley of Fire State Park, Nevada, as an analog for active hydrocarbon reservoirs and groundwater aquifers. Our research comprises three complementary sub-projects: (1) characterization and realistic representation of splay fractures around faults, (2) fault damage zone and their geometric, structural and statistical properties (3) understanding the formation of compaction bands and their impact on fluid flow. The project combining detailed field and petrographic observation, process-based mechanical modeling, and numerical simulation of fluid flow serves to illuminate how a complex suite of brittle structures form and affect fluid flow in a typical sandstone aquifer/reservoir at a variety of length scales.

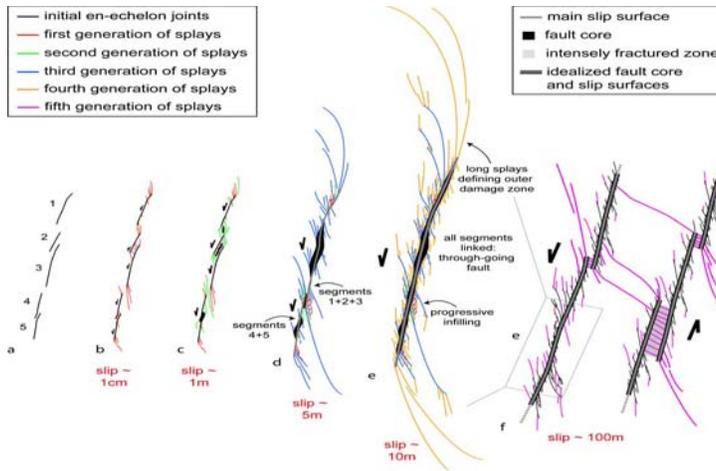
#### **Results: (1) Characterization of fault structure, linkage and fluid-flow effects**

We concluded our study of the geometrical and statistical characterization of faults and fault networks and focused on writing the results as journal papers with the highlights listed below:

(1) The length and angular relationships between strike-slip faults and their splays indicate that the maximum splay length is correlated to the fault length by a power law but shows little correlation with the fault slip magnitude. The kink angle between faults and their splays is small for isolated faults (average 20°) and systematically larger for mechanically interacting faults (average 50°). Analytical models predict that splay length decreases with increasing confinement under biaxial compression. 2D numerical models of isolated faults show that small kink angles correspond to small values of the angle between the fault and the maximum compression ( $\beta$ ) whereas large kink angles require greater  $\beta$  values. Similar models of interacting faults confirm the critical role of  $\beta$  on the kink angles and suggest that fault overlap and fault separation can also induce important variations in the kink angles. These results provide a basis for a better understanding of fault segment linkage via splaying process and may also help to predict the length and orientation of secondary faults formed by splaying associated with first order faults with resolvable slip magnitude in the subsurface.

(2) With increasing slip along faults, their damage zone evolves by progressive fracture infilling and is organized into two components with different characteristics. The first of these components is the inner

damage zone flanking the fault core with a high fracture frequency and a thickness scaling with fault slip. The second of these components is the outer damage zone with a larger and more variable thickness and a lower fracture frequency than the inner zone. The origin and evolution of the inner and outer damage zones are closely related to the history of fault growth by segment linkage, as presented in a



new conceptual model for damage zone evolution (see Figure 1). We characterized the statistical properties of the fault networks by scan line surveys. Well developed fault networks have multifractal properties with important consequences in forecasting and characterizing faults from limited data sets. The conceptual model and statistical data presented here may be used as predictive tools to better estimate the geometrical and statistical properties of the damage zones associated with large faults in the subsurface.

Figure 1. Conceptual model for fault damage zone evolution

## (2) Mechanical models of faults and damage zone structures

Inelastic deformation of brittle rock loaded in compression at the meter to kilometer scale typically involves localized frictional sliding along preexisting weak interfaces that are oblique to the principal stress directions. Associated local stress concentrations can produce secondary opening fractures in the fault damage zone that emanate from the sides of faults as wing cracks (see Figure 1). The formation of wing cracks is closely related to important geological phenomena such as: propagation of shear fractures, fault coalescence and longitudinal growth, the formation of fault damage zones, exfoliation and splitting, fracture propagation across bedding planes, and fluid flow channeling.

The 2D Displacement Discontinuity Method (DDM) is combined with a complementarity algorithm to model the quasi-static formation and patterns of wing cracks that emanate from regions of stress concentration along a sliding frictional flaw in an otherwise homogeneous and isotropic elastic material. Because stress states and geometry change with sliding on the flaw and wing crack propagation, one can not specify the boundary conditions a priori. Under these circumstances complementarity is superior to other well-known contact algorithms because it increases accuracy, enforces the contact constraints strictly, avoids user-defined parameters, reduces the computational time significantly, and significantly improves convergence.

We focus on meter scale phenomena where mineralogical heterogeneity (common to centimeter-scale laboratory samples) and 3D geometry (common to kilometer-scale structures) reasonably can be ignored. Analytical solutions to the elastic boundary value problem of the closed sliding flaw include those that assume no friction, uniform friction, and a cohesive end zone (CEZ), and those that assume infinitesimal or straight wing cracks. We generalize the problem to consider linearly varying friction in the CEZ and curved wing cracks, and we allow the sliding flaw to open when mechanical interaction with the wing crack dictates that it should. Trace lengths of 135 strike-slip faults in sandstone are linearly related to wing crack lengths ranging from 0.16 to 72 m and correspond to a range of remote principal stress ratios from 0.06 to 0.2. Opening displacement profiles of wing cracks from the numerical model can be significantly different from analytical solutions. These solutions may produce significant errors in stable crack length for curved propagation paths. The smeared out stress

concentration in the CEZ and the heterogeneity in strength of rock suggest that multiple wing cracks may form in one slip event. The mechanical interactions of these cracks leads to kink angles that increase with distance from the flaw tip, a relationship commonly observed in nature.

## TEMPLE UNIVERSITY

Department of Chemistry  
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**Grant:** DE-FG02-96ER14644

### **Complexities Affecting the Rate and Mechanism of Pyrite Oxidation: An Interdisciplinary Approach**

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**Objectives:** The primary goal of this research program is to understand the microscopic aspects of pyrite oxidation. Our continuing research strategy is to understand macroscopic observations of pyrite reactivity with an atomic/molecular level view. The results of this research will lead to a better understanding how pyrite reacts in a range of chemical environments.

**Project Description:** The reactivity of pyrite in anoxic and oxic environments is being investigated by integrating aqueous geochemical and modern surface science techniques. An emphasis of the research is to develop *in-situ* techniques to study the mineral surface on a microscopic level in the presence of an aqueous or gaseous phase.

**Results:** Research progress in FY2007 at Temple was into two areas: (A) Probe microscopy and batch reaction experiments that have studied the effect of bacteria (those common to AMD environments) on pyrite with and without adsorbed phosphocholine lipid; and (B) spectroscopic studies of vaesite in the abiotic environment.

#### *Suppression of Pyrite Oxidation under Biotic Conditions*

Research has continued to address the solution of a significant environmental problem referred to as acid mine drainage (AMD), resulting from the oxidation of metal-sulfides, primarily pyrite. This environmental impact includes acidification of rivers and streams as well as leaching of toxic metals from the metal-sulfide material. Prior research from our laboratory has shown that the adsorption of two-tail lipids of phosphocholine lipids, such as L- $\alpha$ -Phosphatidylcholine, Hydrogenated lipid and 1,2-bis(10,12-tricosadiynoyl)-*sn*-Glycero-3-Phosphocholine on pyrite resulted in a marked decrease in oxidation rate. Results from recent biotic-based experiments show that the effects of both autotrophic and heterotrophic bacteria on pyrite oxidation are suppressed.

#### *Vibrational Spectroscopic Study of the Oxidation of Pyrite and Vaesite in Oxidizing Gaseous and Aqueous Environments*

The reaction of FeS<sub>2</sub> (pyrite) and NiS<sub>2</sub> (vaesite) gaseous and aqueous oxidizing condition was investigated using Horizontal Attenuated Total Reflection Fourier-Transform Infrared spectroscopy (HATR-FTIR). Vaesite adopts the pyrite structure and a comparison of the oxidation mechanism and reactivity of these isostructural minerals is allowing us to develop a relationship between reactivity and disulfide electronic structure. Recent results have compared the surface speciation of pyrite and vaesite with FTIR and also the oxidation rates of the minerals. Differences in the influence of defects

(dominated by the presence of Fe<sup>III</sup> on pyrite) and in electrical conductivity are being investigated as reasons for these differences.

## TEXAS A&M UNIVERSITY

Texas Engineering Experiment Station  
College Station TX

**Grant:** DE-FG02-06ER15816

### **Kinetics and Mechanisms of Calcite Reactions with Saline Water**

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**Objectives:** The general objective of this research is to determine the kinetics and mechanisms of calcite reactions with saline waters over a wide range of saline water composition, carbon dioxide partial pressure ( $p\text{CO}_2$ ), and modest ranges of T and P. This will be done by studying both reaction rates and solubility from changes in solution chemistry. Also, nanoscale observations of calcite surface morphology and composition will be made to provide an understanding of rate controlling mechanisms.

**Project Description:** The objectives will be accomplished by studying both reaction rates and solubility from changes in solution chemistry, and making nanoscale observations of calcite surface morphology and composition to provide an understanding of controlling surface mechanisms. The specific tasks necessary to reach the objectives are:

- a) improvement of our Pitzer equation-based ability to deal precisely with the carbonic acid system in complex high ionic strength solutions and at high  $p\text{CO}_2$ ;
- b) determination of how  $p\text{CO}_2$ ,  $\text{Ca}^{2+}$ , ionic strength and “foreign” ions influence reaction rates;
- c) measurement of distribution coefficients of the common saline water components as a function of solution composition, precipitation rate and temperature, as well as their influence on calcite stability; and
- d) investigation of the influence of the parameters in “b” on apparent kinetic solubility from dissolution and precipitation reactions to determine if the apparent solubility differs when approached from super and under saturation.

This knowledge is needed to predict the geochemistry of carbonate mineral-saline formation water interactions. Calcite-saline water interactions will impart a significant influence on processes affecting the post  $\text{CO}_2$ -injection development or destruction of porosity, permeability and mass transport in the subsurface. Experimental studies and numerical models for the responses of saline aquifers to injection of carbon dioxide, under repository conditions, point to the importance of reactions involving carbonate minerals even in non-carbonate-hosted formations. It is consequently necessary to understand the complex factors influencing calcite-solution interactions in saline waters. This information will clearly be central to the construction of reliable reaction-transport models to predict reservoir and formation response to injection of  $\text{CO}_2$  and movement of saline waters.

**Results:** This was the first year of the project and primary efforts went into recruitment and training of personnel, and construction and testing of new experimental systems for the kinetic studies. It was necessary to construct two new systems for the study of calcite reaction kinetics in saline waters. The first was for both dissolution and growth experiments at 1 atm pressure over a range of temperatures,  $p\text{CO}_2$  values and solution compositions. The system was built with both free drift and chemostat modes of operation. It is controlled by 2 computers on which an extensive effort went into writing the needed

LabView language control code. The system is comprised of two major sub-components. The first mixes CO<sub>2</sub> and N<sub>2</sub> gasses using mass flow controllers. The gas mixture is then bubbled through a dilute solution of known alkalinity where the pH is constantly measured. The  $p\text{CO}_2$  of the gas is then computed precisely from pH and alkalinity. Gas control and  $p\text{CO}_2$  computation are done throughout the experiment by the first computer system. The system is regularly tested using standard gases of various fixed accurately known  $p\text{CO}_2$  values. The second major sub-component is the reactor which has a large (2 L) volume to increase stability (based on experience). In the free drift mode, pH (actually mv) is constantly monitored and recorder as a function of time. From pH and a known  $p\text{CO}_2$  saturation state with respect to calcite can be calculated using the Pitzer equation approach to ion activity coefficients. Solubility is checked using the “kinetic solubility” approach. We are currently using this system to investigate if water activity in high ionic strength KCl and NaCl solutions influences reaction kinetics. Parallel experiments are being run where a small cleavage plate of Iceland spar calcite is reacted with a large volume of saline water. This sample is then examined by the nanoscale analytic techniques to determine reaction mechanisms and, in the case of precipitation experiments, composition of the overgrowths. A second similar high pressure system made of titanium is under construction for high  $p\text{CO}_2$  and elevated T and P experiments.

## TEXAS A&M UNIVERSITY

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**Grant:** DE-FG02-00ER15034

### **Time-Lapse Seismic Monitoring and Performance Assessment of CO<sub>2</sub> Sequestration in Hydrocarbon Reservoirs**

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**Objectives:** Our goal is to examine the viability of time-lapse seismic monitoring using an integrated modeling of fluid flow, including chemical reactions, and seismic response. A critical aspect here is computational efficiency so that the approach can be suitable for large-scale field applications using high resolution geologic and seismic models.

**Project Description:** Our work focuses on fully integrating fluid flow and seismic data for monitoring injected CO<sub>2</sub> fronts by developing robust methods for reservoir characterization, coupled fluid flow modeling, including compositional and reactive processes and joint inversion of seismic and fluid flow data. For computational efficiency and suitability for large-scale field applications, we are developing streamline-based compositional modeling of CO<sub>2</sub> sequestration including compressibility, compositional and geochemical effects. We performed comprehensive simulations of the gas injection process accounting for the phase behavior of CO<sub>2</sub>-reservoir fluids, the associated precipitation/dissolution reactions and the accompanying changes in porosity and permeability. The simulation results are then used to model the changes in seismic response with time. Using field data from a CO<sub>2</sub> injection enhanced oil recovery pilot project, we plan to develop a systematic workflow for the detection and location of CO<sub>2</sub> movement using fluid flow and seismic data.

**Results:** We discuss the results from the modeling of reactive transport associated with CO<sub>2</sub> injection and the impact on the seismic response as the CO<sub>2</sub> front propagates in the reservoir. Our primary objective is to examine the feasibility of seismic monitoring of CO<sub>2</sub> movement under the specific conditions studied here. We consider CO<sub>2</sub> injection into a five spot pattern for two different cases. The reservoir properties correspond to a 'vuggy' carbonate reservoir. The permeability distribution for this case has a low spatial correlation with a minimum of 0.1 md and a maximum of 2200 md. CO<sub>2</sub> is injected for 6 years and then all the wells are shut-in. The reservoir conditions are then monitored at 10 years, 100 years and 1000 years.

The gas phase is primarily supercritical CO<sub>2</sub>. The mixing of CO<sub>2</sub> into the reservoir brine changes the brine density and pH due to chemical interactions. Brine salinity change (calculated as TDS) of 10% is noticed after 6 years of injection, and this in turn changes the density of the brine. The oil density also changes because of mixing with CO<sub>2</sub>. CO<sub>2</sub> injection and associated geochemical reactions lead to precipitation of calcite and kaolinite, and dissolution of anorthite. Porosity changes due to these mineral reactions are of order of 0.15%, and 1.5% are observed at times 100 years, and 1000 years respectively.

Changes in seismic properties computed using the Gassmann equation including changes in densities, are measurable. For this model, the reservoir is assumed to be located at a depth of 2 km, overlain by an isotropic and homogenous medium of  $V_p=4.5$  km/s,  $V_s=2.5$  km/s and density= 2.2 g/cc.

Because of CO<sub>2</sub> injection and the mineral precipitation/ dissolution with accompanying porosity changes, the P-wave velocity decreases by 2.73%, 2.75%, 2.765% and 2.87% at t = 6, 10, 100 and 1000 years respectively. The AVO intercept and gradient parameters provide important insights into the seismic detectability of the CO<sub>2</sub> front. The intercept parameter undergoes a decrease of 13.63%, 14.14%, 13.85% and 11.6% at the monitoring times, t = 6, 10, 100 and 1000 years, and the corresponding changes in the gradient are 5.02%, 5.07%, 5.09% and 5.45% respectively. These results are shown in Fig. 1. Not surprisingly, most of the change takes place during the six years of CO<sub>2</sub> injection, but it is important to note that the reservoir continues to undergo changes that affect seismic amplitudes.

Our results show that for accurate time-lapse response, it is important to model the precipitation and dissolution reactions that occur during CO<sub>2</sub> injection. Specifically, the CO<sub>2</sub> dissolution and the acidification of the brine trigger a variety of geochemical reactions that can significantly alter the rock-fluid properties. The gas-liquid dissolution and the intra-aqueous phase reactions are relatively fast and their effects on time-lapse seismic response can be seen at the end of CO<sub>2</sub> injection. The mineral reactions are typically very slow and their effects are detectable only after hundreds of years. Salinity change, which is of order of 10% in this study, changes the brine phase properties significantly. The combination of physical and chemical changes in the sequestration reservoir lead to changes in AVO attributes on the order of 15%, suggesting that these parameters can be very useful tools for monitoring changes in reservoir conditions in a sequestration site.

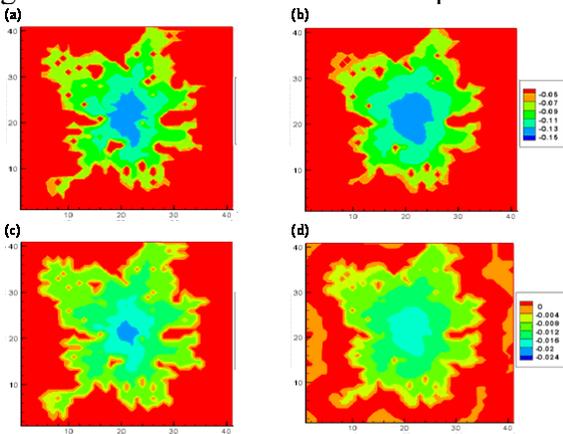


Fig 1: (a) and (b) represent difference of AVO intercept between t = 10 and 1000 years respectively with t = 0 years. (c) and (d) represent same profiles for the AVO gradient.

## UNIVERSITY OF TEXAS

Department of Civil Engineering  
Austin TX 78712

**Grant:** DE-FG02-04ER15496

### **Metal-Anion Pairing at Oxide/Water Interfaces: Theoretical and Experimental Investigations from the Nanoscale to the Macroscale**

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**Objectives:** The objectives of this research are to develop an approach for predicting the types of metal surface complexes that form on mineral surfaces by focusing on the role of metal-anion complexes, and to incorporate these surface complexes into thermodynamic surface complexation models to predict adsorption behavior.

**Project Description:** We combine the use of several techniques including bulk adsorption experiments, X-ray absorption, infra-red, and vibrational sum frequency spectroscopies (XAS, IR, VSGS), and molecular modeling to investigate ion-pairing in solution and at mineral surfaces. XAS provides data on how the metal binds to the surface (e.g., monodentate, bidentate), IR provides data on ion-pairing in aqueous solution, and VSGS provides data on the impact of adsorbed metal-anion pairs on water structure at the mineral surface. Molecular modeling will be used to guide spectroscopic data interpretation by providing information on water structure around ions in solution and the structure of metal-anion complexes in aqueous solution. In addition, molecular modeling can be used to provide insight into water structure at mineral surfaces, the surface sites involved in ion adsorption, and the distribution of ion pairs between aqueous solution and the mineral surface. Our studies have focused on systems involving alkaline earth metal ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ) and heavy metal ( $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ ) cations. The anions we have selected for study include  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{SeO}_3^{2-}$ . Ion adsorption and the potential formation of ternary complexes on silica (quartz, amorphous silica), alumina (corundum and gibbsite), and ferric iron (goethite) oxides are under investigation.

**Results:** Continuing their work on metal ion partitioning at solid/water interfaces, Dr. Katz's research group has focused on alkaline earth metal adsorption on gibbsite surfaces over the last year. In addition to heavy metal ( $\text{Co}^{2+}$  and  $\text{Pb}^{2+}$ ) sorption,  $\text{Sr}^{2+}$  and  $\text{Mg}^{2+}$  sorption on gibbsite have been investigated in the presence of different anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ) over a range of concentrations. Macroscopic experiments of these systems for different metal/solid ratios were employed to study the effect of surface coverage as well as to obtain a broader set of experimental data for modeling purposes. In addition, sorption experiments were conducted at two different temperatures to investigate whether temperature would affect the local coordination structure of adsorbed alkaline earth metals.

$\text{Sr}^{2+}$  adsorption on gibbsite was affected by the concentrations of background electrolyte, similar to that of  $\text{Sr}^{2+}$  on quartz (as we demonstrated earlier in this project). However, reduction of the extent of adsorption in the gibbsite system was not as significant as that observed in the quartz system. In the quartz system, the  $\text{Sr}^{2+}$  removal was reduced from 75% to 15% removal when the background electrolyte concentrations increased from 0.01 M to 0.1 M. Under similar experimental conditions, the

removal of  $\text{Sr}^{2+}$  on gibbsite was reduced from 80% to 60%. In addition, background electrolytes of  $\text{NO}_3^-$  or  $\text{ClO}_4^-$  appeared to have impacted  $\text{Sr}^{2+}$  sorption on gibbsite, while they had little effect on sorption to quartz. For the conditions investigated in this study, however, surface coverage had no significant effect on the sorption behavior of  $\text{Sr}^{2+}$  onto gibbsite.

Preliminary molecular modeling of alkaline earth metals onto gibbsite by the Criscenti group suggests that at higher temperatures, inner-sphere coordination may be significant whereas at lower temperatures outer-sphere coordination is dominant. To test this modeling result, batch experiments were conducted under same experimental conditions except at different temperatures, 25 °C and 90 °C, respectively, for  $\text{Sr}^{2+}$  and  $\text{Mg}^{2+}$  on gibbsite. It was found that  $\text{Sr}^{2+}$  adsorption was enhanced at higher temperature and there was an impact of ionic strength on  $\text{Sr}^{2+}$  adsorption at all temperatures. Preliminary results from  $\text{Mg}^{2+}$  adsorption on gibbsite, however, showed that ionic strength did not have a significant impact on adsorption at the higher temperature.

## UNIVERSITY OF TEXAS

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**Grant:** DE-FG02-03ER15430

### **Predicting Fracture Porosity Evolution in Sandstone**

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**Objectives:** Our goal is to explain how fracture growth and diagenetic alteration interact to create and destroy fracture porosity. We are testing the hypothesis that records of fracture opening can be recovered from fractures formed in the subsurface and that, along with fluid-inclusion data and diagenetic and geomechanical models, these records can help recover duration and rates at which fractures open and rock properties change. We use a diagenetically sensitive geomechanical model to investigate how diagenesis affects development of fracture aperture, length, and spatial arrangement.

**Project Description:** Fluid flow in fractured rock is an increasingly central issue in recovering water and hydrocarbon supplies and geothermal energy, in predicting flow of pollutants underground, in engineering structures, and in understanding large-scale crustal behavior. Yet mechanical models typically neglect cementation in fractures and the rock mass, tacitly assuming that cementation rates are slow relative to fracturing and that fracture growth and fracture filling are decoupled. Our studies show that this assumption is not justified, that important mechanical and chemical feedbacks govern several important aspects of fracture patterning, and that fracture growth patterns, timing, and rate in principle can be recovered from structural diagenetic data.

We are exploring three topics. Each involves cross-disciplinary efforts in rigorous fracture and diagenesis characterization and geomechanical and diagenetic modeling.

1. We are extending a theory of cementation in fractures that predicts fracture porosity evolution as a function of temperature, surface area, and opening history. We use the model along with cement textures to infer patterns, rates, and durations of fracture opening. We take advantage of new, automated, image-collection systems and protocols and fluid-inclusion and sandstone crystallography to rigorously test predictions. We also track rock property evolution in the context of burial history. Core-based studies are under way in the Piceance Basin, Colorado, and the East Texas Basin and outcrop studies in two units. The outcrops allow us to study aspects of fracture size and spatial arrangement that cannot be measured in core.

2. We investigate how diagenesis affects fracture growth by conducting numerical experiments that incorporate diagenesis, using both our geomechanical model, a newly developed hybrid numerical code, and other modeling approaches. The numerical experiments are helping us formulate specific hypotheses about how any feedbacks work, including processes that generate fracture-size distributions

and clustering patterns. Fracture patterns in both models and outcrops are rigorously described, using our newly developed methods for quantifying fracture size and spatial patterning. Palinspastic reconstruction of natural fracture aperture and length profiles allows direct comparison with geomechanical models. We test fracture-growth hypotheses against natural examples using high-resolution fracture-opening histories and fluid-inclusion data keyed to opening increments, allowing rigorous comparison with our diagenetic models.

3. Our research shows that heterogeneous sealing of large, static fractures by carbonate cementation is a widespread phenomenon that blocks fractures that grow concurrently with quartz cementation. We take advantage of the large and diverse core data set from the Piceance and East Texas Basins to investigate how carbonate cementation seals large fractures. Our observations of core and an outcrop analog show that diverse suites of carbonate cements show regional and local variations in composition, distribution, and timing. We delineate these patterns to guide reaction-path modeling. These observations also provide a constraint on fracture timing and duration estimates derived from quartz cementation models and observations.

**Results:** We developed, tested and applied large-area ( $\text{mm}^2$ ) cathodoluminescence (CL) imaging and mapping methods and fluid-inclusion analysis and crystallographic analysis using electron backscatter diffraction methods of partly sealed fractures to reconstruct sequential trapping of fluid inclusions during fracture opening. Bridge observations and realizations using our structural diagenetic model agree. We are quantifying this result and testing for sensitivity to uncertainties in burial history, map resolution and other factors. Results explain how fracture aperture (and porosity) develops and is preserved. We are developing fracture growth models that incorporate diagenesis and explain how fracture-size distributions arise. Core, outcrop, and model studies are in progress to describe and link geomechanical and hybrid models to diagenetic models, field observations of fracture size and spatial arrangement patterns, and opening histories in the context of well-constrained burial histories.

Synkinematic cement bridges are a common fracture attribute in moderately to deeply buried rocks (1+ km depth). We reconstruct fracture-opening history from CL image maps and fluid inclusions trapped within individual cement layers defined by crack-seal texture. In core and outcrop examples, any single bridge may contain many tens to hundreds of generations of fluid-inclusion assemblages (FIAs) that record thermal and chemical characteristics of fluids present during crack-seal events. Analysis of these FIAs across the fracture reveals the history of temperature change; high-resolution CL imaging defines relative ages of FIAs. With a burial history, fracture age is obtained by comparing time-temperature curves. Reconstructions of fracture-aperture development tied to burial-history analysis indicate that fractures grow episodically during as much as tens of millions of years. Geomechanical models incorporating diagenesis produce fracture size and spatial arrangement patterns that cannot be accounted for when diagenesis or mechanics are treated as separate, isolated processes.

## VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

Department of Geosciences  
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**Contract:** DE-FG02-00ER15112

### Investigation of the Physical Basis for Biomineralization

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**Objectives:** To determine principles governing interactions of simple protein analogs and key inorganic impurities with carbonate minerals and the resulting structures/polymorphs that form. A long-term goal is to establish the physical basis for biomineralization and accompanying roles of solutes in natural and engineered Earth systems.

**Project Description:** This work is focused on developing a mechanism-based picture of controls imposed by Asp-rich polypeptides and biomineralizing proteins on the elemental signatures in calcite. We are also probing the transient events and phase evolution during CaCO<sub>3</sub> nucleation at peptide-derivatized templates. In particular, we seek an understanding of the amorphous to crystalline transformation that we recently showed routinely occurs during nucleation at these templates. Growth studies include: AFM and time-of-flight SIMS studies of Mg in calcite grown in the presence of polypeptides and proteins. Nucleation studies include: *in situ* AFM, X-ray absorption spectroscopy, eSEM, *in situ* TEM and molecular modeling of directed CaCO<sub>3</sub> nucleation and transformation on peptide derivatized SAMs. Investigations into the fundamentals of mineral growth and dissolution utilize *in situ* AFM measurements of kink dynamics, kMC simulations, and development of analytical theories.

**Results:** During FY07 we made findings in three areas: (1) biomolecular controls on calcite growth and minor/trace element contents, (2) template directed nucleation and transformation of calcium carbonate, and (3) fundamentals of mineral growth and dissolution.

***From amino acids to proteins: Role of molecular charge and hydrophilicity in regulating the kinetics of crystal growth (Elhadj et al., 2006, Proc. National. Acad. Science).*** The composition of biologic molecules isolated from biominerals suggests that control of mineral growth is linked to biochemical features. This study found a systematic relationship between the ability of biomolecules in solution to promote the growth of calcite (CaCO<sub>3</sub>) and their net negative molecular charge and hydrophilicity. The degree of enhancement is dependent on peptide composition, but not on sequence. Data analysis shows that this rate enhancement arises from an increase in the kinetic coefficient. We interpret the mechanism of growth enhancement to be a catalytic process whereby biomolecules reduce the magnitude of the diffusive barrier,  $E_k$ , by perturbations that displace water molecules. The result is a decrease in the repulsive barrier for attachment of solutes to the solid phase. These findings show that the growth-modifying properties of small model peptides may be scaled up to analyze mineralization processes that are mediated by more complex proteins. We suggest that enhancement of calcite growth may be

estimated *a priori* from the composition of peptide sequences and the calculated values of hydrophilicity and net molecular charge.

***New insights into mechanisms of biomolecular control on growth of inorganic crystals (James J. De Yoreo, A. Wierzbicki, P. M. Dove, CrystEngComm, 9, 1144).*** The interactions of biomolecules with atomic features on crystal surfaces lead to dramatic changes in morphology and growth rate. Molecular scale studies based on atomic force microscopy and computational modeling have provided new insights into the mechanisms that lead to these changes. In this invited feature article, we examine the key factors that are emerging from those studies and link the mechanisms of modification to the underlying structural and chemical relationships between modifier and surface.

***Kinetics of amorphous silica dissolution: Paradox of the silica polymorphs (Dove et al., submitted).*** Amorphous materials lack the structural order that would allow them to be studied by classical terrace, ledge, kink-based models applied to crystal dissolution. This would seem to imply that the surfaces of amorphous phases are atomically rough so that the transfer of SiO<sub>2</sub> to solution leaves the surface free energy of the solid unchanged. As a consequence, dissolution rates of amorphous phases should simply scale linearly with driving force (undersaturation) through the higher probability of detaching silica tetrahedra from the surface. By examining rates for amorphous SiO<sub>2</sub> polymorphs— fused quartz glass, synthetic colloidal, and biological silicas— we find, instead, a paradox. Just as seen for their crystalline polymorph, quartz, dissolution rates of amorphous silicas in electrolyte solutions have an exponential dependence on driving force. We analyze this enigma by considering that silica polymorphs present common types of surface-bonded silica groups. In electrolyte solutions, nucleated detachment of the higher coordinated groups increases surface free energy and the probability of doing so scales exponentially with driving force. The result is a plausible mechanism-based model that is formally identical with the polynuclear theory originally developed for crystal growth. The approach also quantitatively explains dissolution data reported for biogenic silica and growth and dissolution of synthetic colloidal silica. In principle, the insights should be applicable to materials with diverse compositions and structural order.

***Exploring silica chemistry at biological interfaces: Kinetic and thermodynamic drivers of surface nucleation (Wallace, A.F. and Dove, P.M.).*** Insights into how biosilicification occurs within living organisms can be gained by conducting experimental studies with simple model systems that emulate key features of biological systems. Using a novel AFM-based approach, we measured the dependence of amorphous silica nucleation kinetics on the chemical and structural nature of model biological surfaces. Measurements of surface nucleation rate were conducted under conditions that simulate current views of conditions within silica deposition vesicles of major diatom species. Aqueous silicate levels were varied to examine dependencies on saturation state. Analysis of the kinetic data within the framework of nucleation theory quantified the height of the kinetic barrier to silica formation, and net energy of silica substrate/solution interfaces. By conducting experiments for differently functionalized substrates, we determined kinetic and thermodynamic controls of functional chemistry on heterogeneous nucleation of amorphous silica. The findings provide new insights into how biochemical interfaces mediate the onset of silica nucleation.

## VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

Center for NanoBioEarth  
Department of Geosciences  
Blacksburg VA 24061

**Contract:** DE-FG02-06ER15786

### **Frontiers In Biogeochemistry And Nanomineralogy: Studies In Quorum Sensing And Nanosulfide Dissolution Rates**

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**Objectives:** This DOE project is concentrating on two research areas of geochemical importance: mineral-microbe interaction and nanomineralogy. In the field of mineral-microbe interaction, we are examining how bacterial cell-cell communication (quorum sensing) may be involved in geochemical processes. In the field of nanomineralogy, we are conducting a comprehensive study of the dissolution and solubility of nanosulfides as a function of crystal size.

**Project Description:** *Shewanella oneidensis* MR-1 is a potential candidate for bioremediation because of its ability to respire a variety of substances, such as oxygen, iron and manganese oxides, hexavalent chromium and uranium(VI). Since it is unknown if *S. oneidensis* can utilize quorum sensing, our work is focused on understanding the role of a potential quorum sensing signal gene *luxS* in *S. oneidensis* and how this affects its ability to interact with their environment, abiotic or biotic.

Dissolution reactions of galena (PbS) and sphalerite (ZnS) are responsible for a number of environmental problems, such as Zn and Pb releases which result in the incorporation of toxic metals into surface water and groundwater. A detailed understanding of the dissolution of galena and sphalerite is an important key to more accurately predicting and monitoring long-term contaminant metal mobility and bioavailability in natural settings. In particular, the size-dependent dissolution of these minerals has never been studied experimentally.

**Results:** In numerous bacteria, *luxS* catalyzes the formation of a quorum sensing signal called AI-2 (furanosyl borate diester) and it also plays a role in the activated methyl cycle. To evaluate the role of *luxS* in *S. oneidensis*, a full gene deletion was constructed. The mutant, DLΔ13, was verified genetically via DNA sequencing and by testing its ability to produce AI-2. Compared to the wild type (WT), the mutant showed a marked reduction of AI-2 production, similar to non-AI-2 producing strains. AI-2 production was restored in the mutant upon complementation via a plasmid encoded *luxS*. The mutation does not have any effects on aerobic or anaerobic growth. Aerobic flow-through biofilm experiments showed that the *luxS* mutant's ability to form a biofilm is inhibited after 24 hours but not abolished. Anaerobic flow-through biofilm showed that the mutation also affects the cells ability to adhere to a hematite surface. Whether this is related to quorum sensing or the gene's role in central metabolism is still unknown. This idea is being addressed by examining whether the chemical signal AI-2 can restore the mutants biofilm forming abilities.

Preparation of high quality galena nanocrystals of various sizes is a prerequisite to investigate size-dependent dissolution. We have synthesized galena nanoparticles via a Sol-Gel method originally

reported by Joo et al. (2003), in which  $\text{PbCl}_2$  and S are used as the lead and sulfur precursors, respectively, and oleylamine is used as both a surfactant and a solvent. We have synthesized separate and nearly-monodispersed galena nanoparticles in two sizes,  $\sim 5$  nm and  $\sim 12$  nm (crystals from the latter synthesis are shown in Figure 1 below). High Resolution Transmission Electron Microscopy (HRTEM) images indicate that the nanocrystals are single crystals with a nearly perfect lattice. The HRTEM investigations also confirm that the galena nanoparticles are truncated by  $\{100\}$ ,  $\{110\}$ , and  $\{111\}$  facets. This result is consistent with the growth theory of halite-structured crystals like galena, i.e., relatively fast growth can occur along  $[111]$ ,  $[100]$ , and  $[110]$  directions because of the high intrinsic surface energy of the faces perpendicular to these directions. Preliminary dissolution experiments of the 12nm galena shows that the dissolution rate is much slower than bulk galena. This has important implications in lead transport and bioavailability in ground and surface waters.

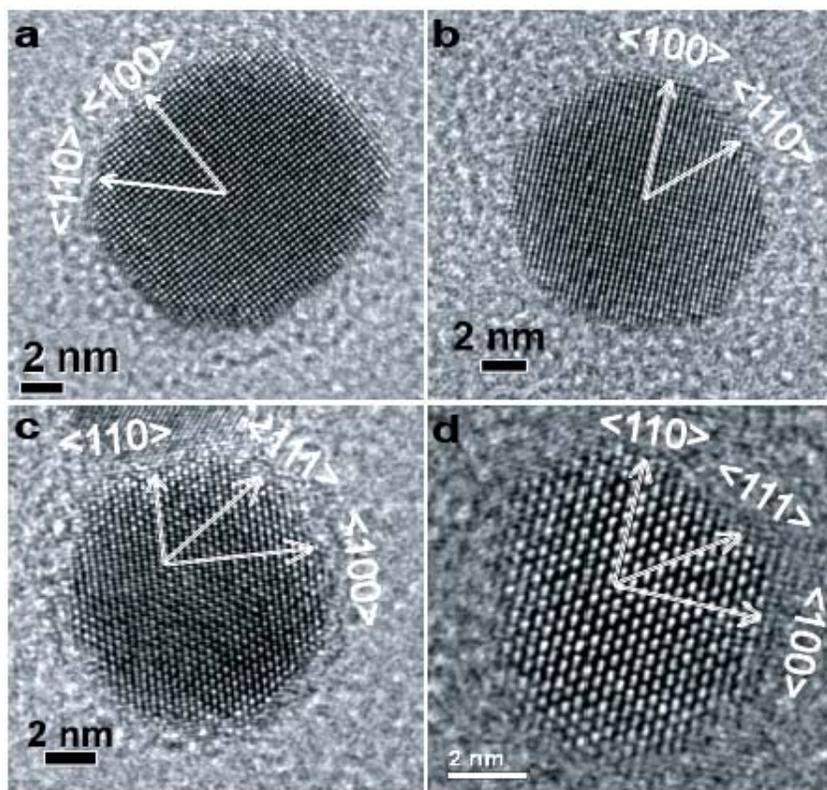


Figure 1. HRTEM images of washed PbS nanoparticles before dissolution (a and c) and washed PbS nanoparticles after 3-hour-dissolution (b and d). (a) and (b) are viewed along  $\langle 100 \rangle$  zone axis; (c) and (d) are viewed along  $\langle 110 \rangle$  zone axis. The more developed  $\{110\}$  faces in (b) and the large  $\{111\}$  faces in (d) indicate the relatively fast dissolution on these faces vs.  $\{100\}$  faces.

## UNIVERSITY OF WISCONSIN

Department of Physics  
Madison WI 53706

**Grant:** DE-FG02-07ER15899

### **Mapping of Temporal and Spatial Phase Transitions of CaCO<sub>3</sub> in Echinoderm Skeletons: Key Insights into Basic Mechanisms in Biomineralization**

*Pupa Gilbert, [pupa@physics.wisc.edu](mailto:pupa@physics.wisc.edu), (608) 358-0164; Steve Weiner (Weizmann Institute of Science)*

**Objectives:** (1) To understand the manner in which the single crystal propagates through the amorphous phase of the larval spicule; (2) To characterize the differences in the phases of the primary formed stereom and the secondary infilling of the adult spine; (3) To characterize the initial, transforming, and mature phases of the adult tooth.

**Project Description:** In biominerals, the use of transient amorphous precursors that subsequently transform into stable crystalline phases may be a widespread strategy for forming skeletal parts in any desired complex shape. This strategy is employed by echinoids to build single calcite crystals with very intricate morphologies presumably adapted to their function. During the process, a small amount of organic material is incorporated within the mature crystal, endowing it with exceptional mechanical properties. Important mechanistic understanding of the formation process, such as the nucleation of the single crystal, its propagation through the amorphous calcium carbonate phase and the roles of associated additives, will be obtained by mapping the various phases at high resolution. Another enigmatic aspect of sea urchin biomineralization that may well be related to the transient mineral formation process is the incorporation of Mg ions into the calcite crystals in concentrations sometimes exceeding thermodynamically stable Mg-calcite. The different phases, e.g. amorphous calcium carbonate, calcite and high Mg-calcite are differentiated spatially at the micrometer-scale. Thus an analytical technique that can provide spectral information with high-spatial resolution, such as X-ray PhotoElectron Emission spectroMicroscopy (X-PEEM), will be used to unravel the different phases and mechanisms. The acquired insights will have a direct bearing on the design of novel materials with complex controlled shapes inspired by nature.

**Results:** The grant was awarded on September 1<sup>st</sup>, 2007, thus only one month before the end of FY2007. We recently successfully optimized sample preparation strategies, and now plan to acquire X-PEEM data on the sea urchin spicules, spines and teeth early in 2008. We have obtained beamtime for these experiments both at the UW-Synchrotron Radiation Center and at the LBNL-Advanced Light Source. The PI is about to spend one month at the Weizmann Institute to collaborate with the Co-PI directly and effectively.

**UNIVERSITY OF WISCONSIN**  
Department of Geology and Geophysics  
Madison WI 53706

**Grant:** DE-FG02-05ER15738

### **Quantifying the Micromechanical Effects of Variable Cement in Granular Porous Media**

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**Objectives:** (1) To quantify grain-scale physical effects of variable cement quantity, composition, and location on the elastic and inelastic deformation of granular porous media.

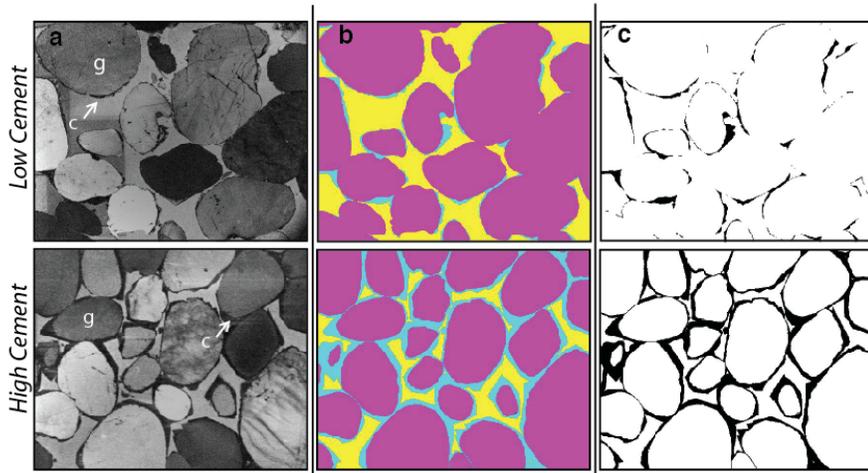
(2) To use the resulting understanding of the fundamental micromechanical processes that govern macroscopic deformation to accurately capture meaningful grain-grain interactions in Discrete Element Model (DEM) simulations.

**Project Description:** The project scope requires us to develop methods of appropriately small-scale experimental deformation and structural characterization of granular porous media. We chose to work with both *natural* and *synthetic* grain-cement systems using novel approaches that provide insight into grain-scale mechanics. We are:

- 1) Developing methods for fabrication of synthetic assemblages of soda-lime silicate beads and both sodium silicate and calcium carbonate cements.
- 2) Designing apparatus to test mechanical properties of synthetic grain-cement assemblages. Use nanoindentation to probe properties such as elastic modulus, hardness, and plasticity of grains and cements in both natural and synthetic systems. Use ultrasonic velocity and uniaxial deformation experiments to characterize variably cemented natural sandstone.
- 3) Integrating microstructural and experimental analyses to relate physical elements of progressively cemented natural and synthetic systems to their structural response to stress.
- 4) Developing quantitative relationships describing the stress-strain response of cemented granular systems and incorporate microscale material response into a DEM.

**Results:** Current understanding of the impact of cement on the mechanical response of granular porous media is largely based on a widely accepted conceptual model of a circular cement “bridge” between two grains. Our observations and literature review indicate, however, that this meniscus-type cement geometry is uncommon in natural materials. The UW group has therefore focused on designing an approach to quantitatively characterize, and determine the mechanical impact of, natural cement morphologies. Because quartz is the most common cement in siliciclastic sediments, our work has focused on the St. Peter Sandstone, a well sorted, quartz-cemented quartz arenite. The St. Peter exhibits considerable variation in cement abundance, with typical quartz overgrowth geometries. Quartz cement morphology changes with progressive cementation (Figure 1). Grains in low-cement samples exhibit

thin, encrusting layers of quartz with isolated crystal facets. Pore spaces are relatively equant and interconnected. In contrast, high-cement samples have an interconnected network of cement with well defined facets, more angular and crack-shaped pores, and diminished pore connectivity. Cathodoluminescence (CL) images allow both cement connectivity and changes in pore geometry with progressive cementation to be quantitatively characterized.

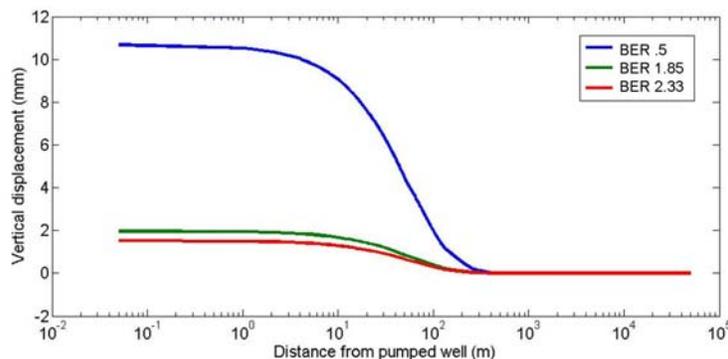


**Figure 1:** Comparison of cement morphology and distribution of areas of low (3.5%) and relatively high (15.6%) cement abundance. (a) CL images in which grains (g) are distinguished from cement (c) by differences in luminescence. (b) False-color images of the same areas. Cement is blue, grains are magenta, and pores are yellow. The intergranular area of the two images is roughly the same, but porosity in the high cement example is less than half that of the low cement location. (c) Images showing only areas of cement within each sample.

The Sandia team has begun to use these morphological observations to construct physically based finite element models to explore grain-cement-grain mechanical behavior. Perhaps not surprisingly, the stress distribution at our modeled grain-cement boundaries is distinctly different from that of the previously studied meniscus-type cement morphologies.

The UMass team’s DEM models provide quantitative insight into the effects of changing grain size and cement content on bulk material properties at a multi-grain scale. To investigate the effects of progressive cementation, a bond length is assigned to each model domain. The assigned length specifies the maximum distance between elements that can be ‘cemented’, leaving ‘grains’ that are further apart ‘uncemented’. Thus, the number of bonds between elements in the domain increases with bond length. Thus, the number of bonds divided by the number of elements (Bond to Element Ratio, or BER) is a proxy for % cement. Increasing the BER increases yield strength. To evaluate the effects of cementation on large-scale fluid removal and resulting reservoir deformation, the theoretical bulk modulus properties from the DEMs were input into 2D, axially symmetric, poroelastic continuum models. Poroelastic model results indicate that the bulk moduli calculated from DEMs with BER= .5 and BER=1.85 resulted in 10.5 mm and 2 mm of subsidence, respectively (Figure 2). BERs calculated from the images shown in Figure 1 are .68 and 1.2.

**Figure 2.** Simulated vertical displacement with distance from a pumped well for bulk moduli calculated for different BERs.



## UNIVERSITY OF WISCONSIN

Department of Geology and Geophysics  
Madison WI 53706



**Grant:** DE-FG02-93ER14389

### **High Precision Ion Microprobe Analysis of Low Temperature Quartz Cements**

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#### **Objectives:**

1. To improve microanalytical techniques for stable isotope analysis.
2. Development of procedures for oxygen isotope analysis by Cameca 1280 ion microprobe.
3. To decipher the complex history of continent-scale migration of hydrothermal brines.
4. To evaluate oxygen isotope thermometry in quartz-overgrowths as a record of paleoclimate.
5. To determine genesis and timing of porosity reducing cements in quartz sandstones that form aquifers and fossil fuel reservoirs.

**Project Description:** This study focuses on microanalysis of diagenetic quartz cements and secondary silica. New techniques employing ion microprobe analysis permit study of oxygen isotope ratio in ultra-small samples. We have contoured  $\delta^{18}\text{O}$  across single crystals and within individual overgrowths at all scales down to sub-one-micron. Mineral zonation patterns provide new insights into timing and processes of water/rock interaction, and migration of fluids through sandstone aquifers.

We are investigating applications of the new analytical technology to paleoclimate studies, and groundwater and hydrothermal systems. We are applying experience gained in the past three year period by microanalysis of quartz overgrowths in the St. Peter sandstone (Kelly et al. 2007) to syntaxial cements from Potsdam sandstone in New York, opal precipitated in the vadose zone of felsic tuffs from Yucca Mtn, and quartz overgrowths in Carboniferous to Jurassic eolian sandstones of the western U.S.

**Results:** The first CAMECA ims-1280, a large radius multicollector ion microprobe/ secondary ion mass spectrometer, was delivered to our lab, Wisc-SIMS, at the University of Wisconsin in 2005. This instrument has many new developments compared to earlier ims-1270's including: 10 electron multiplier and faraday detectors, improved focusing of primary and secondary beams, dedicated detection and monitoring of primary beam intensities, all digital electronics, PC control, and new operating and corrections software. Analytical results are excellent. In situ analyses of 10 micron spots in thin section attain precision of  $\delta^{18}\text{O}$  (quartz, calcite, or zircon) of 0.1‰ for sample volumes that are 100 times smaller (<1 ng) than by single collector ion probe and  $10^6$  to  $10^9$  times smaller than possible by laser fluorination/ mass-spectrometry.

Cathodoluminescence imaging is important to identify fine-scale quartz cements for analysis by ion microprobe. In 2006, we installed a new Hitachi SEM and dedicated high sensitivity CL detector (plus EDA, BSE, EBSD). This \$375K instrument was funded by NSF (70%) and UW (30%), and is located in Geology, near the ion microprobe and electron microprobe labs.

We have completed a detailed oxygen isotope study of detrital quartz (DQ) and authigenic quartz overgrowths from shallowly buried St. Peter Sandstone (SW Wisconsin) to constrain temperature and fluid sources during diagenesis (Kelly et al. 2006, 2007). Quartz overgrowths in these cratonic supermature quartz arenites are syntaxial and show multiple growth generations by cathodoluminescence.

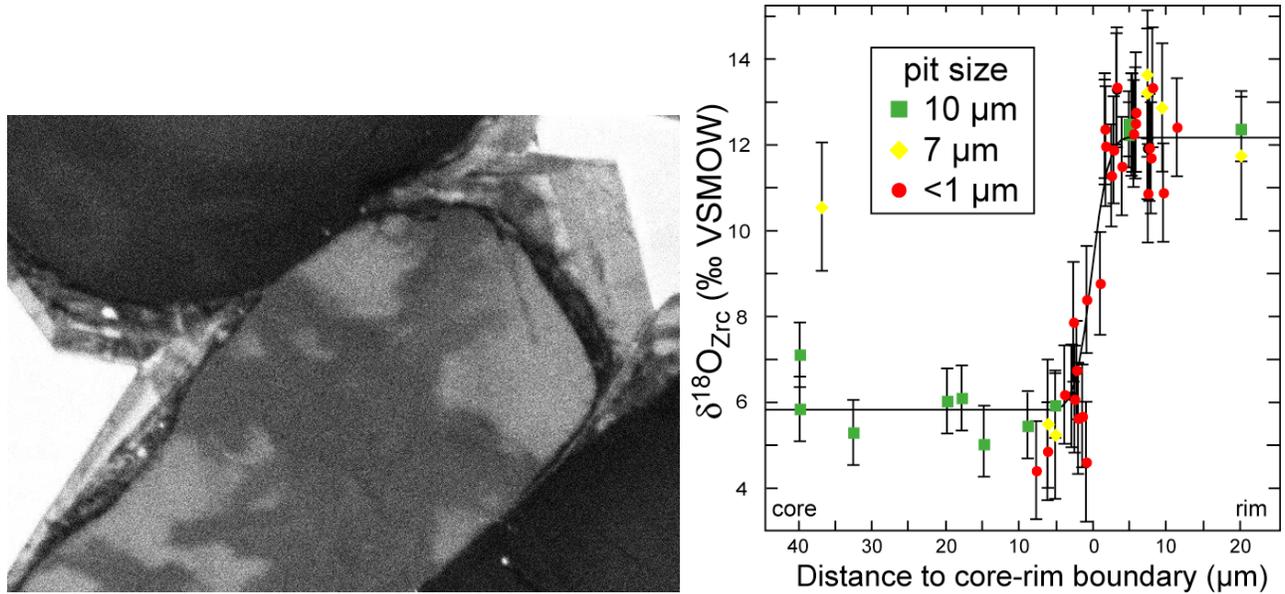


Figure 1. **Left:** CL image of thin syntaxial quartz overgrowths on detrital quartz in Mt. Simon sandstone from the Wisconsin dome (07WI-14, FOV = 250 $\mu m$ ). **Right:** Analysis of oxygen isotope ratio at Wisc-SIMS with spot sizes of 10, 7, and <1  $\mu m$  reveals a sharp diffusion profile within zircon of  $\sim 6\text{‰} / 2\mu m$  (Page et al. 2007).

## WOODS HOLE OCEANOGRAPHIC INSTITUTION

Department of Geology and Geophysics  
Woods Hole MA 02543

**Grant:** DE-FG02-00ER15058

### **Collaborative Research: Evolution of Pore Structure and Permeability of Rocks Under Hydrothermal Conditions**

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**Objectives:** The pore structure and transport properties of rocks, including fluid permeability and electrical conductivity, can be altered by a wide variety of diagenetic, metamorphic, and tectonic processes. Our goal is to provide better understanding of the interrelationships among permeability, mechanical properties, and the pore shape, under hydrothermal conditions, in mineral aggregates, with and without reactions.

**Project Description:** We conduct experimental investigations of the effect of changes in failure modes on transport properties. Specifically, we extend the two-step experiments to a wider range of strain-rates and temperatures, with concomitant permeability measurements. Variations in the time between loading to produce the shear band and the subsequent reloading to produce the compaction band are investigated. We will conduct thorough and detailed image collection and analysis of all deformed samples. Microstructure observations of the pore space in samples before and after alteration will be done using SEM, laser scanning confocal optical microscopy, and the high resolution x-ray CT techniques.

#### **Results:** *Initiation and Growth of Compaction Localization in Porous Sandstones*

Recent field and laboratory studies have demonstrated that different modes of strain localization occur in porous sandstones in response to different stress conditions. Because natural environments often include preexisting heterogeneities that are reactivated during tectonic loading, different modes of strain localization coexist. We continue the experimental investigation on how dilatant shear localization affects the initiation and growth of compaction localization. In our previous study, we demonstrated that under low confining pressures, deformation in porous Bentheim sandstone samples with pre-existing shear fractures is primarily stable sliding along the pre-existing fracture surface. With increasing confinement, sliding along the fracture surface was inhibited, and compaction localization occurred in the fractured rocks. These compaction bands generally initiated at the fracture interface and gradually developed into a series of deformation bands along the fault. The differential stress required to initiate compaction localization in pre-fractured samples are considerably less than that in intact Bentheim sandstone samples. However, in these experiments, there was only one acoustic emission transducer available. Therefore, we were not able to map out the *in situ* nucleation and growth process of the compaction bands and their spatial relation to the pre-existing shear fracture. In collaboration with Drs. Dresen and Stanchits at GeoForschungsZentrum, Potsdam, Germany, we recently conducted a new set of experiments using 12 piezoelectric transducers (PZT) to monitor acoustic emission and elastic wave

velocity (Figure 1). In these new experiments, we followed the two-step experimental approach: First, porous Bentheim sandstone samples were deformed at an effective pressure of 10 MPa until shear localization developed. Second, the fractured samples were reloaded and deformed at effective pressure 190 MPa. Experiments were conducted under both dry and water-saturated conditions. Preliminary mechanical data indicate that the failure behavior is in excellent agreement with our previous results. We are currently processing the velocity data.



Figure 1. Sample assembly. The PZT transducers are installed along the cylindrical surface of the sample.

## WOODS HOLE OCEANOGRAPHIC INSTITUTION

Department of Marine Chemistry and Geochemistry  
Woods Hole MA 02543

**Grant:** DE-FG02-97ER14746

### **Laboratory Constraints on the Stability of Petroleum at Elevated Temperatures: Implications for the Origin of Natural Gas**

*Jeffrey Seewald, (508) 289-2966, [jseewald@whoi.edu](mailto:jseewald@whoi.edu)*

**Objectives:** Laboratory experiments are being conducted to constrain geochemical processes that regulate the hydrogen and carbon isotope composition of low molecular weight organic compounds in natural gas and associated aqueous fluids at elevated temperatures and pressures. This information is being used in conjunction with results from field-based studies aimed at characterizing microbial ecosystems in co-produced fluids from the Potato Hills gas field in southeastern Oklahoma to assess the role of microbes in the generation of natural gas.

**Project Description:** Numerous laboratory and field studies have demonstrated the participation of sedimentary minerals and water as reactants and catalysts in chemical transformations associated with the degradation of oil and the formation of low molecular weight organic compounds that constitute natural gas. The occurrence of such processes in natural environments, however, can be difficult to recognize because the composition of organic alteration products may not be substantially different than those produced by thermal cracking. Our research has focused on the use of laboratory experiments to develop diagnostic tools based on hydrogen and carbon isotopes that can identify specific geochemical and biological processes responsible for the formation of natural gas. We have expanded our approach to include an assessment of microbial activity in relatively low temperature (<70°C) natural gas reservoirs in southeastern Oklahoma because microbial activity may represent a key process regulating the chemical and isotopic composition of natural gas. In general, microbial activity under anaerobic conditions at substantial depth within sedimentary basins has not been considered as factor in petroleum degradation and the formation of natural gas, despite the enormous amounts of chemical energy and temperature conditions compatible with life.

**Results:** Results of laboratory experiments have demonstrated carbon exchange between the carboxyl carbon group in aqueous organic acids and aqueous carbonate species. Subsequent reduction of carboxylic acids to their corresponding alkanes at the relatively reducing conditions of the experiments resulted in the incorporation of carbonate carbon into low molecular weight *n*-alkanes. Accordingly, inorganic carbonate species may contribute to the carbon isotope composition of thermogenic hydrocarbons in reducing natural environments. Additional experiments examining D/H exchange between aqueous C<sub>1</sub>–C<sub>5</sub> *n*-alkanes and water at 325°C and 350 bar in the presence of a pyrite-pyrrhotite-magnetite redox buffer revealed incorporation of water-derived hydrogen by C<sub>2</sub>–C<sub>5</sub> *n*-alkanes on a timescales of months. In contrast, relatively minor incorporation was observed for CH<sub>4</sub>. Isotopic exchange appears to be facilitated by reversible equilibration of *n*-alkanes and their corresponding alkenes. Thus, in reducing aqueous environments, reaction mechanisms may exist that allow rapid D/1H exchange of alkyl-H with water at elevated temperatures and pressures on timescales much shorter than previously assumed.

Microbial communities in co-produced aqueous fluids from actively producing wells in the Potato Hills natural gas field of southeastern Oklahoma were examined to investigate a possible role for microbial activity in regulating the abundance of organic acids and C<sub>2+</sub> hydrocarbons. Fluids from these wells contained substantial numbers of microorganisms ( $\leq 4.9 \times 10^6$  cells ml<sup>-1</sup>). Phylogenetic analysis revealed putative syntrophic communities dominated by heterotrophic bacteria and methanogenic archaea. The bacterial communities consisted predominantly of Clostridiales and Bacteroidales. These bacteria often use fermentative metabolisms that consume and/or produce organic acids and are known to grow syntrophically with methanogens. Archaeal sequences belonged to the Methanomicrobiales and the Methanosarcinales, one of the most metabolically diverse orders of methanogens. Based on sequence similarity, resident microbes are likely thermophiles, with optimum growth at 60-80 °C, which is consistent with the *in situ* production temperatures of the wells. Thus, our data suggest a diverse microbial community, consisting of moderately thermophilic heterotrophic Bacteria and methanogenic Archaea.

Thermodynamic modeling of possible metabolic strategies reveals that autotrophic methanogenesis is energetically unfavorable at *in situ* well conditions, while heterotrophic methanogenic metabolisms involving formic acid, methanol and acetate are energetically favorable. These results suggest that resident thermophilic methanogens likely employ heterotrophic metabolisms in the Potato Hills reservoir.

## WOODS HOLE OCEANOGRAPHIC INSTITUTION

Department of Marine Chemistry and Geochemistry  
Woods Hole MA 02543

**Grant:** DE-FG02-06ER15775

### **Using Comprehensive Two-Dimensional Gas Chromatography to Explore the Geochemistry of the Santa Barbara Oil Seeps**

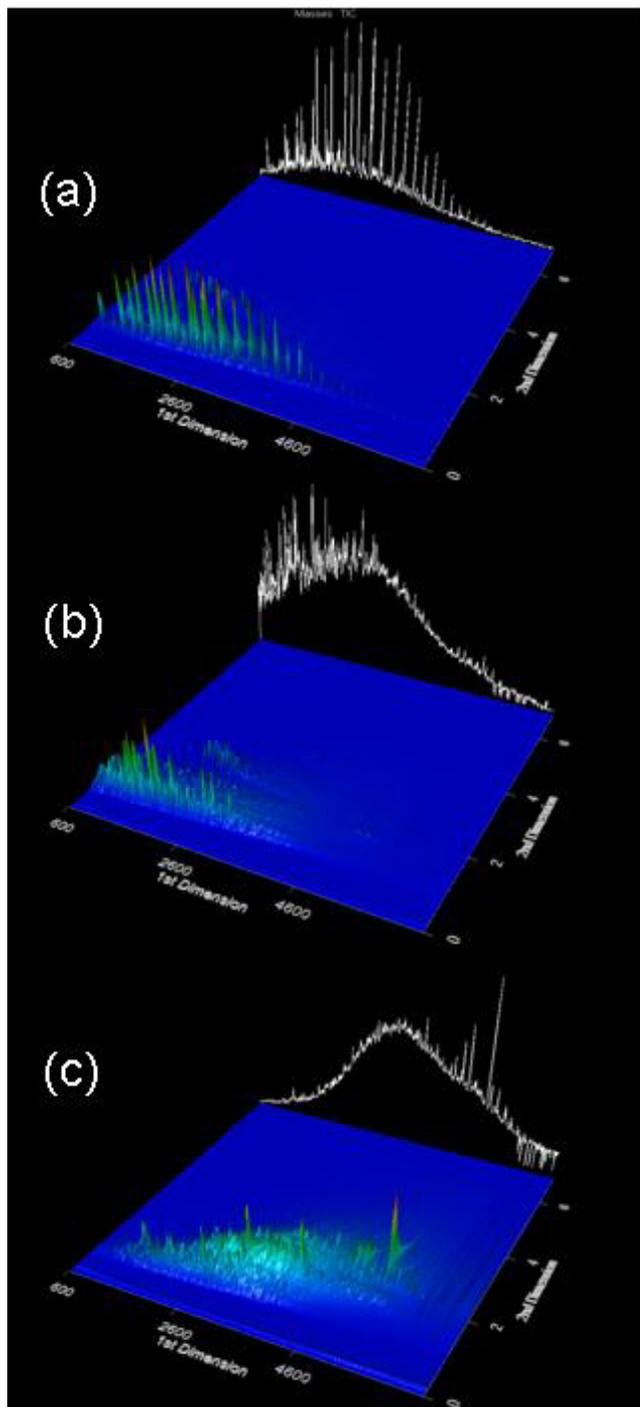
*C.M. Reddy, (508) 289-2316, fax (508) 457-2164, [creddy@whoi.edu](mailto:creddy@whoi.edu); R.K. Nelson*

**Objectives:** To further advance our understanding of the geochemical processes that act on oil that travels from reservoirs and seeps onto the ocean floor.

**Project Description:** The goals of this work are to employ comprehensive two-dimensional gas chromatography (GC × GC) to investigate the geochemistry of the Santa Barbara oil/methane seeps. With the power of GC × GC, we wish to provide unprecedented insights into the processes that act on petroleum in subsurface and surface environments. The results of this work should not be limited to Santa Barbara and ideally can be applied when studying other seeps as well in petroleum exploration and oil spill studies. The Santa Barbara seeps are a natural laboratory and perfect for studying petroleum because of the large volumes of oil seeping, its proximity to critical economic, residential, and recreational areas, and existing collaborative ties with Professor David Valentine at the University of California at Santa Barbara.

**Results:** We have detected with the *DSV Alvin* tar mounds along the California coastline. In particular, we have found “Il Doumo” and “Il Doumito”, which are about 10 km offshore and at a water depth of ~150 meters. Both mounds are closely associated with sediment-laden depressions, suggesting extrusion of liquid petroleum coupled with localized subsidence or gas blowout. They are about ~25 meters in height off the sea floor. Four tar samples were collected from each mound and all show remarkable similarity in their structure and chemical composition. Organic carbon comprises 50% of the mass for each sample, with sulfur, hydrogen and nitrogen comprising another 10% in aggregate. Inclusions of fine-grained sediment and microfossils comprise much of the residual mass. Analysis by GC × GC revealed a highly degraded material, the most we have ever observed in this region (Figure 1), and a suite of biomarkers consistent with Monterey Formation petroleum. We believe that this is the first report of extinct tar volcanoes along the Pacific margin of North America, and it provides an important window into the activity of cold seeps by capturing structures that are unlikely to be preserved in the geologic record.

The overall project is progressing better than expected.



**Figure 1.** GC×GC-TOFMS chromatograms of (a) crude oil from Platform Holly (Well #2342-15; 34°23.370 N by 119° 53.258 W), which is near the tar mounds, (b) crude oil collected as it was emerging from the sea floor and also near the mounds, and (c) tar mound sample collected from Il Duomo. Blue corresponds to the base-plane; the abundance of each molecule is proportional to height above the baseline. Notice the extreme changes in the oil composition in these samples. Only the most trace components in the reservoir oil (a) are present in the tar mound sample (c), revealing that most of the molecules (and mass) have been removed.

## WRIGHT STATE UNIVERSITY

Department of Chemistry  
Dayton OH 45435

**Grant:** DE-FG02-03ER15379

### **Fluid Chemistry, Surface Chemistry and Fracture Mechanics: An Investigation of the Connection at the Nanoscale**

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**Website:** [www.chm.wright.edu/higgins/research.html](http://www.chm.wright.edu/higgins/research.html)

**Objectives:** The project objectives at WSU are centered around two major hypotheses: (1) That the surface chemistry of minerals has a direct influence on the sliding resistance (i.e., friction) between a scanning probe microscope tip and mineral surfaces and (2) that the surface chemistry "signal" in friction force microscopy (FFM) may be amplified through adsorption of chelating surfactants to specific metal sites on mineral surfaces.

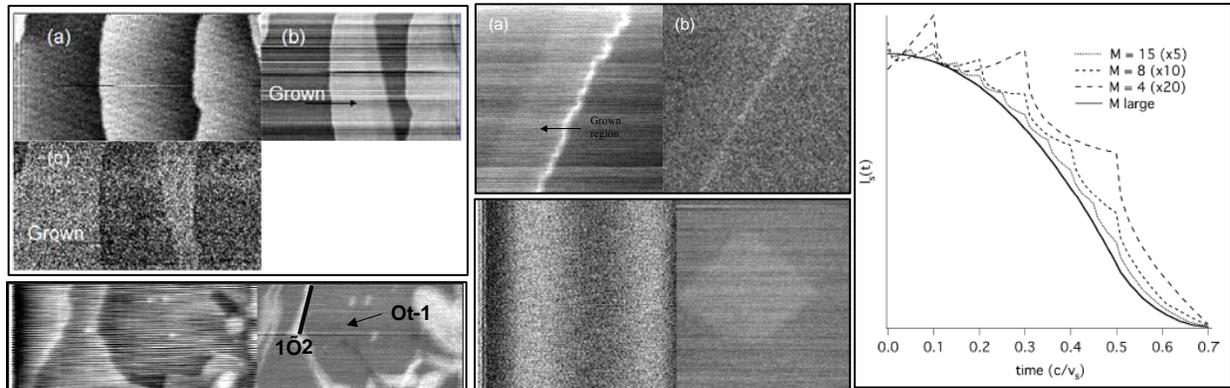
**Project Description:** The project at WSU has two main thrusts toward understanding the principal influences on surface chemistry of carbonate minerals upon exposure to aqueous solutions. These areas include the elucidation of lateral force contrast mechanisms in mineral/water interface systems and ligand/surfactant synthesis for application in chemical enhancement of surface properties. Our approach is to quantify the friction forces between an atomic force microscope (AFM) probe tip and carbonate mineral surfaces of interest using frictional force microscopy (FFM) and force modulation microscopy (FMM). In addition, the surfaces are fully characterized using fluid cell AFM measurements of growth and dissolution kinetics and x-ray reflectivity measurements. These methods of characterization allow us to describe both the thermodynamic properties of the surface layers as well as their atomic-scale structure and composition. The FFM and FMM measurements then enable us to relate the mechanical surface properties to the chemical and physical properties in a manner that could lead to future applications of the AFM as a surface chemistry-mapping tool with nanometer-scale resolution. The results from this project will improve our understanding of the surface chemistry of carbonate minerals relevant to surface and subsurface aquifer systems and on a distance scale (nanometers) that can be computationally modeled at the semi-empirical level.

**Results:** This emphasis, in the last project period, has included the elucidation of lateral force contrast mechanisms in the Atomic Force Microscope (AFM) and the study of morphological relaxation in response to solution perturbations. Addressing the mechanisms for lateral force contrast observed in the previous project period, Friction force microscopy (FFM) and force modulation microscopy (FMM) were used to study monolayer film mechanics on dolomite and calcite in aqueous solutions. The major findings in our study of  $\text{Ca}_x\text{Mg}_{1-x}\text{CO}_3$  films deposited on dolomite, based on FMM observations, were that the mechanical properties of the film (namely the film modulus) were far more significant in affecting the film friction than was the chemical (e.g., adhesive) interactions between the AFM probe and surface. Fig. 1 shows the film modulus (surface stiffness) maps of Ca-rich/dolomite surfaces (top left pane) and Mg-rich/dolomite surfaces (top center pane). The lower stiffness of the Ca-rich film

compared with dolomite is consistent with the observation of higher friction which is here interpreted to result from greater deformation of the softer material under the load of the AFM cantilever. Our working hypothesis, based on earlier observations, was that the relative size of the cations in mixed-cation strained films plays a major role in governing relative friction forces on carbonate minerals. By investigating Cd-rich (Fig. 1 – bottom left pane) and Sr-rich (bottom center pane) carbonate films on calcite, we tested this hypothesis, finding that both the smaller Cd ion (relative to Ca ion) and the larger Sr ion, when introduced into a carbonate film, both yielded relative increases in friction. Therefore, factors beyond ion size, such as film structure and surface charge need to be investigated.

Of particular relevance to the evolving chemistry of mineral-water interfaces is the conventional thought that steady-state approximations are valid, though these assumptions are rarely tested. In the response of any mineral-water interface to changes in environmental conditions, dissolution and mineralization rates undergo rapid changes as the reaction rates at step edges are governed directly by these environmental changes. These rapid responses at step edges tend to produce apparent "steady-state" reaction conditions with a very short relaxation time required for the achievement of the condition of steady reaction rate. This can often lead to incorrect assumptions of steady-state conditions when the production of steps by two-dimensional nucleation (pits in dissolution, islands in growth) factors into the development of surface morphology. Our investigations of the dissolution of celestite, used as a model mineral for these initial studies, have revealed that the topographic relaxation time under near equilibrium conditions can be much longer than the characteristic times of experimental investigations. Furthermore, there is a mechanistic connection between the non-linearity in dissolution rate versus undersaturation and topographic relaxation, a process consisting of changes in the surface microtopography (i.e., step density) resulting from changes in solution conditions. The surface topography (related to total step length or step density), whose lifetime near equilibrium is governed by the step speed ( $v_s$  in Fig. 1, right pane) and the distance between line defects ( $c$  in Fig. 1, right pane), dramatically influenced subsequent near equilibrium dissolution rates. This study led to predicted relaxation times on the order of days for the celestite-water interface, but with simple extension of the concept to the common rock-forming minerals (e.g., feldspars), relaxation times on the order of hundreds of years could be expected. The observations that steady-state approximations may require years to centuries to be valid have serious implications in the prediction of physicochemical behavior in geological systems such as those proposed to be used in CO<sub>2</sub> sequestration and in long-term hazardous waste storage.

Initial syntheses and testing of alkyliminodiacetates (i.e., chelating surfactants) were carried out to begin evaluation of sorptive properties of these ionic species. Dodecyliminodiacetate (DIDA, structure shown in Fig. 1, bottom-left) was dissolved in alkaline aqueous solution (0.05 mM) and a calcite surface was exposed to this solution. AFM topographic and friction force images (Fig. 1, bottom-left) revealed that the binding of these surfactant molecules to calcite was highly favorable, producing surfactant islands of 1.8 nm height (left image) and that these islands had distinctly lower friction than the native calcite (right image). With future developments of this methodology, it may be possible to map surface chemistry on mineral surfaces using AFM as a nanometer-scale chemical probe. This work is an important step in advancing the state-of-the-art in *in-situ* analytical mineral surface science through the synergistic combination of synthetic chemistry, complexation and surfactant chemistry, and *in-situ* probe microscopy.



**Figure 1.** Top left pane:  $\text{Ca}_{0.75}\text{Mg}_{0.25}\text{CO}_3$  film on dolomite. (a) topography, (b) friction, (c) surface stiffness. Top center pane: High-Mg film on dolomite. (a) friction, (b) surface stiffness. Bottom left pane:  $\text{CdCO}_3$  overlayers on calcite. (left) topography, (right) friction map. Friction is highest on the 2<sup>nd</sup>  $\text{CdCO}_3$  layer (Ot-2) and lowest on calcite (Cal). Bottom center pane:  $\text{Sr}_x\text{Ca}_{1-x}\text{CO}_3$  film on calcite. (left) topography, (right) friction. Friction is higher in Sr-bearing film. Right pane: Time-dependent step length,  $l_s(t)$ , with varying depths ( $M$ ) of etch pits. The surface topography relaxes on a timescale of  $\sim 0.5c/v_s$ , independent of  $M$ ;  $v_s$  = step speed,  $c$  = average spacing of linear defects.

## UNIVERSITY OF WYOMING

Department of Geology and Geophysics  
Laramie WY 82071

**Grant:** DE-FG02-06ER15825

### **Waveguide Scanning Photocurrent Microscopy (WaSPM): A New Molecular Imaging and Characterization Tool**

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**Objectives:** The objective of this research is to construct a microscope on the basis of the wavelength-dependent photocurrent response of an iron oxide-coated scanning probe tip interacting with the evanescent light at a waveguide-solution interface. The purpose is to image molecules (such as proteins) at the 10 nm scale.

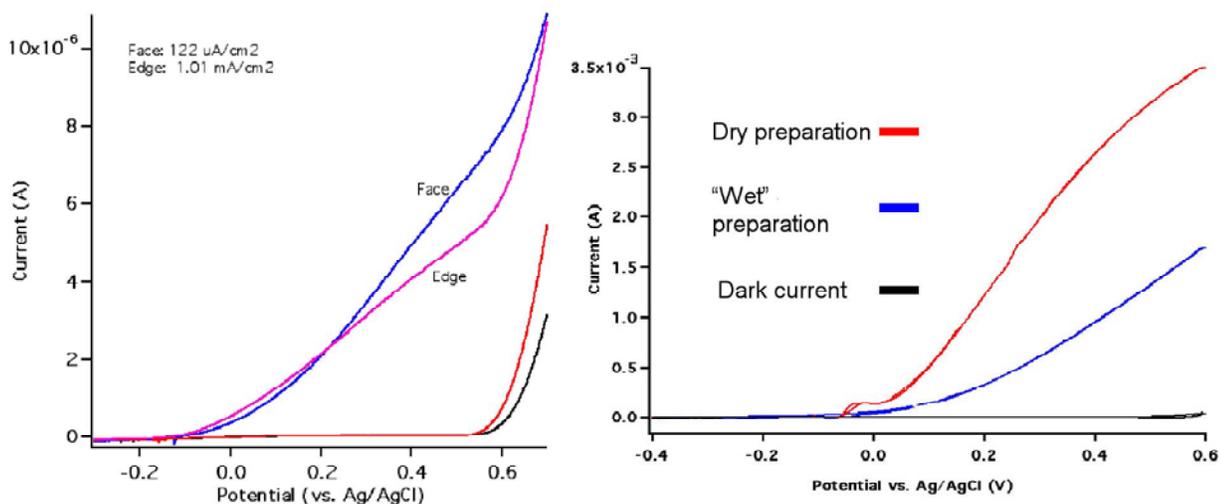
**Project Description:** The construction of the waveguide microscope depends on the successful accomplishment of a number of preliminary steps, including the manufacture of photosensitive tips using various techniques, and testing these tips for their ability to scatter light out of an evanescent light field at the interface between air and a waveguide in which in-coupled light undergoes total internal reflection and their ability to generate photocurrent. We are using chemical vapor deposition (CVD) techniques to form iron oxide (hematite) nanocrystalline films doped with Si that produce substantial photocurrent. Instead of making ultrasonic spray pyrolysis films, we have included within the scope of research the production of MnS and WO<sub>3</sub> films by CVD as alternative approaches if the hematite films prove to be less efficient than ultimately needed at low light intensities.

**Results:** We have acquired the necessary waveguide apparatus, laser, and other equipment, refurbished an existing laser, and set up two new CVD systems in a lab using three fume hoods. We have now manufactured photosensitive tips for the proposed Waveguide Scanning Photocurrent Microscopy (WaSPM). We have apparatus ready to test for light outscattering by these and other tips, and to detect outscattered light. The first full WaSPM apparatus is currently under construction in our machine shop, and will incorporate a commercial electrochemical STM system with the total-internal reflection laser configuration in order to attempt our first microscopic images. A key part of the research is the optimization of the photoelectrochemical properties of the tip. Findings regarding the photocurrent-generating properties of the tip include:

- a) Further work on the anisotropy of photocurrent generation in hematite. In the figure below, the left-hand panel shows that a platelet of hematite produces about the same photocurrent when the large-area crystal face (001) is exposed to a Xenon lamp light source as does the far smaller crystal edge (not a single crystal face), with the result that photocurrent density is between 5 and 10 times greater from illuminated crystal edges than from (001) faces. This is most likely simply a result of anisotropic conductivity in hematite affording more efficient charge separation in directions perpendicular to the [001] direction.
- b) Another problem in optimization is the limitation of photocurrent density by recombination mediated by an "intra-gap" state. One hypothesis is that water impurities, probably in the form of internal OH defects, are the origin of at least some of the intragap states. Hematite films made by atmospheric

pressure chemical vapor deposition using water-saturated air as well as dry air indeed show a difference in photocurrent.

c) Our current “best” Si-doped hematite films rival the best that have been reported in the recent literature with regard to photocurrent generation. This development has implications for solar energy generation as well as the WaSPM microscope.



## UNIVERSITY OF WYOMING

Department of Geology and Geophysics  
Laramie WY 82071

**Grant:** DE-FG02-06ER15823

### **Redox Interaction of Cytochromes and Bacteria with Oxide Surfaces: Probing Redox-Linked Conformation Change**

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**Objectives:** The objective of this research is to better understand the role of conformation change in electron transfer from cytochromes to minerals, a process that underpins respiratory metal reduction by bacteria in nature and in bioremediation strategies, including reductive immobilization of radioactive contaminants.

**Project Description:** This project aims to better understand how outer-membrane and other cytochromes from dissimilatory metal-reducing bacteria change conformation in relation to redox reactions, adsorption, and interaction with other proteins. Conformation change is directly related to protein enzymatic function. We compare the electrochemical behavior of isolated proteins with that of whole-cell suspensions. We focus on cytochromes from two well-characterized organisms, *Shewanella oneidensis* MR-1 and *Geobacter sulfurreducens*. These bacteria are directly implicated in electron transfer to metals and are thus of great interest not only in natural redox cycling of metals but also in bioremediation strategies for contaminant metals including Cr, U, Tc, Np, and others of interest to the U.S. Department of Energy. We are using a combination of electrochemical, scanning probe microscope, optical waveguide lightmode spectroscopy (OWLS), and quartz crystal microbalance (QCM) techniques to detect structural changes in adsorbed cytochromes.

#### **Results:**

1) We have completed an electrochemical study of isolated and purified OmcA and MtrC (provided courtesy of Liang Shi and Brian Lower of PNNL), as well as of both wild-type and OmcA, MtrC, and OmcA+MtrC deletion mutants of *Shewanella oneidensis* MR-1 under aerobic and anaerobic conditions. Cyclic voltammetry of isolated proteins is similar to that of the whole organisms. The midpoint potentials of redox peaks are slightly more negative for isolated OmcA and for the MtrC-deficient mutant (which is presumably not deficient in OmcA) than for MtrC and the OmcA-deficient mutant. The double-deletion mutants show no electrochemical activity.

2) Comparative Optical Waveguide Lightmode Spectroscopy (OWLS) and Quartz Crystal Microbalance with Dissipation (QCM-D) studies are providing a window on the different properties of outer-membrane vs. periplasmic cytochrome. We will concentrate, in this summary, on this comparative data. We have found some very substantial differences in the behavior of MtrC as compared to OmcA. Our findings include:

a) MtrC desorbs readily from oxide surfaces in response to dilution into protein-free buffer, whereas OmcA does not.

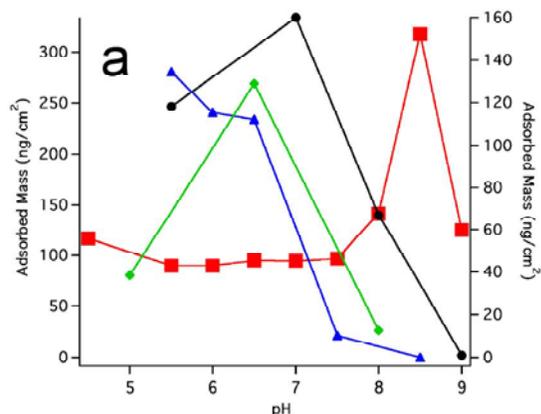
b) MtrC is a very low density protein in the adsorbed state – of the total adsorbed mass, only about 23% is polypeptide and cofactors in the protein. The remainder of the adsorbed mass is the water and

solutes that adsorb to the surface in association with the protein. This percentage is larger than those reported for most other proteins.

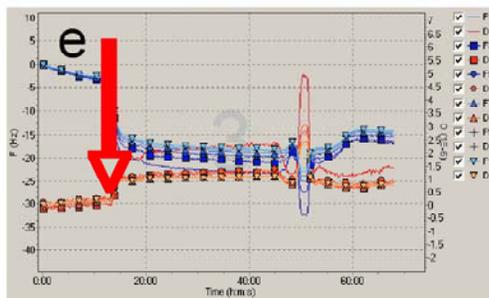
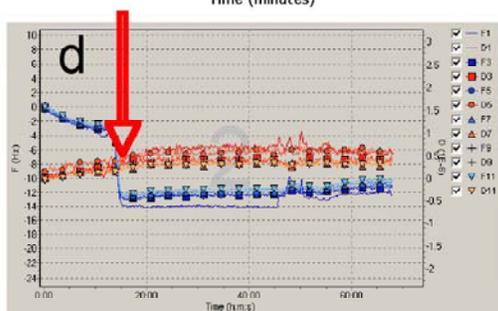
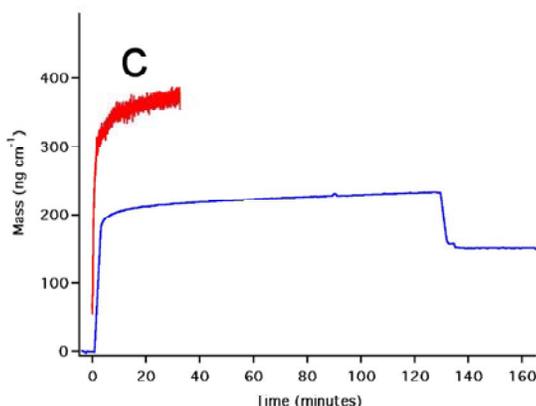
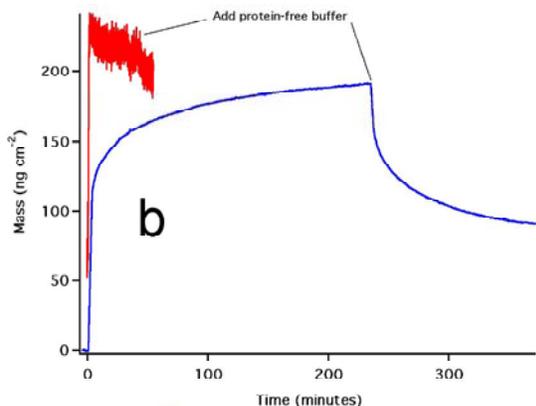
c) MtrC adsorbs to alumina in a different pH range from OmcA (Fig. a).

d) The periplasmic protein PpcA from *Geobacter sulfurreducens* is a compact protein that carries little solvent with it (18%), desorbs readily, and appears to contract slightly upon adsorption (Fig. b), whereas the outer-membrane cytochrome OmcB from the same organism is less dense than PpcA (37% solvent; Fig. c), though it desorbs upon dilution more than does OmcA from *Shewanella oneidensis* MR-1.

e) Energy dissipation results are consistent with the OWLS/QCM results, with relatively little dissipation for PpcA (indicating a more rigid and compact adsorbed molecule; Fig. d) and more dissipation for OmcB (indicating a “floppier” adsorbed molecule; Fig. e).



Figures: a) OWLS adsorption data for OmcA on  $\text{Al}_2\text{O}_3$ , high ionic strength (blue) and low ionic strength (black), and on  $\text{Fe}_2\text{O}_3$  (green), and for MtrC on  $\text{Al}_2\text{O}_3$  (red, right-hand axis); b) PpcA on  $\text{Al}_2\text{O}_3$ , QCM (red) and OWLS (blue); c) OmcB on  $\text{Al}_2\text{O}_3$ , QCM (red), OWLS (blue); d) and e) QCM-D (different overtones = different colors) showing little dissipation for PpcA and more dissipation for OmcB.



## YALE UNIVERSITY

Departments of Geology & Geophysics and Physics  
New Haven CT 06520

**Contract:** DE-FG02-05ER15741

### **Freezing in Porous Media: Phase Behavior, Dynamics and Transport Phenomena**

*John S. Wettlaufer, [john.wettlaufer@yale.edu](mailto:john.wettlaufer@yale.edu), (203) 432-0892.*

**Objectives:** The premelted liquid layers on ice are ubiquitous and important aqueous films. They exist over a wide range of thermodynamic and chemical environments, from the depths of glaciers to stratospheric ice clouds and are particularly important in the dynamics and thermodynamics of soils. Premelted films exist in all classes of solids, where they facilitate crystal growth from vapor and the coarsening of polycrystals. Many experiments have demonstrated that the melting temperatures of materials are depressed below their bulk values,  $T_m$ , in porous media. Our objectives are to understand the role of premelting in controlling the volume fraction of liquid water in subfrozen model and actual soils and then quantify their underlying role in influencing the dynamical and transport phenomena that drive frost heave and related porous media behavior in the natural environment.

**Project Description:** Our approach involves advancing the tenets of the condensed matter physics of the system using theory and experiment and ultimately to bring these advances to bear on the environmental setting. Our experiment investigates the notion that a particle in a partially frozen porous media should undergo Brownian motion within its premelted jacket. As the sample temperature decreases, the premelted layer will shrink and the diffusion constant characterizing the particle's motion should increase. We use Dynamic Light Scattering (DLS) to determine the diffusion coefficient as a function of temperature. DLS encompasses a group of non-invasive optical techniques that have been employed widely in the study of microscopic dynamics of soft condensed matter. All DLS methods involve studying coherent light scattered by a sample. As the light passes through the sample, it is scattered by many different particles. Each scattering event introduces a phase shift, which in the image plane, produce an interference pattern called speckle. As the scatterers move, the phase shift induced by each one changes and the speckle pattern varies in time. The time required for the intensity of a particular speckle spot to become decorrelated from its initial value is related to the effective diffusion coefficient of the particles. Our experimental approach is to use a form of DLS called x-ray photon correlation spectroscopy (XPCS) to explore the dynamics of silica particles frozen inside pure ice at a uniform temperature. The experiments are done at the Advanced Photon Source at Argonne as our modality of DLS. Our theoretical approaches vary widely, from the theory of multiple scattering to the statistical mechanics of confined media.

**Results:** In consequence of our first experiments at the Advanced Photon Source (FY06 Summary) a number of results have led us to (a) develop a system for the study of coarsening here at Yale and to consider its applicability to the problem of subglacial dynamics and thermodynamics (b) investigate the dilute limits of suspensions during directional solidification and (c) harness what we had worried about as radiative heating compromising our system and to use it to advance a problem of materials processing. Therefore, we will return to the APS for further XPCS experiments this March.

(a) Both at the APS and at Yale we have been studying the solidification of model solutions of monodisperse silica spheres of approximately 0.1 micron radius. A surprising consequence of our desire to understand the role of ice grain coarsening in the nature of our scattering data was the recognition that our experimental study can be used as an analogue for subglacial debris entrainment by ice growing into supercooled water. Field studies have identified several processes by which glaciers and ice sheets can accumulate debris-rich basal ice. Although significant effort has gone into modeling these processes and the inferred effects on glacier dynamics, there is a dearth of laboratory investigations. In particular, in several field settings debris entrainment by frazil ice growing in glaciohydraulically supercooled water channels has been suggested as the source of the dirty basal ice. However, the physical mechanisms by which frazil ice actually traps the sediment and then incorporates it into the basal ice remain unclear. In order to clarify this process, we have frozen our XPCS solutions of silica spheres dispersed in water supercooled to between -2 and -6°C. As the ice coarsens over several days, particles migrate through the ice due to temperature gradient induced thermomolecular pressure and they move along with the coarsening grain boundaries.

(b) We have proposed a mechanism for the formation of ice lenses in colloidal clays based on an instability of the ice-clay interface. A mathematical model of freezing saturated montmorillonite is developed which predicts that, given freezing conditions typical of the field, the clay can become thermodynamically supercooled in the same sense as a binary solution such as salt water. We predict that in this case the ice-clay interface is unstable to the formation of a mixed-phase region composed of ice lenses and unfrozen clay.

(c) While we have used silica particles because the density of silica is significantly different from that of water ( $2.21\text{g/cm}^3$  vs.  $1\text{g/cm}^3$  at  $0^\circ\text{C}$ ) and hence because x-rays scatter from electrons the difference in electron density facilitates scattering. However, because there is also absorption, reexamination of our on XPCS data and the calibration of the on site RTD probe led us to consider the importance of radiative heating. While this creates a problem for our understanding of the degree of departure from bulk coexistence, we have also discovered that this effect can be harnessed in another context: We developed a general theory that exploits interfacial premelting to control the distribution of insoluble particles within a host matrix, and to thereby tailor the bulk electrical and mechanical properties of a solid mixture. The redistribution of particles throughout the premelting host material is achieved through careful radiative control of the local temperature field. The particle migration is described by an expression for the effective Brownian diffusion coefficient  $D$  in terms of the appropriately scaled Stokes-Einstein diffusivity  $D_0$  and what is referred to as the thermodynamic buoyancy coefficient, as functions of temperature, particle radius and intermolecular forces.

## YALE UNIVERSITY

Department of Geology and Geophysics  
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**Grant:** DE-FG02-01ER15173

### **Plants, Weathering, and the Evolution of Atmospheric Carbon Dioxide and Oxygen**

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#### **Objectives:**

1. The effect of plants on CO<sub>2</sub> uptake via weathering.
2. The evolution of CO<sub>2</sub> and O<sub>2</sub> over the past 540 million years
3. The effect of varying CO<sub>2</sub> on paleoclimate.

**Project Description:** Field work in the Cascades Mountains of Washington State was completed to examine the weathering of silicate rocks by conifer vs deciduous trees. This included collection of soils and intrusive and extrusive rocks in direct contact with tree roots of varying ages. Rock surface morphology was examined and geochemical and petrological analysis of the rocks and cores is ongoing. Long-term laboratory experiments that parallel this fieldwork have been set up and are nearing completion.

Steady state computer modeling for CO<sub>2</sub> and O<sub>2</sub> over Phanerozoic time (past 540 million years) continued with the construction of a combined interactive model (GEOCARBSULF) that emphasizes rapid recycling via deposition, uplift and erosion. Results for O<sub>2</sub> over time were compared to major evolutionary events, and the model was expanded to examine the effects of varying basalt weathering on the level of atmospheric CO<sub>2</sub>. Results for CO<sub>2</sub> were also compared to independent proxy values to deduce past climate sensitivity to changes in atmospheric CO<sub>2</sub>.

**Results:** Initial electron microprobe analysis and bulk soil chemistry suggests that the weathering of magnesian minerals in granitic rocks by conifers may be more rapid than that by maple and aspen trees. The opposite may be true for calcian minerals. This has major bearing on the evolution of atmospheric CO<sub>2</sub> because the rise of angiosperms between 130 and 80 million years ago may or may not have had an important effect on atmospheric CO<sub>2</sub> and its uptake during silicate weathering.

Use of new carbon isotopic data and consideration of rapid recycling in the GEOCARBSULF model lead to the conclusion that a secondary maximum of atmospheric O<sub>2</sub> occurred near the Silurian/Devonian boundary. This coincided with the first invasion of the land by organisms, chiefly arthropods, and may be a contributing cause for this major evolutionary event. Consideration of varying amounts of basalt weathering over time has resulted in calculation of lower values for atmospheric CO<sub>2</sub> during the Jurassic period which coincide in time with cooling episodes. Calibration of the GEOCARBSULF model against proxy CO<sub>2</sub> data for the past 420 million years has resulted in the conclusion that the warming response of global mean temperature to a doubling of CO<sub>2</sub> was approximately 3°C. This agrees with many independent estimates of future global greenhouse warming.

## YALE UNIVERSITY

Department of Geology and Geophysics  
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**Grant:** DE-FG02-07ER15838

### Code and Documentation Release for Fluid-Rock Interaction Models

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**Website:** <http://www.geology.yale.edu/crustal-fluids>

**Objectives:** The objective is to prepare code and documentation for a public release of several reactive-transport models. Included in the release will be four separate codes, for: oxygen transport and consumption in shales, weathering, metamorphism, and isotope diffusion.

**Project Description:** Code and documentation on how to use the codes are being prepared for release to the public. Each of the four crustal fluid flow models planned for release by late 2007 involves reactions and transport in porous media. Each also involves kinetic control of mineral reactions and dynamic permeability based on sub-grid-scale grain models. The models include: 1) KINFLOW: An aqueous phase flow and transport in two dimensions (2D) for simple mineral reactions involving the elements Na-Al-Si-O-H in heterogeneous media; 2) META-KINFLOW: A supercritical H<sub>2</sub>O-CO<sub>2</sub> fluid flow and reaction model in 2D for metamorphism of a dolomite-quartz initial composition; 3) DIG: A model for intragranular diffusion of isotopes or trace elements during recrystallization; and 4) OMPYR: A model for oxygen diffusion and reaction in soils that accompany weathering of black shales.

**Results:** The various codes are being prepared for public release. The input files have been simplified and a “how-to” usage manual for each code is being prepared. In-line documentation of the Fortran codes has been extended so that users can gain a better understanding of reactive-transport codes. Both KINFLOW codes allow the calculation of flow and transport in heterogeneous media in 2D with dynamic changes in mineral compositions and permeability that affects the flow field. To efficiently and repeatedly solve Darcy’s law for the evolving flow field, the user may choose between a sparse-matrix technique or a spectral-transform technique (each accommodate a variety of boundary conditions). Heterogeneous permeability creates distributions of reaction rates that imply that laboratory kinetic rates may be applicable to field problems without surface area corrections. The DIG code involves solving a moving boundary problem at the mineral surface when grains are growing or dissolving. The solution of equilibrium fractionation at the fluid-mineral surfaces does not preclude the calculation of the kinetic isotope effect. The OMPYR code has been used to estimate oxygen consumption of eroding shales, with implications for models of the long-term evolution of atmospheric oxygen. For release under a BSD or Open Source free license, I have encountered a copyright problem with some subroutines for solving linear systems, so I am incorporating other choices for these routines.

**DOE/OBES Geosciences Research: Historical Budget Summary**  
**(Thousands of dollars)**

ON-SITE INSTITUTION	FY03	FY04	FY05	FY06	FY07
Argonne National Laboratory	445	480	535	758	461
Idaho National Laboratory		50	50	50	60
Los Alamos National Laboratory	1353	1409	1320	963	1050
Lawrence Berkeley National Laboratory	2045	2758	3240	2939	4063
Lawrence Livermore National Laboratory	1523	1598	1335	1141	1270
Oak Ridge Institute for Science and Education				105	12
Oak Ridge National Laboratory	1190	1250	2075	1750	1750
Pacific Northwest Laboratory	875	920	860	910	975
Sandia National Laboratory	1355	1274	980	975	1130
total, on-site published	8786	9739	10395	9591	10771
total, off-site published	10513	10410	10492	9544	9869
total, operating published	19299	20149	20887	19135	20640
total, equipment	1023				
Total GEOSCIENCES-published	20322	20149	20877	19135	20640
OFF-SITE INSTITUTION					
Alabama, Univ. of (Dixon)				47	48
Alabama, Univ. of (Dixon)					58
American Chemical Society (Brandes)		5			
American Society for Microbiology (Colwell)			5		
Arizona, Univ. of (Roth)		25			
Arizona State Univ. (Shock)		239	101		
Arizona State Univ. (Hervig/Williams)	108	133	132	135	

Boston Univ. (Klein)	132	126	130	134	
Caltech (Stolper)	156	162		167	172
Caltech (Wasserburg)	225	215	200		
Calif., Univ. of Berkeley (Banfield)			200	200	200
Calif., Univ. of Berkeley (Banfield)		150	153	123	
Calif., Univ. of Berkeley (Helgeson)	164	163	167		100
Calif., Univ. of Berkeley (Wenk)			150	150	150
Calif., Univ. of Davis (Rock)	171				
Calif., Univ. of Davis (Navrotsky)	198	202	194	197	215
Calif., Univ. of Davis (Rustad)		97	78	82	85
Calif., Univ. of Davis (Rustad)			136	137	68
Calif., Univ. of Davis (Casey)	109	113	319		135
Calif., Univ. of Davis (Rundle)	141	135	143	151	
Calif., Univ. of Los Angeles (Harrison/McKeegan)	135	148	79		
Calif., Univ. of Santa Barbara (Meiburg)	66				
Calif., Univ. of Santa Barbara (Boles)	78	86	79	95	95
Calif., Univ. of Santa Cruz (Wu)	388	306	318	327	
Calif., Univ. of San Diego (Weare)	125	125		269	
Chicago, Univ. of (Sutton/Rivers)	550	575	600	697	718
Chicago, Univ. of (Sutton)		143	125	148	139
Chicago, Univ. of (Richter)	99	102	138	143	148
Clark Univ. (Kudrolli)	45	47		59	54
Clay Minerals Society (Cygan)					10
Colorado School of Mines (Batzle)	140	117	114		
Colorado School of Mines (Tsvankin)	239	249	150		75
Colorado School of Mines (Snieder)				97	101
Colorado School of Mines (Benson)					79

Colorado, Univ. of (Rajaram)	70	72			
Colorado, Univ. of (Spetzler)	143	155	55	58	60
Connecticut, Univ. of (Torgersen)	35	33		32	34
Delaware, Univ. of (Wood)	138	142			
Florida, Univ. of (Ladd)	89		155	108	111
George Washington Univ. (Teng)			98		48
George Washington Univ. (IPA Lesmes)		225	150	6	5
Georgia State Univ. (Elliott)	21		22		
Georgia Tech (Stack)					210
Gordon Res. Conf. (Kronenberg, Jessell)		10			
Gordon Res. Conf. (Hirth)				10	
Harvard Univ. (Martin)	85	83	81	96	99
Houston, Univ. of (Weglein)			101		51
Idaho, Univ. of (Wood)	10	10	10		
Idaho State Univ. (Magnuson)				88	90
Illinois, Univ. of (Kirkpatrick)	233	241	248	216	
Illinois, Univ. of (Bethke)	214	92	270		135
Illinois, Univ. of Chicago (Sturchio)	59	60	62	51	53
Illinois, Univ. of Chicago (Nagy)		148	145		
Indiana, Univ. of (Ortoleva)	124				
Indiana, Univ. of (Schimmelman)	119	112	119	141	133
Johns Hopkins Univ. (Garven)	89	80	88	124	
Johns Hopkins Univ. (Veblen)	160	289	205	205	250
Johns Hopkins Univ. (Sverjensky)	140	137	153	158	163
Johns Hopkins Univ. (Jahren)				101	105
Louisiana State Univ. (White)	40	46			
Louisiana State Univ. (Dutrow)	9	9	9		

Maryland, Univ. of (Lower)	67				
Maryland, Univ. of (Tossell)	79	99	99		
Maryland, Univ. of (Zhu)					130
Mass. Inst. Tech. (Evans)	209	222	235	304	318
Mass. Inst. Tech. (Rothman)	158	160		160	168
Mass. Inst. Tech. (Durham)					40
Massachusetts, Univ. of (Boutt)			145		41
Michigan Tech Univ. (Turpening)	114		144		
Mineralogical Society of America (Speer)	30	20		35	10
Mineralogical Society of America (Speer)				5	
Minnesota, Univ. of (Kohlstedt)		38	39	176	185
NAS/NRC (Schiffries/DeSouza)		90	90	90	90
NAS (Linn)				200	
Nevada, Univ. of (EPSCOR - McCall)	6				
New England Res. (Brown)	199	206	100		
New Mexico Inst. Min. Tech. (Wilson)	101	108			
NY, City Univ. of CC (Koplik)	98	102		107	109
NY, City Univ. of CC (Makse)	85	85		85	100
NY, State Univ. of Stony Brook (Schoonen)	65	66		87	83
NY, State Univ. of Stony Brook (Wong)	120	124	128	125	128
NY, State Univ. of Stony Brook (Lindquist)	64		64	87	66
North Texas, Univ. of (Bagus)		35	35	35	50
Northwestern Univ. (Rudnicki)	120	118	123	113	114
Northwestern Univ. (Geiger)			3	49	50
Notre Dame, Univ. of (Maurice)	174	178			
Notre Dame, Univ. of (Maurice)		6			
Ohio State Univ. (Lower)		71			

Ohio State Univ. (Allen)		41	42	44	80
Oklahoma, Univ. of (Elmore)	103		47		
Oregon State Univ. (Haggerty)					
Oregon State Univ. (Egbert)	89	86		98	95
Penn State Univ. (Elsworth)	98				
Penn State Univ. (Brantley)	145		174	176	223
Penn State Univ. (Brantley)		9			
Princeton Univ. (Peters)			114	160	169
Purdue Univ. (Pyrak-Nolte)	105	109		288	
Rensselaer Polytech. Inst. (Newell)	45	47			
Rensselaer Polytech. Inst. (Watson)	199	247	208	215	
Society of Exploration Geophysics (Smith)				5	
South Carolina, Univ. of (Wilson)		50	54	54	
Southern California, Univ. of (Maxworthy)	84				
Stanford Univ. (Mavko)	149	150			
Stanford Univ. (Borja)	99		99	102	110
Stanford Univ (Knight)	143	139	146		
Stanford Univ. (Nur)	200	208	217		207
Stanford Univ. (Pollard/Aydin)	267	261	261		273
Temple Univ. (Strongin)	87	91		91	83
Tennessee, Univ. of (Thonnard)	146				
Texas A&M Univ. (Morse)	130	133	135	157	149
Texas A&M Univ. (Datta-Gupta)	130	138	140	143	142
Texas, Univ. of (Katz)		71	75	78	75
Texas, Univ. of (Laubach)	196		227	197	241
Texas, Univ. of Dallas (McMechan/Bhattacharya)	95	96			
Texas Tech Univ. (Graham)	9				

Tufts Univ. (Garvin)					227
Virginia Tech (Rimstidt)	114	118	124		
Virginia Tech (Dove)	126		178	226	250
Virginia Tech (Hochella)		104	98	122	127
Wisconsin, Univ. of (Alumbaugh)	101	96			
Wisconsin, Univ. of (Haimson)	106				
Wisconsin, Univ. of (Goodwin)			108		73
Wisconsin, Univ. of (Valley)		204	210	217	234
Wisconsin, Univ. of (Gilbert)					325
Woods Hole OI (Whelan)	206	204			
Woods Hole OI (Zhu)	46	48	50	61	
Woods Hole OI (Seewald)		179	177	184	
Woods Hole OI (Reddy)				157	164
Wright State Univ. (Higgins)	70	71	73	98	110
Wyoming, Univ. of (Eggleston)	52	45	46		
Wyoming, Univ. of (Eggleston)				154	131
Wyoming, Univ. of (Eggleston)				100	102
Yale Univ. (Rye/Bolton/Ague)	327		157		
Yale Univ. (Wettlaufer)			115	100	100
Yale Univ. (Berner)	110	130	130	130	
Yale Univ. (Bolton)					77
Other				1	
OFF-SITE TOTALS	10513	10410	10492	9544	9869