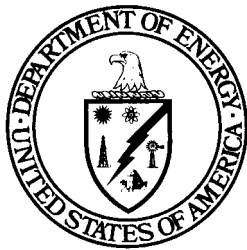


Summary of FY 2004 Geosciences Research

May 2008



U.S. Department of Energy

Office of Science
Office of Basic Energy Sciences
Chemical Sciences, Geosciences, and Biosciences Division
Washington, D.C. 20585

TABLE OF CONTENTS

TABLE OF CONTENTS	2
FORWARD	10
THE GEOSCIENCES RESEARCH PROGRAM IN THE OFFICE OF BASIC ENERGY SCIENCES.....	11
ARGONNE NATIONAL LABORATORY.....	12
Mineral-Fluid Interactions: Synchrotron Radiation Studies at the Advanced Photon Source.....	12
IDAHO NATIONAL LABORATORY.....	13
Multi-Resolution Structure and Reactivity of Kinetically Roughened Oxide Surfaces	13
LAWRENCE BERKELEY NATIONAL LABORATORY.....	14
Center for Isotope Geochemistry	14
Reactive Chemical Transport in Structured Porous Media.....	14
Clay Mineral Surface Geochemistry.....	15
Rate Controls in Chemical Weathering: A Reactive Transport Approach	15
Prediction and Evaluation of Coupled Processes.....	16
Molecular-Level Studies of Fe-Al Oxyhydroxide Coating Formation on Quartz.....	16
Experimental, Theoretical, and Model-Based Studies of Crystallographically Controlled Self-Assembly During Nanocrystal Growth.....	17
Development of Isotope Techniques for Reservoirs.....	18
Kinetic Isotope Fractionation.....	18
Imaging Shear in Rocks	19
Scattering and Intrinsic Attenuation in Rock with Heterogeneous Multiphase Fluids.....	20
Permeability Dependence of Seismic Amplitudes.....	20
Imaging Permeability and Fluid Mobility.....	20
Air-Derived Noble Gases in Sediments.....	21
Colloid Transport in Unsaturated Fractured Rocks and Porous Media	21
Faster and Better Solutions to Three Dimensional Electromagnetic Inversion Problems.....	22
LAWRENCE LIVERMORE NATIONAL LABORATORY.....	23
Investigation of the Physical Basis for Biomineralization.....	23
Mineral Dissolution and Precipitation Kinetics.....	23
Reactive Transport of CO ₂ Rich Fluids	24
Geological CO ₂ Sequestration	25
Kinetic Isotope Fractionation.....	25
Analysis of Physical Properties for Heterogeneous Rocks Containing Fluids.....	26
Electrical Properties of Rocks.....	27
Deposition of Carbons	27
Rheology of the Earth's Interior.....	28

Three Dimensional Analysis of Seismic Signatures & Characterization of Fluids & Fracture in Anisotropic Formations	28
Application of Geophysical Tomographic Imaging	29
LOS ALAMOS NATIONAL LABORATORY.....	31
High Resolution/High Fidelity Seismic Imaging.....	31
Nonlinear Elasticity in Rocks	31
Elastic Wave Effects on Colloid Interactions and Their Influence on Porous Fluid Transport	32
Summer of Applied Geophysical Experience (SAGE).....	33
Improved Sensitivity Uranium-Series Measurements	33
Controls on Molecular-Scale Microbial Responses to Metals: Interactions of Bacteria, Metals and Environmental Nanoparticles.....	34
Energy Transport in Space Plasmas.....	34
OAK RIDGE NATIONAL LABORATORY	35
Nanoscale Complexity at the Oxide/Water Interface	35
Fundamental Research in Isotope Geochemistry: Experimental, Molecular-Based Simulation, and Neutron-Scattering Studies of Fluids and Minerals.....	35
Ion Microprobe Studies of Fluid Rock Interactions – Multi-Scale Studies of Fluid-Rock Interaction.....	36
Mechanisms and Rates of Isotope Exchange in Mineral-Fluid Systems – Investigation of Mineral Reaction Zones and Associated Interfaces	36
Experimental Studies of Hydrothermal Fluid Speciation and Fluid/Solid Interactions Employing Potentiometric Methods – Experimental Studies of Hydrothermal Processes Employing In Situ pH Measurement.....	37
Volumetric Properties, Phase Relations & Reaction Kinetics - Molecular Structures and Adsorption Behavior of CO ₂ -CH ₄ +H ₂ O Fluids at Upper Crustal Temperatures and Pressures.....	37
Experimental Studies of Fundamental Stable Isotope Exchange in Experimental Mineral-Fluid Systems - Nanoscale Structure and Dynamics of Biomolecule - Mineral Interactions in Solution and their Role in Biomineralization.....	38
PACIFIC NORTHWEST NATIONAL LABORATORY	39
Electron Transfer at the Fe(111) Oxide-Microbe Interface	39
Molecular Basis for Microbial Adhesion.....	39
Multi-Resolution Structure and Reactivity of Kinetically Roughened Oxide Surfaces	40
Reaction and Transport of Toxic Metals in Rock-Forming Silicates at 25°C	40
Experimental, Theoretical, and Model-Based Studies of Crystallographically Controlled Self-Assembly During Nanocrystal Growth.....	41
Computational Investigation of Acid-Base, Surface Complexation and Oxidation/Reduction Mechanisms	42
First Principles Simulation of the Supercritical Behavior of Ore-Forming Fluids.....	43
SANDIA NATIONAL LABORATORY/ALBUQUERQUE.....	44
Molecular Simulations of Layered Minerals & Their Interactions with Hazardous Material	44
Metal-Anion Pairing at Oxide/Water Interfaces	44
Interactions of Pore Fluid Pressure	45
Micromechanical Processes in Porous Geomaterials	46
Role of Fracture Intersections in the Flow and Transport Properties of Rocks.....	46

Two-Phase Immiscible Fluid Flow	47
Laboratory Investigation of Constitutive Property Upscaling	48
PART II: OFF-SITE.....	49
AMERICAN CHEMICAL SOCIETY.....	49
Interfacial Phenomena: Linking Atomistic and Molecular Level Processes - Symposium March 28 - April 1, 2004	49
UNIVERSITY OF ARIZONA	50
Seismic Absorption and Modulus Measurements in Porous Rocks in Lab and Field: Physical and Chemical Effects of Fluids.....	50
ARIZONA STATE UNIVERSITY	51
Development of an Experimental Data Base and Theories for Prediction of Thermodynamic Properties of Aqueous Electrolytes and Nonelectrolytes of Geochemical Significance at Supercritical Temperatures and Pressures.....	51
A SIMS Study of the Chemical Dynamics of Organic/Inorganic Interactions in Sedimentary Basins.....	52
BOSTON UNIVERSITY.....	53
Collaborative Research: Analysis and Interpretation of Multi-Scale Phenomena in Crustal Deformation Processes: Using Numerical Simulations of Complex Nonlinear Earth Systems	53
CALIFORNIA INSTITUTE OF TECHNOLOGY	54
Infrared Spectroscopy and Stable Isotope Geochemistry of Hydrous Silicate Glasses.....	54
Isotope Tracer Studies of Diffusion in Silicates and of Geological Transport Processes Using Actinide Elements.....	55
UNIVERSITY OF CALIFORNIA, BERKELEY.....	56
Precipitation at the Microbe-Mineral Interface.....	56
Experimental, Theoretical, and Model-Based Studies of Crystallographically Controlled Self-Assembly During Nanocrystal Growth.....	57
Diffusion/Dispersion Transport of Chemically Reacting Species	58
UNIVERSITY OF CALIFORNIA, DAVIS.....	59
Thermodynamics of Minerals Stable Near the Earth's Surface.....	59
Size and Shape Effects on Surface Charging and Energetics of Goethite Nanoparticles.....	60
Tailored Crystal Growth and Impurity Control Using Nanocluster Adsorbates	61
Collaborative Research: Analysis and Interpretation of Multi-Scale Phenomena in Crustal Deformation Processes Using Numerical Simulations of Complex Nonlinear Earth Systems	62
Electrochemical Measurements and Theoretical Predictions of the Thermodynamic Properties of Carbonate and Oxide Minerals	63
UNIVERSITY OF CALIFORNIA, LOS ANGELES.....	64
Application of ⁴⁰ Ar/ ³⁹ Ar Thermochronometry and Ion Microprobe Stable Isotope Geochemistry to the Evolution of Petroleum Reservoirs and Hydrothermal Systems	64
UNIVERSITY OF CALIFORNIA, SANTA BARBARA.....	65

Fluid Flow in Faults: Processes and Effects from Modern and Paleo Systems in a Transpressional Tectonic Setting, Southern California.....	65
UNIVERSITY OF CALIFORNIA, SANTA CRUZ	66
High Resolution/High Fidelity Seismic Imaging and Parameter Estimation for Geological Structure and Material Characterization.....	66
UNIVERSITY OF CALIFORNIA, SAN DIEGO.....	67
First Principles Simulation of the Supercritical Behavior of Ore Forming Fluids	67
UNIVERSITY OF CHICAGO	68
GeoSoilEnviroCARS: A National Resource for Earth, Planetary, Soil and Environmental Science	
Research at the Advanced Photon Source	68
Synchrotron X-ray Microprobe and Microspectroscopy Research in Low Temperature Geochemistry	69
Kinetic Isotope Fractionation by Diffusion in Liquids	70
CLARK UNIVERSITY	71
Physics of Channelization: Theory, Experiment, and Observation	71
COLORADO SCHOOL OF MINES	72
Inversion of Multicomponent Seismic Data and Rock-Physics Interpretation for Evaluating Lithology, Fracture and Fluid Distribution in Heterogeneous Anisotropic Reservoirs.....	72
Optical Measurement of Seismic-Frequency Attenuation and Velocity Dispersion at In-Situ Conditions	73
UNIVERSITY OF COLORADO	74
Seismic Absorption and Modulus Measurements in Porous Rocks in Lab and Field: Physical and Chemical Effects of Fluids.....	74
The Physics of Two-Phase Immiscible Fluid Flow in Single Fractures and Fractured Rock	75
UNIVERSITY OF CONNECTICUT.....	76
Air-Derived Noble Gases in Sediments: Implications for Basin Scale Hydrology	76
UNIVERSITY OF DELAWARE	77
Development of an Experimental Data Base and Theories for Prediction of Thermodynamic Properties of Aqueous Electrolytes and Nonelectrolytes of Geochemical Significance at Supercritical Temperatures and Pressures.....	77
UNIVERSITY OF FLORIDA	78
Evolution of Surface Morphology During Dissolution of a Rough Fracture	78
GEORGE WASHINGTON UNIVERSITY	79
A Comparative Study of Dissolution Processes on Growth/Cleavage Surfaces and at Near/Far-from Equilibrium Conditions.....	79
GEORGIA STATE UNIVERSITY	80
Development and Application of a Paleomagnetic/Geochemical Method for Constraining the Timing of Burial Diagenetic Events	80

GORDON RESEARCH CONFERENCES	81
Rock Deformation Conference	81
HARVARD UNIVERSITY	82
Dissolution Mechanisms of the Carbonate Minerals	82
UNIVERSITY OF ILLINOIS	83
Computational and Spectroscopic Investigations of the Molecular Scale Structure and Dynamics of Geologically Important Fluids and Mineral-Fluid Interfaces	83
Field-Constrained Quantitative Model of the Origin of Microbial and Geochemical Zoning in a Confined Fresh-Water Aquifer	84
UNIVERSITY OF ILLINOIS AT CHICAGO	85
Mineral-Fluid Interactions: Synchrotron Radiation Studies at the Advanced Photon Source.....	85
Nanoscale Reactivity of Clays, Clay Analogues (Micas), and Clay Minerals	86
INDIANA UNIVERSITY	87
Significance of Isotopically Labile Organic Hydrogen in the Thermal Maturation of Source Rocks	87
JOHNS HOPKINS UNIVERSITY	88
Fluid Flow in Faults: Processes and Effects from Modern and Paleo Systems in a Transpressional Tectonic Setting, Southern California.....	88
Reactions and Transport of Toxic Metals in Rock-Forming Silicates at 25°C.....	89
Predictive Single-Site Protonation and Cation Adsorption Modeling.....	90
LOUISIANA STATE UNIVERSITY	91
3D Sedimentological and Geophysical Studies of Clastic Reservoir Analogs: Facies Architecture, Reservoir Properties, and Flow Behavior within Delta Front Facies Elements of the Cretaceous Wall Creek Member, Frontier Formation, Wyoming.....	91
UNIVERSITY OF MARYLAND	92
Theoretical Studies on Heavy Metal Species in Solution.....	92
MASSACHUSETTS INSTITUTE OF TECHNOLOGY	93
Collaborative Research: Evolution of Pore Structure and Permeability of Rocks under Hydrothermal Conditions	93
Physics of Channelization: Theory, Experiment, and Observation	94
MINERALOGICAL SOCIETY OF AMERICA	95
Support of MSA and GS Short Courses and the Companion Reviews Volumes.....	95
UNIVERSITY OF MINNESOTA	96
Rheology of Earth's Interior	96
NATIONAL ACADEMY OF SCIENCES	97
Board on Earth Sciences and Resources.....	97
NEW ENGLAND RESEARCH	98

Evolution of Fracture Permeability.....	98
NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY	99
A Systematic Study of Heterogeneity, Instrumentation, and Scale Using Physical and Numerical Experimentation.....	99
THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK	100
Fluid and Particulate Transport in Self-Affine Fractures	100
Stress-Dependent Acoustic Propagation and Dissipation in Granular Materials	101
STATE UNIVERSITY OF NEW YORK, STONY BROOK	102
An Inter-Disciplinary Study of the Surface Reactivity of Pyrite	102
Microscale Processes and Macroscopic Behavior of Porous Geomaterials	103
Pore Scale Geometric and Fluid Distribution Analysis	104
UNIVERSITY OF NORTH TEXAS.....	105
Reaction and Transport of Toxic Metals in Rock-Forming Silicates at 25°C	105
NORTHWESTERN UNIVERSITY.....	106
Interactions of Propagating Compaction Fronts and Pore Fluids in Porous Rock	106
UNIVERSITY OF NOTRE DAME	107
Controls on Molecular-Scale Microbial Responses to Metals: Interactions of Bacteria, Metals, and Environmental Nanoparticles.....	107
THE OHIO STATE UNIVERSITY.....	108
Metal-Anion Pairing at Oxide/Water Interfaces: Theoretical and Experimental Investigations from the Nanoscale to the Macroscale	108
Nanobiogeochemistry of Microbe/Mineral Interactions: A Force Microscopy and Bioinformatics Approach.....	109
THE UNIVERSITY OF OKLAHOMA.....	110
Development and Application of a Paleomagnetic/Geochemical Method for Constraining the Timing of Burial Diagenetic Events	110
OREGON STATE UNIVERSITY	111
Efficient Inversion of Multi-Frequency and Multi-Source Electromagnetic Data	111
PENNSYLVANIA STATE UNIVERSITY.....	112
Nanoscale Characterization of Corrosion at the Microorganism-Glass Interface	112
Critical Chemical-Mechanical Couplings that Define Permeability Modifications in Pressure Rock Fractures.....	113
PRINCETON UNIVERSITY	114
In-Situ Evaluation of Soil Organic Molecules: Functional Group Chemistry Aggregate Structure, and Metal and Mineral Surface Complexation Using Soft X-Ray Synchrotron Methods	114
PURDUE UNIVERSITY.....	115

Scaling of Seismic Wave Propagation Across Fractures Subjected to Time-Dependent Processes	115
RENSELAER POLYTECHNIC INSTITUTE	116
Transport Properties of Fluid-Bearing Rocks	116
Application of Geophysical Tomographic Imagery to the Development of Subsurface Flow and Transport Models	117
UNIVERSITY OF SOUTH CAROLINA	118
Understanding Long-Term Solute Transport in Sedimentary Basins: Simulating Brine Migration in the Alberta Basin, Canada	118
UNIVERSITY OF SOUTHERN CALIFORNIA.....	119
Three-Dimensional Miscible Porous Media Flows with Viscosity Contrast and Gravity Override	119
STANFORD UNIVERSITY	120
Three-Invariant Non-Coaxial Elastoplastic Constitutive Modeling and Its Implications on the Localization Properties of Rocks	120
Geochemical Controls on Nuclear Magnetic Resonance Measurements	121
Porous Reservoir Rocks with Fluid: Seismic and Transport Properties	122
Structural Heterogeneities and Paleo Fluid Flow in an Analogue Sandstone Reservoir	123
Inversion of Multicomponent Seismic Data and Rock Physics Interpretation for Evaluating Lithology, Fracture and Fluid Distribution in Heterogeneous Anisotropic Reservoirs.....	124
TEMPLE UNIVERSITY.....	125
An Inter-Disciplinary Study of the Surface Reactivity of Pyrite	125
UNIVERSITY OF TENNESSEE	126
Completion of Kr-81 and Kr-85 Analysis Development for Hydrogeology and Testing its Validity by Assessing Aquifer Recharge Rates	126
TEXAS A&M UNIVERSITY	127
Experimental and Analytical Studies to Model Reaction Kinetics and Mass Transport of Carbon Dioxide Sequestration in Depleted Carbonate Reservoirs.....	127
Time-Lapse Seismic Monitoring and Performance Assessment of CO ₂ Sequestration in Hydrocarbon Reservoirs	128
UNIVERSITY OF TEXAS.....	129
Metal-Anion Pairing at Oxide/Water Interfaces: Theoretical and Experimental Investigations from the Nanoscale to the Macroscale	129
Predicting Fracture Porosity Evolution in Sandstone	130
UNIVERSITY OF TEXAS AT DALLAS.....	131
3-D Sedimentological and Geophysical Studies of Clastic Reservoir Analogs: Facies Architecture, Reservoir Properties, and Flow Behavior within Delta Front Facies Elements of the Cretaceous Wall Creek Member, Frontier Formation, Wyoming.....	131
VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY.....	132
Investigation of the Physical Basis for Biomineralization.....	132

Nanobiogeochemistry of Microbe/Mineral Interactions: A Force Microscopy and Bioinformatics Approach.....	133
Electron Density Distributions as a Guide for Understanding the Reactivity of Silicate Earth Materials	134
UNIVERSITY OF WISCONSIN.....	135
Resolving Complex Hydrothermal/Magmatic Events in Caldera Environments: MicroAnalysis of Oxygen Isotope Ratios.....	135
A 3D Numerical Analysis of the Grounded Electric Source, Transient Electromagnetic Geophysical Method.....	136
WOODS HOLE OCEANOGRAPHIC INSTITUTION	137
Collaborative Research: Evolution of Pore Structure and Permeability of Rocks Under Hydrothermal Conditions.....	137
Laboratory Constraints on the Stability of Petroleum at Elevated Temperatures: Implications for the Origin of Natural Gas.....	138
Organic Geochemistry of Continental Margin and Deep Ocean Sediments	139
WRIGHT STATE UNIVERSITY	140
Multiscale Reactive Transport in Processes Related to CO ₂ Sequestration: Nanoscale Dynamics, Upscaling and Non-steady State Kinetics.....	140
UNIVERSITY OF WYOMING.....	141
Multiscale Reactive Transport in Processes Related to CO ₂ Sequestration: Nanoscale Dynamics, Upscaling, and Non-Steady State Kinetics	141
YALE UNIVERSITY	142
Plants, Weathering, and the Evolution of Atmospheric Carbon Dioxide and Oxygen.....	142
Integrated Studies of Coupled Flow, Reaction, and Diffusion in Earth's Crust	143
DOE/OBES GEOSCIENCES RESEARCH: HISTORICAL BUDGET SUMMARY	144

FORWARD

The Department of Energy supports research in the geosciences in order to provide a sound foundation of fundamental knowledge in those areas of the geosciences that are germane to the Department of Energy's many missions, and those which provide stewardship for geosciences research capabilities at the DOE National Laboratories. Excellent fundamental science that can improve and support DOE's mission needs will also provide basic knowledge 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. 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

Chemistry Division, Building 200

Argonne, IL 60439

CONTRACT: DE-AC02-06CH11357

PERSON IN CHARGE: P. Fenter

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

Paul Fenter (630)252-7053; fax (630)252-9570, Fenter@anl.gov

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 the mineral-fluid interfaces. This is crucial to establishing the relation between atomic-scale processes and macroscopic geochemical transport in natural systems. The principle approach is to observe single-crystal mineral surfaces in situ during chemically controlled reactions with fluids using X-ray scattering, standing wave and absorption techniques with high brilliance synchrotron radiation. Phenomena of interest include mineral-water interface structure (including mineral surface structure and the perturbations of near-surface water structure induced by the mineral), adsorption/desorption of metal 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. Progress includes determination of the systematic variation of orthoclase dissolution kinetics with temperature and pH through *in-situ* and real-time measurements of dissolution at well-defined cleavage surfaces. Determinations of surface hydration structures of various mineral surfaces (e.g., orthoclase, fluorapatite, calcite) were also made. In particular, the structures of orthoclase (001) and (010)-water interfaces were found to be similar and do not explain differences in apparent activation energies for dissolution observed for these two surfaces. Direct measurements were also performed on cation adsorption sites (e.g., on muscovite). A new approach that directly reveals model-independent element-specified site density profiles with X-ray standing waves was demonstrated for the first time. The site distributions of impurities in muscovite (e.g., Fe, Mn, Ba) were used to illustrate the approach.

IDAHO NATIONAL LABORATORY

Idaho Falls ID

CONTRACT: ID13727

PERSON IN CHARGE: P. Meakin

Multi-Resolution Structure and Reactivity of Kinetically Roughened Oxide Surfaces

Paul Meakin, Paul.Meakin@inl.gov

Surfaces of minerals in natural settings usually exhibit a significant degree of morphological heterogeneity. On scales from the molecular-scale to micron scales, surface roughness can be an important factor in growth, dissolution, and adsorption processes. Despite this fact, the relationships between these processes and roughness have not lent themselves to easy quantification because of their inherent complexity. To address this complexity we are studying the dissolution behavior of various mineral surfaces at various length scales of observation accessible by atomic force microscopy (AFM). For example, the dissolution of prismatic and rhombohedral quartz surfaces by hydrothermal KOH/H₂O solution leads to the development of a variety of overlapping etch features each etching at different rates (Yanina, Rosso, Meakin, 2005, *Geochimica et Cosmochimica Acta*, in review). The spatial density and characteristics of these features, as well as their interaction upon coalescence, affects the total dissolution rate for overall surface. The prismatic surface dissolves almost two orders of magnitude faster than the rhombohedral surface, mostly due to the difference in the number and the rate of dissolution of extended defects, such as dislocations. Crystal voids etched almost one order of magnitude faster on the prismatic surface than on the rhombohedral surface due to differences in the number and the density of steps formed by voids on the different surfaces. Studying the step-wise dissolution of isolated etch pits is the current paradigm; however this approach fails when dissolution features overlap and interact. By examining the surfaces at various length scales between 10 nm and 100 microns, we have been successful at separating the contributions of various overlapping dissolution processes. In addition to AFM topographic analysis of the evolving surfaces, wavelet image processing has been a useful tool for helping to categorize etch features on a length scale basis. Also, kinetic Monte Carlo simulations have provided a basis for making a linkage between the AFM observations and the molecular-scale (Meakin, Rosso, Yanina, 2005, *Journal of Chemical Physics*, in prep). Current efforts are focused on adapting these tools to address the scaling behavior of a variety of low-index hematite surfaces dissolving in various media.

LAWRENCE BERKELEY NATIONAL LABORATORY

Earth Sciences Division
Berkeley CA 94720

CONTRACT: CH11231

PERSON IN CHARGE: E. Majer

Center for Isotope Geochemistry

*Donald J. DePaolo, 510-486-4975, 510-643-5064, Fax 510-642-9520, depaolo@eps.berkeley.edu
or djdepaolo@lbl.gov*

Funding is requested to support research on geochemical processes using isotope ratios and trace element concentrations in natural materials. Natural isotopic tracers provide critical calibration of process models used in environmental management, radioactive waste management, geothermal technology development, global climate change, and energy exploration. A major focus of the proposed work involves using multi-collector ICP mass spectrometry to investigate natural isotopic variations of Fe, Ca and other elements. This work may provide new perspectives on the role of Fe and Ca in the carbon cycle and in weathering processes. Cr isotopic variations will also be investigated as a way to better understand the mobility and environmental effects of Cr contamination. Ca, Sr and U isotopes will be used to study in situ rates of weathering reactions in fluid-rock systems, and evaluated as measures of groundwater velocity and infiltration flux. U-Th-He geochronology will be investigated as a geochronologic tool for the Late Pleistocene and Holocene. Noble gas concentration measurements will be developed for continental paleo-temperature studies, and their use as a global change monitor explored. Modeling studies are aimed at relating isotopic variations to reservoir characteristics, atmospheric moisture transport, and drainage rates in deep soils of arid regions.

The primary research area of concern to the BCIG is the use of isotopic ratio measurements of natural materials to monitor geological processes. The impetus for our studies is the fact that most geological transport processes cannot be modeled accurately starting from first principles in the absence of observations to provide constraints. This limitation stems from heterogeneity on many scales and complex coupling between processes. The tracers provided by natural isotopic variations measure the net effects of these complex processes, and ultimately provide the critical calibration of models that can make the models useful for prediction. Our aim is to advance the state of the art of the isotopic approaches, partly by demonstrating or improving isotopic measurement methodology, and partly by advancing isotopic data analysis strategies.

Reactive Chemical Transport in Structured Porous Media

Tetsu K. Tokunaga, 510-486-7176, tktokunaga@lbl.gov

Diffusion can exert strong and often unrecognized influences on subsurface solute transport and reactions. Many aspects of reactive chemical transport in diffusion-limited domains remain poorly

understood, despite the fact that the various possible reaction mechanisms are often known. Since the spectrum of microenvironments are coupled and stratified through diffusive mass transfer in interior regions of sediment blocks, soil aggregates, and even within sand grains, these diffusion-limited domains are the simplest systems within which the full range of geochemical transformations can occur. Moreover, when such stratification occurs, systems cannot be understood based on commonly employed bulk measurements that average across important geochemical gradients. This research proposal is directed at improving understanding of reactions within diffusion-limited domains. Two categories of reactions are considered, redox and sorption. For the redox case, the role of aqueous ferrous iron in reducing chromium(VI) will be examined. The hypothesis to be tested is that local Fe^{2+} concentrations in diffusion-limited regions largely account for Cr(VI) reduction. For the sorption case, intragranular diffusion of uranium(VI) will be examined. The hypothesis for this part of the project is that intragranular diffusion accounts for most of the time-dependence observed in U(VI) sorption. The processes to be investigated require determination of chemical profiles with high spatial resolution. Therefore, key measurements will be obtained with spatially resolved synchrotron x-ray techniques including the x-ray microprobe, micro- x-ray absorption near-edge structure spectroscopy, and chemical microtomography.

Clay Mineral Surface Geochemistry

Garrison Sposito, (510) 643-8297, fax (510) 643-2940, gsposito@lbl.gov

The objective of this project is to characterize and elucidate the dual hydrophilic-hydrophobic properties of smectite clay mineral surfaces that figure in the attenuation of pollutant hydrocarbons and the sequestration of organic matter. This objective will be accomplished through state-of-the art computer simulations and spectroscopic experiments on molecular structure in the interlayer region between smectite particles where intercalation of organic compounds takes place. The simulations will involve tested codes, applying density functional theory, Monte Carlo or molecular dynamics techniques, and molecular mechanics methods, while making full use of the NERSC supercomputers. The results of the project will contribute directly to fundamental understanding of clay mineral structure and reactivity; the sequestration of carbon in gas hydrates or natural organic matter; and the fabrication of composite nanoparticles based on clay mineral-organic complexes.

Rate Controls in Chemical Weathering: A Reactive Transport Approach

Carl I. Steefel 510-486-7311; CISTeefel@lbl.gov

The purpose 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 CO₂ sequestration in deep aquifers, and even to determine the fundamental controls on the rates of chemical weathering, an important long-term regulator of atmospheric CO₂ levels.

A major focus of this project is to use the X-ray microtomography beamline at the Advanced Light Source (8.3.2) to create 3D images of the pore structure of weathered basalt at the 2-4 micron scale. This information is then used to establish the correlation between porosity and pore connectivity, which control the percolation and diffusion behavior of the material.

Prediction and Evaluation of Coupled Processes

Kartsten Pruess, k_pruess@lbl.gov

The purpose of the research proposed here is to develop a systematic, rational, and mechanistic understanding of the coupled physical and chemical phenomena that would be induced by injection of CO₂ into aquifers. This will be accomplished by means of conceptual, mathematical, and numerical models that are based on rigorous continuum theories of fluid dynamics, coupled with detailed rock fracture mechanics and chemical speciation and reaction path analyses. By developing a mechanistic understanding of the relevant processes, this research will provide a sound basis for evaluating the feasibility of CO₂ disposal in different hydrogeologic environments, including fractured rock systems, and will provide engineering tools for the design, implementation, and monitoring of CO₂ disposal systems in aquifers.

The analysis demonstrates how a large-scale CO₂ injection operation results in a gradual increase of aquifer pressure, which could reach close to the lithostatic stress after years of injection. Such aquifer pressure increase will induce a number of hydromechanical interactions and geomechanical responses through changes in the effective stress field in both the injection aquifer and the overlying semi-permeable caprock. A general reduction in the vertical effective stress induces vertical expansion of the aquifer, which can be significant and can be monitored on the ground surface. A relatively slow increase of the aquifer pressure during a typical constant rate injection will induce poroelastic stresses in the caprock which prevent catastrophic mechanical rock failure in the form of hydraulic fracturing through a caprock. Instead, the principal rock mechanics effect will be shear-slip along pre-existing faults and fractures occurring in the lower part of the caprock near the injection aquifer. The analysis shows that although shear-slip would be induced in the lower part of the caprock, it is not likely to propagate a rock failure zone through the upper part of the cap if preventive operational actions are taken. Thus, monitoring of seismic events in the lower part of the cap together with monitoring of ground surface movement are essential for controlling the hydromechanical responses during a CO₂ injection operation.

Molecular-Level Studies of Fe-Al Oxyhydroxide Coating Formation on Quartz

Glenn Waychunas, gawaychunas@lbl.gov; 510-495-2224

Synchrotron-based spectroscopy and chemical analysis are used to characterize the nature of sorbates, precipitates and coatings formed on quartz and other mineral surfaces. This is important for the prediction of environmental processes that sequester natural and anthropogenic toxic ions, as these processes are affected not only by the type of mineral surface, but also by coatings that render the surfaces more or less reactive. Grazing-incidence x-ray absorption spectroscopy (GIXAS), which

enables extreme surface sensitivity, is used to obtain the molecular structure and chemistry of precipitates on quartz single crystal surfaces. Both model surfaces prepared in the laboratory, and single crystals exposed to natural aquifer conditions, are utilized. In the former case the conditions affecting Fe oxyhydroxide formation can be examined selectively, while in the latter case the coating formation and composition are studied as a function of duration within well sites. Other synchrotron spectroscopy experiments are aimed at understanding the reactivity towards precipitation and sorption with other toxic species and utilizing differing surfaces of corundum and hematite. These minerals serve as analogs of a wide range of naturally occurring reactive mineral surfaces. The precise nature of the mineral-water interface is also being evaluated by x-ray diffraction studies of the surface structure of mineral surfaces equilibrated with water. Such surfaces are found to be different from analogous surfaces equilibrated in vacuum, and from models based on terminations of the bulk structure. Knowledge of the true surface structure termination is necessary to understand the nature of sorption topology and the initiation of precipitation, and further allows comparison with molecular dynamics (MD) simulations of the wet mineral interfaces. Another part of the investigation examines the nature of water molecular structure at the quartz and other mineral surfaces as a function of surface structure and preparation, solution pH, and the presence of sorbing ions. This work is done using sum-frequency vibrational spectroscopy (SFVS), a non-linear laser-scattering technique that allows collection of water vibrational spectra from a few molecular layers at the mineral-water interface region. All of these interface studies are combined to draw an improved picture of particular surface-mediated processes.

Experimental, Theoretical, and Model-Based Studies of Crystallographically Controlled Self-Assembly During Nanocrystal Growth

Glenn Waychunas, gawaychunas@lbl.gov; 510-495-2224

The growth of ZnS nanoparticles with both water and mercaptoethanol was found to occur predominantly via crystallographically-specific oriented attachment (OA). The growth mechanism determines particle morphology and microstructure. Twins and stacking faults form in the coarsened mercaptoethanol-capped ZnS, whereas more complex, closely spaced twins, stacking faults, and polytypic intergrowths form in coarsened water-ZnS. At long reaction times, diffusion-controlled growth removes surface irregularities arising from OA to yield rounded particles with complex internal structures. The character of the surface ligands affects both phase transformation pathway and temperature of phase transformation. Methanol desorption and rewetting, and water binding cause structural changes, reversible in the case of methanol ligands. Aggregation and disaggregation also cause reversible structural modification. Dispersed nanoparticles in suspension have a more distorted internal structure than aggregated nanoparticles of the same size. Reversible switching between distorted and crystalline structures can be induced by changing the aggregation state at room temperature, implying a low activation energy for the transformation. The results are believed to be the first surface-driven room temperature transitions observed in nanoparticles. The results indicate that nanoparticle structure is not kinetically trapped, but responsive to environmental changes. The growth of goethite nanoparticles was explored with a variety of synthesis methods, including a flash annealing technique to create nanoparticles in the range from 5-80 nm with differing crystallinity, habit and surface properties. TEM characterization shows aggregation in the more equant particles that is suggestive of initial face-to-edge impingement. This mode of aggregation was further suggested in large scale 10,000 atom MD simulations that showed positive charge buildup at the edges of goethite nanoparticles and negative

charge buildup in the centers of the faces. We thus infer a possible mechanism for OA in these nanoparticles that mitigates the problem of particle-particle electrostatic repulsion. Other work has measured the growth of goethite nanoparticles in real time via synchrotron-based wide and small angle x-ray scattering (WAXS and SAXS, respectively). As with ZnS there is evidence for a change of mechanism with nanoparticle size in the tens of nm regime, possibly from OA to diffusion-controlled growth.

Development of Isotope Techniques for Reservoirs

B. Mack Kennedy, 510-486-6451, bmkenedy@lbl.gov

The primary sites being considered for underground sequestration of anthropogenic CO₂ are active or depleted oil and gas reservoirs, deep aquifers, and underground coal beds. Efficient and safe sequestration of large quantities of CO₂ will require reliable characterization of potential storage formations, reservoirs and aquifers. Many deep aquifers and oil and gas reservoirs are complexly partitioned by differing structural, petrologic, stratigraphic, and hydrologic controls that will inhibit efficient injection and limit reservoir potential. Hydrodynamic processes such as advection, dispersion, and mixing/dilution, as well as chemical processes such as diffusion into low permeability matrix rocks, phase partitioning, and mineral dissolution and precipitation bear directly on the transport efficiency and fate of injected CO₂. To maximize the safety and efficiency of geologic sequestration, it will be necessary to address these and similar issues related to reservoir and aquifer characterization.

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, 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 will be required.

The goal of this project is to develop geochemical and isotope techniques for reservoir and aquifer characterization in support of CO₂ geologic sequestration studies and measurement of groundwater ages. Three projects will constitute the main focus of our proposed research for the next three years. (1) We will conduct a noble gas isotopic study of an oil and/or gas field to test the feasibility of using the conservative nature of noble gases to evaluate fluid compartmentalization and leakage from a reservoir. (2) We will use noble gas abundances to study water-CO₂ interaction along a flow path as part of planned CO₂ pilot injection tests. (3) We will evaluate, verify, and apply isotopic techniques for placing time constraints on groundwater flow.

Kinetic Isotope Fractionation

John N. Christensen, 510-486-6735, jnchristensen@lbl.gov

High-precision measurements of isotopic ratios in natural materials are combined with mathematical models to understand the spatial and time scales of geochemical processes of interest for energy management. Natural isotopic tracers provide critical calibration of process models used in environmental management, radioactive waste management, geothermal technology development, global climate change, and energy exploration. Isotopic measurements represent a means to interrogate complex natural fluid-rock-microbe systems to improve conceptual models of the chemical and physical processes that affect their behavior. The aim is to advance the state of the art and to use these advances to investigate fundamental issues in geochemistry. Modeling and systematic measurements of natural systems are supplemented by efforts to improve sampling methodologies and measurement techniques. A major focus of the work involves using multi-collector ICP mass spectrometry to investigate natural isotopic variations of Fe, Ca, U, Th, Ra, Sr, Pb, and Cr. Recent results demonstrate that helium production by alpha decay of U and Th can be used to date volcanic eruptions over an age range from a few thousand years to several million years. Alpha-recoil effects on U isotopes in natural systems are being used to measure the rates of mineral dissolution in active low-temperature groundwater systems. The same recoil effects are being investigated as a means of measuring the timescale of sediment transport. Noble gas concentration measurements are being developed for continental paleotemperature studies, and as a global change monitor. Measurements suggest that there is systematic fractionation of Fe and Ca isotopes associated with weathering of silicate rock material. Modeling studies are aimed at relating isotopic variations to reservoir characteristics such as matrix versus fracture flow, to atmospheric moisture transport and moisture sources, and drainage rates in deep soils of arid regions. Discrepancies between isotopically-measured natural mineral dissolution rates and theoretically predicted rates are being investigated with numerical models that account for pore scale transport effects.

Imaging Shear in Rocks

Seiji Nakagawa, 510-486-7894, snakagawa@lbl.gov

The primary objective of this project is to develop a basic understanding of the seismic properties of fractures and faults that are being subjected to and have been subjected to shear stress in the past. The focus of the research is on the (1) anomalous seismic wave scattering and mode conversion off a sheared fractures and faults, (2) seismic wave scattering by a heterogeneous fracture and a fault, and (3) laboratory measurements on fractures and faults at field employed frequencies.

When a fracture with rough, partially contacting surfaces is subjected to statically applied shear loads, seismic waves scattered by the fracture exhibit unique signatures that can be related to the magnitude and orientation of the shearing. This effect can be seen most dramatically when a normally incident plane compressional (P) wave is scattered by a plane infinite fracture, which results in co-generation of transmitted and reflected plane shear (S) waves. This project investigated the effect of fracture surface geometry and stress via 2D dynamic boundary element models and the discrete-particle dynamics method. Also, laboratory experiments using both natural rock and steel blocks containing single fractures were conducted to examine the effect of stress history on the anomalous scattering of seismic waves. For the case of fractures within steel blocks, the fractures were mediated by synthetic fault gouge (glass beads); and changes in the seismic responses were measured until the fracture (fault) failed under increasing shear stress. The effect of heterogeneous compliance distribution along fractures and faults

was investigated by theoretical and numerical models that expanded a conventional model for seismic wave scattering by a homogeneous fracture. Finally, to examine the effect of fluid and clay in a fracture at field-related frequencies in the laboratory, a resonant bar-test device for fractured, small rock samples was developed and used on dry and water-saturated sandstone cores containing single fractures.

This project is currently continued by a renewed project (with an extended scope) to investigate the effect of poroelasticity on seismic wave scattering by fractures and faults.

Scattering and Intrinsic Attenuation in Rock with Heterogeneous Multiphase Fluids

Kurt Nihei, ktnihei@lbl.gov

The proposed research is a fundamental investigation of scattering and intrinsic attenuation of seismic waves in rock with heterogeneous distributions of fluids and gas. This research represents a departure from past studies on seismic attenuation in that the focus here is not a detailed study of a specific attenuation mechanism, but rather to investigate theoretical and laboratory methods for obtaining separate estimates of scattering and intrinsic attenuation in heterogeneous rock.

This project combines laboratory, numerical, and theoretical studies to the investigation of scattering and intrinsic attenuation in rock with heterogeneous gas and fluid distributions. The objectives of this project are threefold: (1) to adapt and further refine methods for decomposing scattering and intrinsic attenuation in rock with heterogeneous multiphase fluids, (2) to apply these methods to laboratory seismic measurements and compare these results with numerical viscoelastic and poroelastic simulations, and (3) to examine a new method for focusing seismic waves in heterogeneous media using elastic time reversal mirrors. These objectives are addressed in four tasks to be performed over a period of three years.

Permeability Dependence of Seismic Amplitudes

Steven R. Pride, (510) 495-2823, fax (510) 486-5686, srpride@lbl.gov

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 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.

Imaging Permeability and Fluid Mobility

D. W. Vasco, (510) 486-5206, dwwasco@lbl.gov

We are 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.

Air-Derived Noble Gases in Sediments

B.M. Kennedy, 510-486-6451, bmkenedy@lbl.gov

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 smooth mass dependent abundance patterns have led to an adsorption hypotheses, three observations argue against single stage 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) Laboratory heating experiments suggests the enriched component is tightly bound, counterintuitive to a simple adsorption history. And (3) many sedimentary rocks (~half) and some oil field gases contain excess Ne in conjunction with excess Xe.

The goal of this project is to isolate and identify the various air-derived noble gas components in sediments, particularly, but not exclusively, those sediments associated with hydrocarbons. The project is designed to (1) characterize the noble gas carrier phases in sediments and address how noble gas elemental patterns are acquired and retained, (2) how noble gases are transferred to basin fluids in which they have been measured, and (3) to improve the application of noble gas isotope studies to multiphase fluid processes in the Earth's crust.

Colloid Transport in Unsaturated Fractured Rocks and Porous Media

Jiamin Wan, (510) 486-6004, jmwan@lbl.gov

Although there is now a general appreciation for the importance of colloid transport in the subsurface, most of the fundamental understanding in this area is limited to the saturated zone, and most of that understanding is largely borrowed from filtration theory. The basic physics and chemistry unique to vadose zone colloid transport is a consequence of the existence of a second immiscible fluid phase, gas. Traditional filtration theory can not be directly applied in the vadose zone colloid transport because of the coexistence of air and water. The concept of particles being strained by becoming trapped within thin water films in unsaturated porous media, "film straining", was recently introduced. A clearer

understanding for flow and transport in unsaturated fractures has also recently emerged with the identification of film flow. A quantitative method for measuring colloid partitioning between bulk water and the air-water interface has also recently been presented. These recent developments in combination provide the basis for understanding the physics and chemistry unique to colloid transport in the vadose zone. With this background, it now appears possible to make significant progress towards understanding vadose zone colloid transport in a thorough manner, encompassing both porous media and fractures, and accounting for differences in surface chemistry of different types of colloids. This research proposal is directed at reaching these goals.

Faster and Better Solutions to Three Dimensional Electromagnetic Inversion Problems

Gregory A. Newman, gnewman@lbl.gov

Inversion of transient electromagnetic (TEM) data sets to image the subsurface three-dimensional electrical conductivity and magnetic permeability properties can be done directly in the time domain. The technique, first introduced by Wang et al. (1994) for causal and diffusive electromagnetic fields, is based upon imaging methods originally developed for seismic wavefields (Claerbout, 1971; Tarantola, 1984), but was not correctly formulated for the full treatment of 3D TEM fields. In our work we modify the original theory of Wang et al. (1994), to overcome this limitation as well as extend the method to treat non-causal TEM fields. Our algorithm uses a conjugate-gradient search for the minimum of an error functional involving EM measurements governed by Maxwell's equations without displacement currents. Treatment for magnetic field, voltage (time derivative of the magnetic field) and electric field data are given. The functional can be computed by propagating the data errors back into the model in reverse time along with a DC field, sourced by the integrated data errors over the measurement time range. By correlating these fields, including the time-integrated back-propagated fields, with the corresponding incident field and its initial value at each image point, efficient computational forms for the gradients are developed. The forms of the gradients allow for additional efficiencies when voltage and electric field data are inverted. In such instances the combined data errors can be back-propagated jointly, significantly reducing the computation time required to solve the inverse problem. The inversion algorithm has already been applied to the long offset transient electromagnetic measurement (LOTEM) configuration thereby demonstrating its capability in inverting non-causal field measurements of electric field and voltage, sourced by a grounded wire.

LAWRENCE LIVERMORE NATIONAL LABORATORY

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

CONTRACT: SFENG48

PERSON IN CHARGE: F. Ryerson

Investigation of the Physical Basis for Biomineralization

Jim DeYoreo, (925)423-4240, fax: 925-424-4820, devoreo1@llnl.gov

Through biomineralization, living organisms utilize organic modifiers and molecular scaffolds to control nucleation and growth of both shaped single crystals and crystal composites. The purpose of this project is to explore the physical mechanisms, energetic factors, and stereochemical relationships that enable this process to proceed. Our approach is to apply scanned probe microscopy and molecular modeling to well-defined model systems in order to quantify the effects of growth modifiers on the energetic and thermodynamic parameters controlling crystallization. Our research has focused on calcite growth in the presence of simple amino acids, poly-amino acids, Mg, and Sr. Our work on pure calcite established the thermodynamic and kinetic parameters governing the advance of atomic steps. We found that introduction of simple amino acid enantiomers resulted in a chiral modification of growth morphology due to step-specific interactions altering the step edge energetics. The change in step shape was reflected in the macroscopic crystal habit. Molecular modeling confirmed the step-specific binding and provided a stereochemical basis for the interaction. Changing from simple to amino acids to poly-peptides strongly altered the effects on growth. While Asp(2) had little impact on calcite growth except at high concentrations, Asp(6) was a potent inhibitor even at sub-micromolar concentrations. Introduction of Mg also produced a step-specific modification due to its incorporation into the lattice, but we found that calcite inhibition by Mg was due to a simple shift in solubility rather than changes in step kinetics. Because Mg was incorporated at dramatically different levels at the two types of step edges on calcite, the resulting strain retarded growth near the corners of the calcite rhomb and led to elongation along the {001} axis. In contrast to Mg, Sr accelerated growth at low concentrations and then strongly inhibited it at high concentrations through a step pinning mechanism. These results argue for a model of growth modification in which step-specific interactions on existing crystal faces drives the modification of crystal shape. It contrasts with the accepted paradigm of stereochemical recognition in which the modifier binds to an otherwise unexpressed face of the crystal and stabilizes it thermodynamically.

Mineral Dissolution and Precipitation Kinetics

Kevin G. Knauss, knauss1@llnl.gov

This project concerns a multi-scale study of mineral/fluid interaction that is designed to improve our understanding of, and ability to predict the course of, mineral dissolution and precipitation processes specifically affecting carbonate precipitation and primary mineral dissolution expected as part of CO₂

sequestration either by injection into deep aquifers or by conversion into carbonates in a surface facility designed for the purpose. We are studying the effects of impure and non-stoichiometric solute systems on the fundamental surface thermodynamics and kinetics of carbonate precipitation, the scaling of these microscopic properties over larger distances, and the effects of imposed non-steady state conditions on the rates of silicate dissolution (which provides solutes for incorporation into carbonates). Specific areas of study include the growth of calcite and magnesite (at the nanometer to centimeter scale) in the presence of solute impurities such as Mg^{2+} , Ca^{2+} , Al^{3+} , $Si(OH)_4$, and SO_4^{2-} and under non-stoichiometric conditions, the dissolution of a primary mineral coupled with the growth of a secondary mineral, and the enhancement of calcic and mafic silicate dissolution kinetics through imposition of non-steady state conditions.

The experimental approach explores processes at a broad range of spatial scales. Our nanoscale studies utilize a Hydrothermal Atomic Force Microscope (HAFM) for molecular-level experiments on the kinetics of nucleation, step edge motion and other phenomena on carbonate mineral surfaces under conditions relevant to CO_2 -sequestration. The HAFM was developed and improved under previous funding. The same conditions used in HAFM experiments are also investigated with one-dimensional hydrothermal plug-flow reactors (PFR) and geochemical reactive transport codes.

The parallel macro/micro approach allow us to address many still-open questions concerning the form of rate equations near and far from equilibrium, the microscopic interpretation of these equations, the activation energies and formation energies for key microscopic surface structures (*e.g.*, steps, kinks), and the impact of specific aquifer solute catalysts and inhibitors on the dissolution and growth processes. The HAFM data provide the requisite microscopic data for understanding the complex kinetics associated with carbonate precipitation.

This research has broad application to many geochemical problems of interest to DOE beyond the geologic sequestration of CO_2 .

Reactive Transport of CO_2 Rich Fluids

Russell Detwiler, 925-422-6229, fax: 925-423-1057, detwiler1@llnl.gov

Flow of reactive fluids through fractured media can lead to dissolution and precipitation of minerals along fracture surfaces causing localized changes in fracture aperture. Because local regions of large aperture tend to coincide with locally larger flow rates and rock/water mass transfer rates, small perturbations in fracture aperture fields can develop into large-scale features that control the transport properties of fractured systems.

By integrating experimental and computational techniques, we are exploring the processes that lead to the geochemical alteration of fracture permeabilities over a range of scales. We have developed a novel experimental approach involving the fabrication of transparent analog fractures by mating a rough, non-reactive glass surface with an optically smooth, reactive surface (potassium dihydrogen phosphate). These 10 x 15 cm fractures allow us to reproduce experiments and systematically vary parameters such as flow rate and influent fluid chemistry in fractures with identical geometry and mineral composition.

Furthermore, well-established light transmission techniques provide unprecedented measurements of changing fracture apertures across the entire flow field at high spatial resolutions during experiments.

Dissolution experiments in these analog fractures demonstrated the influence of the dimensionless Peclet and Damkohler numbers ($Pe = \text{advection/diffusion}$ and $Da = \text{reaction/advection}$) on alteration of the fracture aperture field. Experiments at low flow rates (low Pe , high Da) result in the formation of distinct dissolution channels with breakthrough of a single channel at the downstream boundary. At higher flow rates (high Pe , low Da) lead to a more uniform increase in aperture across the fracture, with the largest changes occurring at small aperture locations and an overall reduction in short wavelength aperture variability.

These experimental results have allowed us to evaluate a depth-averaged model of reactive flow and aperture alteration through direct comparison of simulations to experimental results. This computational model reproduces the large-scale behavior of the experiments, including the nature of the dissolution channels and the rate of change of fracture permeability with time. Our rigorous evaluation of this efficient computational model suggests that it is an effective tool for extending laboratory results to considerably larger scales.

Geological CO₂ Sequestration

Susan Carroll (925) 423-5694, fax (925) 422-0540, carroll6@llnl.gov

Objectives: The objective of this research is to measure dissolution and precipitation rates important to the mineralization of dissolved carbon at conditions relevant to CO₂ sequestration. Determination of mineral dissolution and precipitation kinetics is fundamental to the successful disposal of greenhouse CO₂-rich gases in aquifers, because reservoir storage capacity is directly related to the conversion rates of CO₂ to carbonate minerals. The reaction of CO₂ and water with unstable silicate minerals to produce more stable silicates (e.g. clays) and solid carbonates is the natural weathering process which is a dominant part of the long-term global geochemical cycling process. Our kinetic research will feed directly into promising reaction-transport codes that will evaluate aquifer storage of dissolved CO₂ and mineral carbonates, and resulting changes in porosity and permeability.

Project Description: Our approach is to conduct single and multi-mineral dissolution and precipitation experiments and reaction transport experiments in Ca-Al-Si-CO₂ and CaCO₃ systems as a function of pCO₂, pH and temperature. Supercritical CO₂ experiments simulate the reactive front of CO₂ plume and aquifer water and are designed to measure the available source of calcium for storage of CO₂ as carbonates and the source of aluminum and silica for the precipitation of secondary minerals that will effect aquifer porosity and permeability.

Kinetic Isotope Fractionation

Ian Hutcheon, (925) 422-8841, fax: (925) 422-3160, hutcheon1@llnl.gov

The overall objective is to document and quantify kinetic isotope fractionations during chemical diffusion in a variety of liquids. One set of experiments was designed to measure the isotopic fractionation of Ca and Li in annealed diffusion couples juxtaposing molten basalt and rhyolite. The experiments confirmed and quantified our previous contention that chemical diffusion in silicate liquids can significantly fractionate isotopes in a mass-dependent way - in the case of $^{44}\text{Ca}/^{40}\text{Ca}$ by more than 6‰, and for $^7\text{Li}/^6\text{Li}$ by more than 40‰. Chemical and isotopic fractionation of dissolved species by diffusion in water was also studied using small spherical chambers filled with salt solutions (KCl, LiCl, MgCl_2) connected to a much larger water-filled reservoir by a cylindrical diffusion tube. If the dissolved species diffuse through the connecting tube at different rates, the residue of salt in the smaller chamber will become progressively enriched in the more slowly diffusing species. The validity of our experimental design was confirmed by reproducing the already known ratio of the diffusion of K to that of Li. In the case of MgCl_2 we found no measurable isotopic fractionation of Mg (<0.5‰ for $^{26}\text{Mg}/^{24}\text{Mg}$) even when less than 5% of the original Mg remained in the inner chamber. If the mass-dependence of Mg isotope diffusion in water had been similar to that in molten silicate, we would have measured a fractionation of about 25‰. In the case of Li, we did measure a 5‰ fractionation of $^7\text{Li}/^6\text{Li}$ when 5% of the Li remained in the inner chamber, but again this is very significantly less than fractionation that would have occurred under similar circumstances in a molten silicate liquid. We interpret the much-diminished isotopic fractionation associated with diffusion in water relative to that in molten silicate liquids as being due to the dissolved ion plus its hydration sphere being the diffusion species in the water experiments. We are testing this suggestion by a new set of diffusion experiments involving dissolved noble gases in water.

Analysis of Physical Properties for Heterogeneous Rocks Containing Fluids

James G. Berryman, berryman1@llnl.gov

Modeling the full complexity of seismic waves in the Earth is too difficult to realize as it requires that elasticity be replaced by one of its generalizations: viscoelasticity, thermoelasticity, poroelasticity, or the still more complex models such as the double-porosity/dual-permeability. Models should also allow for other sorts of complexity as well, such as granularity. Fluids play a key role in all problems of interest. Resolution of various practical and scientific issues in the earth sciences depends on knowledge of fluid processes underground. In environmental cleanup applications, contaminants to be removed from the earth are often liquids such as gasoline or oil, or ground water contaminated with traces of harmful chemicals. In commercial oil and gas exploration, the fluids of interest are hydrocarbons in liquid or gaseous form. In all cases analysis of fluid content depends on measurements of seismic (compressional and shear) wave velocities in the earth. The sources of these waves may be naturally occurring such as earthquakes, or man-made such as reflection seismic surveys at the surface of the earth, vertical seismic profiling, or still more direct measurements using logging tools in either shallow or deep boreholes. When a liquid or gas completely fills interconnecting voids among solid earth grains, seismic velocities should depend on the fluid and drained rock elastic constants and densities. Gassmann's formulas are low frequency results and both laboratory and well-log measurements of wave velocities have been observed to deviate markedly from Gassmann's predictions at higher (sonic to ultrasonic) frequencies. For partial saturation conditions, deviations can in particular be attributed to "patchy saturation," meaning that some pores are fully saturated with liquid and others are filled with gas. Neither Gassmann's formulas nor the "patchy saturation" model seem to apply to all laboratory ultrasonic data.

So various explanations for the observed velocity discrepancies have been put forward, including viscoelastic effects (velocity decrement due to frequency-dependent attenuation), fluid-enhanced softening of intragranular cementing materials, chemical changes in wet clays that alter mechanical properties, etc. The main purpose of this project is to provide the analysis and computational tools required for treating many of these difficult problems.

Electrical Properties of Rocks

Jeffery J. Roberts, (925) 422-7108, fax (925) 423-1057, roberts17@llnl.gov

The electrical properties of fluid-bearing materials are dependent on a number of factors including temperature, porosity, mineralogy, and clay content, as well as fluid content and pore fluid salinity. Electrical measurements are an important tool in probing the physical and chemical properties of rocks in the laboratory and in the field. Because electrical properties are sensitive to so many factors, and because many of these factors are parameters of geophysical interest, careful laboratory measurements are needed to improve the information available from field electrical measurements. The goal of this project is to measure the electrical properties of clay-bearing rocks as a function of confining and pore pressure, temperature, and pore saturant.

In FY04 the research has focused on experimental measurements of dielectric constant, electrical resistivity, and zeta potential of clay-water mixtures. We carried out electrical impedance measurements over the range of 1 Hz to 1 MHz on mixtures of swelling and non-swelling clay samples in NaCl solutions ranging from zero to 0.35 molar. The purpose of the measurements was to try to identify possible differences in the impedance response of the two clays under controlled conditions that could be exploited in the field. Results indicate that fluid salinity strongly affects surface conduction of swelling and non-swelling clays and the two types of clay respond very differently. For both clays, the d.c. conductivity follows Archie's Law down to very low brine concentrations [0.001 molar – 0.01 S/m for Na-montmorillonite (swelling) clay; 0.0001 molar – 0.001 S/m for kaolinite (non-swelling) clay]. At lower NaCl concentrations the conductivity of the mixture is constant at a level consistent with the relative cation exchange capacity of each clay. For a dispersed clay mixture in brine, once the brine concentration exceeds the threshold conductivity, both the d.c. and complex conductivity is the same as that of a pure brine solution and the clay mixtures are indistinguishable.

Deposition of Carbons

Jeffery J. Roberts, (925) 422-7108, fax (925) 423-1057, roberts17@llnl.gov

An enduring question facing students of the Earth is what happens to rocks during the time leading up to catastrophic failure along a fault. The question has potentially enormous societal import for the obvious reason that an understanding of brittle failure may lead to better estimates of earthquake probabilities. This is a collaborative research project with investigators from Texas A&M (Kronenberg, Karner), The AMNH (Duba and Mathez), and LLNL (Roberts).

The basis of our project is that a systematic study of carbon deposition on fracture surfaces in rocks deformed through laboratory experiments may improve the understanding of processes in rocks that lead

to electrical precursory phenomena. Accordingly, our interdisciplinary experimental study investigates the interaction between carbon-bearing fluids and mineral surfaces under crustal conditions. The key goals are to determine if carbonaceous films deposited on freshly generated surfaces affect rock deformation and to test the assertion of Roberts et al. (1999) that rapid deposition of carbon on new surfaces increases electrical conductivity.

Rheology of the Earth's Interior

William B. Durham, durham1@llnl.gov

The overall scope of this research is to determine the high-temperature, high-pressure flow law for olivine, an essential step in understanding the dynamics of Earth's deep interior. A series of twelve deformation experiments have been conducted using the D-DIA apparatus at synchrotron radiation facilities. Polycrystalline samples were hot-pressed from powders of olivine plus 5% enstatite. Experiments were carried out at constant displacement rates of 1×10^{-5} to 4×10^{-4} /s to shortening strains of ~15% with temperatures between 1273 and 1573 K and pressures of 3 to 6 GPa. The chemical environment of the olivine samples is fixed; the oxygen fugacity is buffered by the existence of both Ni and NiO, and silica activity is set by the presence of enstatite.

Precise measurements at high pressure of stress, strain, strain rate, pressure, and temperature are a distinct feature of this study. During a deformation experiment, x-ray radiographs taken periodically of the sample column yield the change in length of the sample as a function of time, from which strain and strain rate are calculated. Pressure is determined based on the spacing of x-ray diffraction peaks from a small amount of well-characterized proxy material, MgO, inserted into the deformation column, while differential stress is obtained from the strain of various lattice planes in the sample measured as a function of orientation with respect to the stress field.

Analyses of our data yield an activation volume for creep of $4-8 \times 10^{-6}$ m³/mol. Although this result is only preliminary, because additional analyses of the microstructures as well as the water contents of our samples are still in progress, it indicates that previously reported values are a factor of two too large. These first results are very exciting, as they indicate that the D-DIA experiments have adequate resolution to determine important flow parameters such as activation volume.

The techniques used for both D-DIA experiments and x-ray diffraction measurements are breakthrough technologies compared to conventional deformation experiments. Significant effort on cell design now permits experiments to 12 GPa at 1500 K. Our software package greatly simplifies data reduction, reducing the time by a factor of ten.

Three Dimensional Analysis of Seismic Signatures & Characterization of Fluids & Fracture in Anisotropic Formations

P.A. Berge, bergel@llnl.gov

Seismic anisotropy caused by layering, foliation, or aligned fractures is pervasive in sediments and rocks such as silty sands, clay-bearing sandstones, shales, and fractured igneous rocks. Earth materials with interconnected pores or fractures can behave mechanically as poroelastic media. Recent advances in laboratory and field techniques allow measurement of all the constants needed to characterize mechanical behavior of some earth materials that are either anisotropic or poroelastic. Current research efforts in the oil industry and university collaborations may provide ways to measure the many anisotropy parameters and poroelastic constants needed to characterize poroelastic, anisotropic sediments and rocks. These earth materials are important in many environmental cleanup, energy resource, and civil engineering applications. The availability of reliable lab and field data gives incentive for developing better theoretical methods for analyzing poroelastic, anisotropic earth materials. Some models do exist but they have significant limitations. Incorporating fluid effects into some of the common anisotropy models yields insight into the implicit assumptions in the models as well as into material behavior.

Our major objective is to obtain constraints on lithology in fluid-filled anisotropic rocks by using rock physics theories for anisotropic and poroelastic media. We are collaborating with investigators on related OBES projects at the Colorado School of Mines and Stanford University, who are developing techniques for obtaining anisotropy parameters from seismic reflection data (CSM) and relating laboratory measurement information to modeling and field data (Stanford). By using our theoretical methods to model the anisotropy parameters recovered from seismic data, we can find ways to improve analysis of seismic reflection data collected in areas where the geology is complicated by anisotropy and heterogeneity.

Application of Geophysical Tomographic Imaging

Charles Carrigan, carrigan1@llnl.gov

A major environmental concern at many DOE sites is the degree to which the unsaturated or vadose zone acts as a barrier that prevents previously spilled or leaked contaminants from reaching the water table. The principal focus of this project has been to combine subsurface electrical imaging with numerical simulations to aid the understanding of vadose zone transport processes. However, linking field observations to field-scale models of subsurface flow and transport processes remains a significant challenge, particularly in the vadose zone. Previous LLNL Vadose Zone Observatory (VZO) experiments provide a source of Electrical Resistance Tomography (ERT) data obtained during the infiltration of water and brine from the near-surface to an 18-m deep water table. ERT observations suggested, surprisingly, that infiltrated contaminants might rapidly reach the water table within only hours, which is a concern where the vadose zone has been assumed to act as a barrier to contaminants. To better understand this behavior, we have integrated several LLNL 3-D computer models (listed in parenthesis below) together to investigate the combined complexity of geologic heterogeneity (TSIM), variably saturated flow and transport (NUFT), flow of electrical current due to ERT (ParFlow), and ERT inversion (MultiBH). This integrated simulation approach, involving stochastic models, permits linkage between the ERT observations and 3-D flow and transport process models. While our simulations compare reasonably to some types of monitoring data (e.g. gypsum blocks), they do not exhibit rapid changes in electrical resistivity at the water table as indicated by the ERT observations. The models indicate that strong preferential pathways, such as fracturing or vertically oriented sand lenses, may be

required to explain the rapid communication between the infiltration point and the water table. Alternatively, recent bench-scale lab experiments involving resistivity measurements in a partially saturated sand-filled test section performed as part of this project (Parekh, et al., 2004, Rensselaer Polytechnic Institute) suggest the existence of air-water interfacial conduction processes strongly decreasing the formation resistivity in the unsaturated zone during infiltration (Knight, Geophys., 56, p. 2139-2147, 1991) that are independent of resistivity decreases caused by the downward migration of a brine tracer.

LOS ALAMOS NATIONAL LABORATORY

CONTRACT: NA25396

PERSON IN CHARGE: D. Janecky

High Resolution/High Fidelity Seismic Imaging

Michael Fehler, fehler@lanl.gov

The purpose of the current project is developing new methods for wave equation based imaging and extending these techniques for the estimation of subsurface model parameters. In the 2004/2005 project year, our research focuses on the following areas:

We extended the thin-slab method for elastic wave propagation from the isotropic media to the VTI media. The elastic thin-slab approximation is a dual-domain formulation for modeling wide-angle forward- and back-scattering using the De Wolf approximation. We introduced the anisotropy parameters based on the elastic perturbation theory and derived the formulation for anisotropic scattered qP and qSV waves. Numerical simulations proved the validity of the method.

We developed a wave equation based method for seismic illumination analysis. A one-way wave-equation based generalized screen propagator is used to extrapolate the wavefields from sources and receivers to the target. A local plane wave analysis is used at the target to calculate localized directional energy fluxes for both source and receiver wavefields. Using these energy fluxes, we construct an illumination matrix to quantify the target illumination conditions. The information about target geometry is used to manipulate illumination matrix and generate different types of illumination maps. Unlike illumination analyses based on ray-tracing, the wave equation based approach avoids difficulties due to the high-frequency approximation of the ray-based method. This new method is flexible and practical for illumination analysis in complex 2D and 3D velocity models with different acquisition and target geometries.

Using beamlet decomposition of the wavefield, we developed an angle-domain amplitude correction method for wave-equation based true-amplitude, true-reflection imaging. First, local image matrix and local illumination matrix are obtained. The amplitude correction is carried out in the local angle domain using common-dip-angle image gathers. With this correction, the effects from limited acquisition geometry, the path effect from propagation through complex overburden and the reflector dip angle are all considered. Numerical examples show that the image quality of subsalt structures is greatly improved and the image amplitudes are more balanced. Meanwhile, the noise and migration artifacts are effectively compressed.

Nonlinear Elasticity in Rocks

Paul Johnson, 505-667-8936, paj@lanl.gov

The basic premise of this work is the modern theory of critical phenomena can be applied to the

description of the nonlinear elastic behavior of all or most geomaterials. In short, we are testing whether or not geomaterials represent a nonlinear elasticity universality class, and determining the defining characteristics of these materials. Our work entails extracting experimentally-derived scaling relations indicating anomalous nonlinear elastic behavior. Establishing a universal description offers a vast simplification in describing nonlinear elasticity over a huge number of length scales, in a huge range of dissimilar materials. The materials we are studying are remarkably disparate in their physical, meso-geometrical and chemical makeup. These are materials that owe their elastic behavior to a fabric of elastically soft material within a hard matrix ("the bond system") that exists within a small fraction of the total material volume. They contain nanoscopic-to-mesoscopic scale elastic features that are responsible for the unique behavior. Recently, we broadened the class significantly to include certain ceramics and metals, all damaged material and rocks, to date. We have carefully analyzed the effects of fluids in the porous members of the class that strongly affect the elastic nonlinear response. We have developed a sophisticated model to describe these behaviors, and, over the past year we have carefully explored the transition behavior from (a) linear elastic, to (b) "classically" nonlinear elastic, to (c) "nonclassically" (hysteretic) elastic. It appears that slow dynamics appears only in tandem with nonclassical behavior. It seems, in fact, that nonclassical behavior could be the integral response induced by classical nonlinearity plus slow dynamics. In addition, we have begun to explore the linear and nonlinear elastic behavior of granular media. Granular media are extremely nonlinear in comparison to rock, but simpler to describe, by application of Hertz-Mindlin theory for instance. Further, we believe that the nonlinear response of granular material plays a significant role in earthquake processes, including earthquake triggering. We are currently exploring this role.

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

Peter M. Roberts (505-667-1199, proberts@lanl.gov)

This project is investigating the effects of dynamic stress oscillations on the behavior of fluids and sub-pore-size particles (colloids) in porous media. It is important to understand this phenomenon because low-frequency (1 to 1000 Hz) stress waves have been observed to influence porous fluid-flow behavior in the Earth. Potential applications include enhanced oil production from depleted reservoirs, accelerated contaminant extraction from groundwater aquifers, and controlling colloid transport at waste facilities. The majority of observations to date have been mixed, unpredictable and anecdotal because the physics coupling stress waves to colloid and fluid-flow behavior in porous media is poorly understood. This project focuses on experimental basic research to advance our knowledge in this undeveloped intersection of three scientific fields: elastic-wave propagation, porous fluid-flow dynamics, and colloid electrokinetics. Improved understanding of the stress-stimulated-flow phenomenon will accelerate technology developments for application to numerous practical problems. Experimental approaches are being used to investigate the basic physics of coupled stress-wave and porous-flow phenomena. The major goals are 1) to obtain improved experimental data that will be used to validate and quantify proposed physical mechanisms, and 2) to define the hydrogeological, geophysical, and physicochemical conditions under which stress waves couple efficiently to porous fluid flow and colloidal transport. Experimental laboratory studies are being performed on fluid-flow and colloid behavior under the influence of applied stress oscillations. Two Los Alamos facilities are being used in these studies: The Dynamic Stress Stimulation Laboratory (DSSL) and the Automated Video Microscopic Imaging and Data Acquisition System (AVMIDAS). The DSSL is used to study low-frequency (1-1000 Hz) effects

on core-scale fluid-flow and colloid behavior in porous material. AVMIDAS is used to visualize colloid behavior in parallel-plate glass cells and porous micro-models under the influence of high-frequency (10 kHz to 10 MHz) acoustic waves. Data from these two systems are compared to investigate possible scaling mechanisms that can be used to predict similar behavior in the Earth's crust.

Summer of Applied Geophysical Experience (SAGE)

W. Scott Baldrige, (505) 667-4338, sbaldrige@lanl.gov

SAGE (Summer of Applied Geophysical Experience) is an ongoing, five-week long, field-based geophysical program for undergraduate- and graduate students, involving teaching and research on basic and applied geophysical problems. Approximately 30 students each year attend SAGE from a wide range of large and small colleges and universities. The purpose is to enhance students' understanding of geophysics, introduce them to careers in the geophysical sciences and employment opportunities, and conduct leading edge research. Techniques include seismic reflection and refraction, gravity, ground-penetrating radar, electrical resistivity, magnetics, transient electromagnetics, and magnetotellurics.

The work and training undertaken at SAGE apply to stratigraphy and structure of continental basins, environmental-restoration and waste-disposal issues, characterization of groundwater and economic resources, CO₂-sequestration, and defense-related methodologies. SAGE is leveraged by funding from the Los Alamos National Laboratory, from the U.S. National Science Foundation, and from a consortium of small and large companies.

Improved Sensitivity Uranium-Series Measurements

Michael T. Murrell, 505-667-4299, mmurrell@lanl.gov

The goal of our project is to apply mass spectrometric methods to answer basic questions in Quaternary dating and geochemistry using uranium-series disequilibria techniques. In the last year we have studied 1) the temporal and spatial evolution of MORB at the Northern Gorda Ridge and the East Pacific Rise, 2) the chronology of glacial ice, 3) the dating of hot springs deposits, and 4) we have contributed a chapter to a new book – Uranium Series Geochemistry. This work provides information on the recent evolution of magmatic systems and also has application to natural hazard risk assessment, paleoclimate studies, and the carbon cycle.

We have emphasized integrating our new multi-collector ICP mass spectrometer into current research. This new instrument comes with a steep learning curve but it has greatly improved our sensitivity for the U-series members. One project that has benefited from these new capabilities involves dating of hydrothermal calcite, opal and quartz hot spring deposits from Dixie Valley, Nevada. This is an active geothermal system located 160 km NE of Fallon in west-central Nevada within the Basin and Range tectonic province that is fed by geothermal fluids arising from about 3000m depth. Samples were purified by handpicking, and were separated into calcite, quartz or opal-rich fractions. Many of the measurements were obtained with our GV Isoprobe MC-ICP in the "soft extract" mode using the Cetac Aridus nebulizer. We observe a cluster of relatively young ages close to 5 ka that are consistent with expectations based on the presence of active fumaroles that indicate a current heat source, as well as

geologic observations for recent faulting that has provided conduits for fluid flow. The observed older ages in excess of 100 ka for travertine deposits are also consistent with expectations, as cold seeps and the absence of fumaroles indicate a lesser degree of hydrothermal activity in these areas. These results show that U-series chronology is an important tool for understanding the longevity of hydrothermal systems and the time-scales of fluid-flow in the crust. In addition, the new ICP demonstrated its greatly improved sensitivity and accuracy relative to previous studies.

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

Larry Hersman, hersman@lanl.gov

The interactions of bacteria with metals and environmental nanoparticles can play an important role in the mobility of metals through porous media. In this first year of the study, we made significant progress on several aspects of our study. First, we made significant progress on a study of the effects of siderophores on metal adsorption to kaolinite. Siderophores are metal-complexing ligands with high affinities for Fe(III), produced by many microorganisms in Fe-deficient environments. Siderophores can also form strong complexes with other metals such as Pb and Cd; hence, siderophores may play an important role in controlling metal mobility in porous media. This study compared the effects of siderophores desferrioxamine-B (DFO-B), desferrioxamine-D (DFO-D1), desferrioxamine-E (DFO-E), as well as siderophore-like ligand acetohydroxamic acid (aHA) on Pb and Cd adsorption to kaolinite (KGa-1b) at pH 4.5 to 9, in 0.1 M NaClO₄, at 22°C, in the dark. At pH > 6.5 all of the siderophores plus aHA, inhibited Pb adsorption, with inhibition increasing in the order aHA < DFO-D1 < DFO-B.

Energy Transport in Space Plasmas

S. Peter Gary, pgary@lanl.gov

The long-term goal of this research is to understand the flow of plasma and energy in the near-Earth space environment both from small- and large-scale points of view. The objective of this research is to use plasma theory, simulations, and data analysis to investigate the consequences of plasma microinstabilities on the large-scale models of space plasmas that describe the solar-terrestrial interaction, to further the understanding of the large-scale structure and evolution of the magnetosphere through theory and simulations, and to improve our understanding of the acceleration and transport of energetic particles within the magnetosphere. Particle velocity distributions and parameters observed by Los Alamos plasma and energetic particle instruments on various spacecraft as well as computer simulations are used to carry out fundamental studies of plasma instabilities and associated transport in and near the solar wind, the Earth's bow shock, and the terrestrial magnetosphere.

OAK RIDGE NATIONAL LABORATORY

CONTRACT: OR22725

PERSON IN CHARGE: D. Cole

Nanoscale Complexity at the Oxide/Water Interface

D.J. Wesolowski (865) 574-6903; Fax (865) 574-496; wesolowskid@ornl.gov

A multidisciplinary, multi-institutional effort is focused on achieving a quantitative understanding of the structure and properties of the interface between aqueous solutions and the surfaces of metal oxide nanoparticle and macrocrystal surfaces over a wide range of temperatures and solution chemistries. This research impacts a broad range of DOE mission areas, including catalysis, nanoscience, waste migration, energy production, and biological processes. The pH- and temperature-dependent charging of oxide surfaces by reaction with water, and the association of solution counterions with the charged surface, form an interfacial domain termed the electrical double layer (EDL), which results from a complex interplay of electrostatic and van der Waals forces, quantum effects, lattice strain, ion hydration and hydrogen bonding, and specific binding of solute ions with the surface and one another. The experimental studies in this project are intended to quantify every aspect of the EDL for the selected solid phases and aqueous species, including degree of surface protonation and the total concentrations of counterions within the EDL, mineral surface structure, detailed geometrical information on ions and water molecules, and local bonding environments using non-perturbing, in situ measurements wherever possible. These are coupled with advanced “classical” multisite models, *ab initio* calculations and molecular dynamics simulations. The experimental and modeling studies are divided into five parts: (1) Surface pH titrations and ion adsorption studies to 300 degrees centigrade using oxide powder suspensions, coupled with temperature-dependent multisite complexation modeling; (2) Electrokinetic measurements on oxide powders to 250 degrees centigrade; (3) X-ray standing wave, absorption and reflection studies on single crystal surfaces into the hydrothermal regime; (4) *Ab initio* and molecular mechanics calculations, and large-scale molecular dynamics simulations of the EDL structure, integrating the results of all experimental approaches; (5) Developmental studies of the use of neutron scattering and reflection for probing the EDL structure using existing neutron sources and detectors, and advanced facilities under construction. Integration of a variety of macroscopic and microscopic experimental results with molecular theory and simulation will permit scaling and transfer to a wide range of disciplines and applications, and will yield new conceptual models and fundamental understanding of interfacial phenomena.

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

J. Horita (865) 576-2750; Fax 865-574-4961; E-mail horitaj@ornl.gov

The purpose of this research is to conduct quantitative theoretical, experimental, and simulation studies of isotope partitioning of the most fundamental reactions and processes in geologic systems relevant to

energy resource developments. Simple analogs for complex natural systems (gaseous molecules, aqueous fluids, and minerals) are studied in great detail to elevated temperatures and pressures with the most advanced and precise experimental techniques and theory-simulation methodologies available in order to provide a solid foundation for the understanding and modeling of various geologic systems including sedimentary and geothermal systems. During the current funding period, our activities have been focused on the effect of pressure and fluid composition on isotope partitioning between brines, steam, and minerals at elevated temperatures, both experimental and theoretical.

Ion Microprobe Studies of Fluid Rock Interactions – Multi-Scale Studies of Fluid-Rock Interaction

D. R. Cole, 865-574-5473, Fax 865-574-4961, coledr@ornl.gov; Lee Riciputi, riciputilr@ornl.gov

We are investigating the mechanisms associated with mass transport during fluid-rock interactions, at a variety of spatial and temporal scales, in both natural and experimental settings. Our work follows the following major themes: (1) linking nanotextures and isotopic signals in uranium minerals from basinal settings to large scale thermal events and global tectonics; (2) experimental studies of the mechanisms and rates of isotope transport and exchange in uraninite; (3) experimental studies of nanotextures and element mobility during dissolution of geologically significant minerals to identify mechanisms associated with mineral transformation during fluid-rock interactions; (4) collaborative efforts with academic and industrial partners examining fluid-rock mass transport in variety of settings; and (5) continued technical (instrumental) development in support of previously outlined research areas. Integration of experimental and field studies will allow us to link nano- and micro-textures in minerals with associated isotopic and elemental signatures, using analytical techniques such as secondary ionization mass spectrometry (SIMS), high-resolution transmission electron microscopy (HRTEM) and inductively coupled mass spectrometry (ICP-MS) to provide a more detailed understanding of the processes occurring during mass transport in regional fluid events.

Mechanisms and Rates of Isotope Exchange in Mineral-Fluid Systems – Investigation of Mineral Reaction Zones and Associated Interfaces

D.R. Cole, 865-574-5473, Fax 865-574-4961, coledr@ornl.gov, L.R. Riciputi and J. Horita

The major goal of the research is to determine the mechanisms and rates of isotope exchange between minerals and fluids (gases) over a broad range of temperatures and pressures. Our primary focus has been on the experimental determination of rates of isotopic exchange controlled by one of two general mechanisms: surface reactions leading to recrystallization or mineral transformation and volume (lattice) diffusion. Results obtained during the current period have led to a quantitative understanding of the importance of pressure and f_{CO_2} in controlling the diffusion mechanism and rate of exchange of carbon and oxygen between calcite and carbon dioxide. The influence of crystal growth on oxygen isotope exchange between magnetite-water and hematite-water has been examined from 0.1 to 100MPa at a temperature of 800°C. We have also investigated the oxygen isotope exchange behavior of systems

where chemical reaction and solid-state diffusion are coupled (e.g., cation exchange between alkali feldspars and salt solutions). This latter effort will form the theme of our follow-on effort, which emphasizes new methods to image and/or quantify both the isotopic and chemical behavior during replacement rim formation. The use of neutron and X-ray scattering and NanoSIMS methods will complement more conventional approaches such as scanning and transmission electron microscopy, and gas source isotope ratio mass spectrometry.

Experimental Studies of Hydrothermal Fluid Speciation and Fluid/Solid Interactions Employing Potentiometric Methods – Experimental Studies of Hydrothermal Processes Employing In Situ pH Measurement

D.J. Wesolowski, (865) 574-6903, Fax (865) 574-4961, wesolowskid@ornl.gov

This project investigates aqueous reactions of critical importance in modeling a variety of fluid-rock interaction and related hydrothermal processes which impact oil, gas, and geothermal resource formation and exploitation, contaminant migration and remediation, deep subsurface fluid/rock interactions, and a wide range of general geochemical and industrial processes. The effort is focused on experimental studies using the unique capabilities of ORNL's high temperature pH-measurement, flow-through and rocking-autoclave hydrothermal facilities. With these capabilities, we are investigating the speciation of metals (Al, Fe, Zn, Mg, Ca, Rare Earths, etc.) in low to high temperature brines, the dissociation constants, thermal stabilities, and complexing characteristics of naturally-occurring organic acids, and the thermodynamics of low to high temperature brine solutions in the system Na-K-Ca-Mg-Al-Si-Fe-O-C-H-Cl-S. Recent developments have enabled us to address the surface charge, sorptive properties, dissolution/precipitation kinetics, and solubilities of important minerals and energy-production materials. We are also developing new pH sensors for oxidizing environments and temperatures above 300 degrees centigrade, and initiating studies involving geobiological materials. This research includes extensive collaboration with visiting professors, graduate students and postdoctoral fellows who wish to take advantage of our unique capabilities and expertise.

Volumetric Properties, Phase Relations & Reaction Kinetics - Molecular Structures and Adsorption Behavior of CO₂-CH₄+H₂O Fluids at Upper Crustal Temperatures and Pressures

J.G. Blencoe, 865-574-7041, Fax 865-574-4961, blencoejg@ornl.gov

Published thermophysical data for carbon dioxide-methane-hydrogen-water (CO₂-CH₄-H₂-H₂O) mixtures at 35-500°C, 0-100 MPa, are too sparse to permit formulation of accurate equations of state (EOSs) for these fluids. Reliable expressions could be used to solve many important petrologic, geochemical and societal problems. Applications of particular relevance to the energy and technological needs of the United States include: modeling the hydrodynamics of natural waters circulating through sedimentary basins, understanding how secondary porosity develops in oil and gas fields, modeling global cycling of greenhouse gases, and quantifying the phase behavior and chemical reactivity of CO₂ sequestered in geologic reservoirs.

To gain an improved understanding of the behavior of CO₂-CH₄-H₂-H₂O fluids in subsurface environments, more accurate thermophysical data are needed for these mixtures at elevated temperatures and pressures. Accordingly, we are using several unique experimental devices to measure, with unprecedented precision and accuracy, the densities, excess molar volumes and vapor-liquid equilibrium (VLE) relations of CO₂-CH₄-H₂-H₂O fluids at 35-500°C, 0-100 MPa. Coupled with suitable data from the literature, the new experimental results will spur development of more comprehensive and reliable EOSs for predicting the thermodynamic excess properties of CO₂-CH₄-H₂-H₂O fluids over wide ranges of temperature, pressure and composition.

Experimental Studies of Fundamental Stable Isotope Exchange in Experimental Mineral-Fluid Systems - Nanoscale Structure and Dynamics of Biomolecule - Mineral Interactions in Solution and their Role in Biomineralization

J. Horita, (865) 576-2750, Fax (865) 574-4961, horitaj@ornl.gov

Detailed, systematic laboratory experiments are proposed in order 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 CO₂-rich fluids at conditions encountered in various geologic settings (groundwater, deep aquifers, sedimentary basins, geothermal systems, etc.). Such information is vital to our understanding of numerous dynamic geochemical processes involving CO₂, on time-scales ranging from hours to thousands of years, ensuing from the injection of large volumes of CO₂ into the subsurface.

Our specific objectives in this proposal are to investigate 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.”

PACIFIC NORTHWEST NATIONAL LABORATORY

CONTRACT: RL01830

PERSON IN CHARGE: A. Felmy

Electron Transfer at the Fe(III) Oxide-Microbe Interface

J.M. Zachara, (509) 376-3254, john.zachara@pnl.gov

Fe(III) oxides poise the oxidation/reduction potential of subsurface materials and act as electron acceptors for redox reactions. Dissimilatory metal reducing bacteria (DMRB) utilize these oxides as electron acceptors under anoxic conditions, and transform them to other mineral phases. Past research has identified the nature and properties of biosynthetic Fe(II), Fe(II/III), and Fe(III) mineral phases, and their formation pathways driven primarily by biogenic Fe(II) flux. Current research is investigating how DMRB access Fe(III) oxides in multi-mineral grain coatings and lithic fragment interiors. These characteristic microenvironments limit direct organism-Fe(III) oxide contact, and provide a unique physicochemical setting for biotransformation that has not been scientifically explored. Laboratory physical models involving the precipitation of nanoparticulate Fe(III) oxides in the internal pore space of porous silica, and the coating of quartz slides with mixtures of Fe(III) oxides and other relevant accessory phases are being used to study biotransformation reactions under controlled conditions that simulate more complex lithic fragment and grain coating interiors. Experimentation involves batch and flow systems incubated with Fe(II), bio-reduced anthraquinone disulfonate, or DMRB that have been cultured anaerobically under controlled conditions. Physical model results allow interpretation of the biotransformation behavior of Fe(III) oxides in a set of subsurface sediments containing particle coatings and intragrain precipitates of Fe(III) oxides in association with other secondary phases. High resolution transmission electron microscopy with focused ion beam sample preparation, Mössbauer spectroscopy, conventional and synchrotron x-ray diffraction, XANES and X-PEEM spectromicroscopy, and atomic force microscopy are being used to monitor reductant and microbe induced changes to the Fe(III) oxides. Fundamental new insights are being provided on how DMRB access solid-phase electron acceptors in restricted physical environments.

Molecular Basis for Microbial Adhesion

Tjerk P. Straatsma, 509-376-4079, tps@pnl.gov

Outer membranes of Gram-negative bacteria have important structural, signaling, and transport functions that play a role in geochemical processes. Among these proteins are several types of porins. These are passive transport proteins for small solute molecules such as sugars and solvated ions. These proteins and other peptides associated with the cell surface, therefore, play an important role in the interaction of microbes with the environment and the uptake of solvated ions. Using threading techniques and crystal structures of structurally homologous proteins from other bacteria, models of the three-dimensional structure for a number of outer membrane proteins for *Pseudomonas aeruginosa* have been suggested. We are now incorporating models for the outer membrane porins in the model for our LPS membrane to study the electrostatic field in the pore region and corresponding effect on ion

selectivity. Simulations of a complex protein channel of *Escherichia coli* incorporated in a bilayer membrane were first reported by Tieleman and Berendsen, and revealed complex non-bulk behavior of water molecules in the trans-membrane pore. In our current work, we performed the first molecular dynamics simulations of a porin in the LPS outer membrane of *P. aeruginosa*. Because of the asymmetric nature of these membranes and the resulting asymmetric charge distribution analysis of these simulations is expected to reveal a significant effect on the transport properties through trans-membrane porins. Our goal in carrying out these simulations is to understand how the structure of the channel provides a low-energy pathway for environmental ions across the membrane. Ultimately, estimates will be made for the potential and free energy profile along such pathways for environmental ions of importance. In addition, models for the outer membrane of *Shewanella oneidensis* are being developed for the study of outer membrane cytochromes through which metal and mineral reduction outside of the cell can take place.

Multi-Resolution Structure and Reactivity of Kinetically Roughened Oxide Surfaces

Kevin M. Rosso, Kevin.Rosso@pnl.gov

Surfaces of minerals in natural settings usually exhibit a significant degree of morphological heterogeneity. On scales from the molecular-scale to micron scales, surface roughness can be an important factor in growth, dissolution, and adsorption processes. Despite this fact, the relationships between these processes and roughness have not lent themselves to easy quantification because of their inherent complexity. To address this complexity we are studying the dissolution behavior of various mineral surfaces at various length scales of observation accessible by atomic force microscopy (AFM). For example, the dissolution of prismatic and rhombohedral quartz surfaces by hydrothermal KOH/H₂O solution leads to the development of a variety of overlapping etch features each etching at different rates (Yanina, Rosso, Meakin, 2005, *Geochimica et Cosmochimica Acta*, in review). The spatial density and characteristics of these features, as well as their interaction upon coalescence, affects the total dissolution rate for overall surface. The prismatic surface dissolves almost two orders of magnitude faster than the rhombohedral surface, mostly due to the difference in the number and the rate of dissolution of extended defects, such as dislocations. Crystal voids etched almost one order of magnitude faster on the prismatic surface than on the rhombohedral surface due to differences in the number and the density of steps formed by voids on the different surfaces. Studying the step-wise dissolution of isolated etch pits is the current paradigm; however this approach fails when dissolution features overlap and interact. By examining the surfaces at various length scales between 10 nm and 100 microns, we have been successful at separating the contributions of various overlapping dissolution processes. In addition to AFM topographic analysis of the evolving surfaces, wavelet image processing has been a useful tool for helping to categorize etch features on a length scale basis. Also, kinetic Monte Carlo simulations have provided a basis for making a linkage between the AFM observations and the molecular-scale (Meakin, Rosso, Yanina, 2005, *Journal of Chemical Physics*, in prep). Current efforts are focused on adapting these tools to address the scaling behavior of a variety of low-index hematite surfaces dissolving in various media.

Reaction and Transport of Toxic Metals in Rock-Forming Silicates at 25°C

Eugene S. Ilton, Eugene.Ilton@pnl.gov

This project is an investigation of reactions between silicate minerals and toxic metal-bearing aqueous fluids. We are specifically exploring mechanisms of oxidation-reduction reactions at the mineral-fluid interface involving reductants structurally bound in minerals and sorbed to mineral surfaces. The project has three main components: experimental investigation of U reduction and sorption by phyllosilicates; transmission electron microscopy (TEM) characterization of reaction products; and development of new characterization techniques. Technique development includes X-ray photoelectron spectroscopy (XPS) and atomistic-scale TEM methodologies to probe sorption behavior and redox reactions. Experiment design and sample characterization is aimed at elucidating crystallographic and solution controls on heterogeneous electron transfer between phyllosilicates and multivalent metals in the environment.

The research has focused on heterogeneous reduction of uranyl by Fe(II)-bearing micas (Ilton et al., 2004). The valence state of uranium strongly influences its solubility and sorption behavior thereby determining its mobility in environmental systems. Recent results include: differentiation of reactivity of basal surfaces, edges, and interlayer regions; identification of effects of alkali cations in solution on heterogeneous reduction of uranyl by micas; and the unexpected discovery that heterogeneous reduction of uranyl on Fe(II)-mica surfaces produces pentavalent uranium as a major sorbed species. Pentavalent U has been ignored for most aqueous systems because U(V) has only a small stability field in water and rapidly disproportionates. Previous work, however, did not consider the role of mineral surfaces in stabilizing U(V). Our research suggests that pentavalent U may play an important, but hitherto unrecognized, role in the U geochemical cycles. One of the long range goals of this project is to determine whether other mineral surfaces can stabilize U(V).

This project has utilized electron microscopy, x-ray photoelectron spectroscopy (XPS), and x-ray absorption spectroscopy (XAS) in order to determine the valence state and location of metals sorbed to phyllosilicates. In this regard, we have been developing strictly ab initio theoretical models to better interpret the fine structures in the 2p, 3s, and 3p XPS of transition metals (Bagus et al., 2004a and 2004b). Our long-range goal is to be able to simulate complex bonding environments that represent sorption at surfaces and nanosized particles.

Experimental, Theoretical, and Model-Based Studies of Crystallographically Controlled Self-Assembly During Nanocrystal Growth

Andrew R. Felmy, (509) 376-4079, ar.felmy@pnl.gov

The growth of ZnS nanoparticles with both water and mercaptoethanol was found to occur predominantly via crystallographically-specific oriented attachment (OA). The growth mechanism determines particle morphology and microstructure. Twins and stacking faults form in the coarsened mercaptoethanol-capped ZnS, whereas more complex, closely spaced twins, stacking faults, and polytypic intergrowths form in coarsened water-ZnS. At long reaction times, diffusion-controlled growth removes surface irregularities arising from OA to yield rounded particles with complex internal structures. The character of the surface ligands affects both phase transformation pathway and temperature of phase transformation. Methanol desorption and rewetting, and water binding cause

structural changes, reversible in the case of methanol ligands. Aggregation and disaggregation also cause reversible structural modification. Dispersed nanoparticles in suspension have a more distorted internal structure than aggregated nanoparticles of the same size. Reversible switching between distorted and crystalline structures can be induced by changing the aggregation state at room temperature, implying a low activation energy for the transformation. The results are believed to be the first surface-driven room temperature transitions observed in nanoparticles. The results indicate that nanoparticle structure is not kinetically trapped, but responsive to environmental changes. The growth of goethite nanoparticles was explored with a variety of synthesis methods, including a flash annealing technique to create nanoparticles in the range from 5-80 nm with differing crystallinity, habit and surface properties. TEM characterization shows aggregation in the more equant particles that is suggestive of initial face-to-edge impingement. This mode of aggregation was further suggested in large scale 10,000 atom MD simulations that showed positive charge buildup at the edges of goethite nanoparticles and negative charge buildup in the centers of the faces. We thus infer a possible mechanism for OA in these nanoparticles that mitigates the problem of particle-particle electrostatic repulsion. Other work has measured the growth of goethite nanoparticles in real time via synchrotron-based wide and small angle x-ray scattering (WAXS and SAXS, respectively). As with ZnS there is evidence for a change of mechanism with nanoparticle size in the tens of nm regime, possibly from OA to diffusion-controlled growth.

Computational Investigation of Acid-Base, Surface Complexation and Oxidation/Reduction Mechanisms

Andrew R. Felmy, (509) 376-4079, ar.felmy@pnl.gov; J. Rustad

This work addresses two major areas: (i) molecular simulation of oxygen exchange processes in aqueous Keggin ions, which serve as well-characterized aqueous oxide surface surrogates, and (ii) ferric-ferrous electron transfer in hydrolyzing aqueous solutions, which is the first step towards looking at electron transfer reactions on mineral surfaces.

A new mechanism has been postulated to explain the reactivity trends for oxygen-isotope exchange reactions between sites in the aluminum polyoxocations of the ϵ -Keggin type and bulk solution. Experimentally, the molecules have four oxygens that differ considerably in reactivity both within a molecule, and between molecules in the series: Al_{13} , GaAl_{12} and GeAl_{12} [$\text{MO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{n+}(\text{aq})$; with $M = \text{Al(III)}$ for Al_{13} , $n = 7$; $M = \text{Ga(III)}$ for GaAl_{12} , $n = 7$; $M = \text{Ge(IV)}$ for GeAl_{12} , $n = 8$]. A partly dissociated, metastable intermediate molecule of expanded volume is necessary for exchange of both sets of $m_2\text{-OH}$ and that the steady-state concentration of this intermediate reflects the bond strengths between the central metal and the $\mu_4\text{O}$. This mechanism explains the reactivity trends for oxygen-isotope exchange in $m_2\text{-OH}$ and $h\text{-OH}_2$ sites in the ϵ -Keggin aluminum molecules, and also explains the observation that the reactivities of minerals tend to reflect the presence of highly coordinated oxygens, such as the $\mu_4\text{-O}$ in boehmite, α -, and $\gamma\text{-Al}_2\text{O}_3$ and their Fe(III) analogs. The partial dissociation of these highly coordinated oxygens, coupled with simultaneous activation and displacement of neighboring metal centers, may be a fundamental process by which metals atoms undergo ligand exchanges at mineral surfaces.

A molecular model has been developed for ferrous-ferric electron transfer in a hydrolyzing solution. The model predicts that increasing pH reduces the potential of mean force between the ferrous and ferric ions. The magnitudes of the calculated contributions from the barrier heights and the potential of mean force nearly cancel each other at the canonical transfer distance of 0.55 nm. There is a surprising amount of overlap in electron transfer reorganization energies for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, and $\text{Fe}(\text{OH})_2(\text{H}_2\text{O})^+$, indicating that fluctuations in hydrolysis state can be viewed on a continuum with other solvent contributions to the reorganization energy.

First Principles Simulation of the Supercritical Behavior of Ore-Forming Fluids

Eric J. Bylaska, (509) 376-9114, fax (509) 376-3650, eric.bylaska@pnl.gov

Simulations of aqueous metal ions, their counter ions and their oxo-hydroxo hydrolytic polyions are proposed. 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 subcritical to supercritical conditions. The metals included in the study, Al^{3+} , Fe^{3+} , Cr^{3+} , Ca^{2+} and Ni^{2+} , were chosen because of their geochemical importance and because they display a rich range of properties such as very different hydrolysis constants, ligand residence times (e.g., in Cr^{3+} and Fe^{3+}), and ligand field stabilization.

Car-Parrinello molecular dynamics simulations of the hydration shells surrounding Al^{3+} ions were carried out for temperatures near 300°C. The predicted six waters in the octahedral 1st hydration shell were found to be trigonally coordinated via hydrogen-bonds to 12 2nd shell waters in agreement with the putative structure used to analyze the X-ray data, but in disagreement with results reported from conventional molecular dynamics using two- and three-body potentials. Bond lengths and angles of the waters in the 1st and 2nd hydration shells and the average radii of these shells also agreed remarkably well with the results of the X-ray analysis. Water transfers into and out of the 2nd solvation shell occurred on a ps time scale via an associative mechanism. Beyond the 2nd shell the bonding pattern substantially returned to the tetrahedral structure of bulk water.

The first hydrolysis species of aluminum was also simulated using Car-Parrinello simulations. The first hydrolysis species, $\text{AlOH}_{(\text{aq})}^{2+}$ has traditionally assumed to be hexacoordinate. However, in this work published in Science (Swaddle, T.W., J. Rosenqvist, P. Yu, E.J. Bylaska, B.L. Phillips, and W.H. Casey. 308: 1450-1453, 2005), it was shown that the kinetics of proton- and water exchange of aqueous Al^{3+} extracted from high-pressure ^{17}O -nuclear magnetic resonance (NMR) data, coupled with our Car-Parrinello simulations, support a five-coordinate $\text{Al}(\text{H}_2\text{O})_4\text{OH}^{2+}$ ion as the predominant form of $\text{AlOH}_{(\text{aq})}^{2+}$ under ambient conditions. This result contrasts Al^{3+} with other trivalent metal aqua ions, for which there is no evidence for stable pentacoordinate hydrolysis products.

SANDIA NATIONAL LABORATORY/ALBUQUERQUE

CONTRACT: AL85000

PERSON IN CHARGE: J. Merson

Molecular Simulations of Layered Minerals & Their Interactions with Hazardous Material

Randall T. Cygan, 505-844-7216; rtcyan@sandia.gov

An atomic level understanding of mineral-water interactions is important for the evaluation and prediction of numerous properties for clays and other minerals, especially in the treatment of environmental waste. In particular, the behavior of water at the clay-water interface controls many processes including solvation, adsorption, precipitation, and growth. Our ability to understand these complex processes is provided by a few experimental and analytical methods such as X-ray absorption, vibrational, and NMR spectroscopies. However, due to complexities in the structure, composition, and nano-size of clays it is important to apply theoretical molecular models to obtain a fundamental understanding and interpretation of these phenomena. We have developed a general forcefield Clayff suitable for the simulation of hydrated mineral systems, including several clay and double layered hydroxide phases. Interatomic potentials for Clayff were derived from parameterizations incorporating structural and spectroscopic data from a variety of simple hydrated compounds. A flexible water model is used to describe the water and hydroxyl behavior.

Molecular simulations of clay-water-methane systems were extended to determine the structure and behavior of methane-water in the interlayer of various montmorillonite clays. Molecular dynamics using NPT ensembles and large simulation supercells provide atom trajectories for simulation times up to 500 ps. Ordering of methane-hydrate structure is examined within the interlayer and is related to formation of methane clathrate structures with water and the clay surfaces, and the formation of a hydrogen bonded network in the interlayer. The theoretical results support recent experimental observation of a stable methane hydrate intercalate with Na-montmorillonite.

Layered double hydroxide phases, such as hydrotalcite, were also simulated with energy minimization and molecular dynamics methods. These materials, often called inverse clays, are characterized by magnesium and aluminum layers with a net positive charge leading to the intercalation of anions and water within the interlayer. We completed a series of calculations demonstrating the relative stability of various hydrotalcite compositions and initiated a theoretical analysis of the vibrational modes for comparison with experimental studies.

Metal-Anion Pairing at Oxide/Water Interfaces

Louise J. Criscenti, 505-284-4357, ljcrisc@sandia.gov

Objectives: The objective of this research is 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 and vibrational sum frequency spectroscopies (XAS, VSGS), and molecular modeling to investigate the potential formation of ternary metal-anion complexes at mineral surfaces in different solution compositions over a range of surface coverages. XAS provides data on how the metal binds to the surface (monodentate, bidentate) and VSGS will provide data on the anions adsorbed with the metals, polyatomic anion orientation in some cases, and water structure at the mineral surface. Molecular modeling will support data from both spectroscopic techniques by providing information on water structure at the surface, the surface sites for metal-binding and the orientation of any associated ions, and the relative energetics of different surface complexes. We initially focused on investigating water structure and Sr^{2+} , Co^{2+} , and Pb^{2+} adsorption from NaCl, NaNO_3 , and NaClO_4 solutions onto quartz, amorphous silica, corundum, and gibbsite.

Interactions of Pore Fluid Pressure

William A. Olsson, waolss@sandia.gov

When subjected to non-hydrostatic, compressive stresses, some porous sandstones exhibit non-uniform compaction. The compaction occurs as a localization process, analogous to shear localization, but results in a thickening, tabular zone of compaction as opposed to culminating in a shear fracture. Simultaneous measurements of stress, strain, acoustic emission locations, and permeability allow the interaction between fluid flow, pressure and compaction localization to be studied. A major result to date is that compaction localization produces up to a two-order-of-magnitude decrease in permeability. A model of the compaction process was developed that incorporates the moving boundary between compacted, low-permeability regions and un-compacted, higher-permeability regions, and compaction-induced fluid injection at the boundaries. Because of the inhomogeneous nature of compaction produced by compaction localization, and its temporal evolution, a number of phenomena related to fluid flow are predicted by the model: locally increased pore pressures and spatial changes in the effective permeability. Implications of the results for future experimentation and for reservoirs are, briefly, that the interaction between compaction-induced fluid pressure and compaction localization should lead to a phenomenon analogous to dilatancy hardening, impeding the propagation of compaction bands. Experiments designed to detect pore pressure evolution and compaction hardening have been completed on saturated, undrained specimens. In addition to the previous suite of measurements, pore pressures were measured at three points along the length of the cylindrical sample. Large, compaction-induced, increases in pore pressure were observed as the effective stress state evolved into a regime where shearing should dominate compaction. However, the AE measurements showed that the dominant deformation mechanism remained compaction localization. A new theoretical model for localized compaction based on spinodal phase decomposition is being developed that includes initial formation of the compaction bands as well as the propagation and interaction of the bands to complete compaction of the specimen. Hertzian grain contact fracturing is a consistent micromechanism that leads to the phenomenology of the theoretical model.

Micromechanical Processes in Porous Geomaterials

Joanne T. Fredrich, fredrich@sandia.gov

The primary objective is systematic investigation of the microscale characteristics of earth materials, and how these microscale characteristics control the macroscopic behavior. Our approach integrates experimental rock mechanics tests, quantitative microscopy, and theoretical and numerical analyses. The research focuses on the porous earth materials that are central to geoscience applications, including geologic sequestration of greenhouse gases and hydrocarbon exploration and production.

Highlights:

A state of the art laser scanning confocal microscopy laboratory was set up. The facility allows for 3D imaging of porous media and fluid flow processes and direct visualization of two-phase flows, dissolution, and flow in fractures. A miniaturized combined flow/load cell was designed to enable visualization of flow in fractures.

Hydromechanical tests were performed with a transparent epoxy fracture replica. We found that with increasing normal stress, fracture aperture is reduced. The frequency distribution is bimodal and “squeezed” to lower values with increased normal stress. Deformation under normal load is not uniform, but instead depends upon the geometry of the contact areas. With increased shear stress, the average aperture increases as the fracture becomes dilatant with increased surface mismatch. The aperture distribution shifts to larger values, but maintains its bimodal shape, and is consistent with the mechanical behavior of rock joints observed during laboratory shear tests, where at low normal stresses the area in contact during shearing is a small percentage of the entire surface. Results are reported in Grasselli & Fredrich, “Direct Imaging of flow in fractures,” Proc. 2004 Eurock and 53rd Geomechanics Colloquium, 2004.

We considered eight data sets collected during synchrotron microtomography experiments performed at the GSECARS 13-BM beamline at the Advanced Photon Source. Four data sets were collected for synthetic sandstones, and the other four were collected from Castlegate sandstone. The data were analyzed and applied in massively parallel numerical simulations of single phase flow. The numerical calculations are compared to experimental measurements on core samples, and results offer insight into the significance of the micron-scale roughness of the pore-grain interface, the locally heterogeneous nature of pore-scale flow, and representative length scales and volumes necessary to predict bulk macroscopic fluid flow behavior.

Role of Fracture Intersections in the Flow and Transport Properties of Rocks

Harlan W. Stockman, hwstock@sandia.gov

This work continues a previous study of dispersion at fracture junctions, by adding a set of laboratory experiments and advanced numerical modeling. Coupled flow and dissolution experiments in fractures were performed at New England Research (NER). Sandia provides numerical modeling of the experiments, via the lattice Boltzmann (LB) method, and measurements of dissolution rates for modeling.

Experiments at NER used flat walls of high-density (low porosity) dental plaster; these flat walls were mated to transparent rough “fracture” walls to provide a varied velocity field. Initial rotating disk experiments were completed, and establish limits on the dissolution rates of the dental plaster. The flat-wall experiments produced high (uneroded) areas directly opposite asperities in the textured surfaces, and high areas and long “stringers” in the lees of obstacles. The specific dissolution patterns in the experiments were reproducible. Results were presented as “Evolution of fracture geometry,” presented at "Dynamics of Fluids in Fractured Rocks" Symposium at Berkeley (LBL) CA, Feb 11-14, 2004.

The 3D LB models reproduced the experimental patterns of dissolution, including the development of the long stringers in the lees of obstacles. The new capabilities of the code were benchmarked, and a robust precipitation model added. The 3D models have a broad application, and have also been applied to the formation of clots in arteries and the growth of artificial bone. The latter results are published in the Journal of Biomechanics [2004, in press].

Two-Phase Immiscible Fluid Flow

Robert J. Glass, rjglass@sandia.gov

The objective of this research is to develop quantitative understanding of the critical processes controlling two-phase flow and transport in rock fractures, with potential applications in radioactive waste isolation, CO₂ sequestration and petroleum engineering. Our previous research identified the importance of phase structure in controlling system behavior. We have developed experimental systems to create and measure a wide range of phase structures, and flow and transport through them. Current efforts focus on models of phase structure, parametric relationships for flow, transport and inter-phase transfer, and behavior in fracture-matrix networks.

Our previous experimental studies have demonstrated two important classes of phase structures in variable aperture fractures: satiated structures, wherein the invading phase fully entraps the defending phase, and fingered structures resulting from gravity destabilization. Both classes are accurately modeled using modified invasion percolation (MIP) algorithms that account for the influence of gravity, in-plane curvature and simultaneous invasion-reinvasion of two phases.

The MIP algorithm with simultaneous invasion-reinvasion of two fluids was shown to reproduce the dynamics of gravity-driven wetting fingers in variable-aperture fractures. Fragmentation behind the fingertip, pulsating flow and the stop-and-go dynamic of fingers were simulated, closely following experimental observations. Average finger widths are within 20% of experimental measurements. (Water Resources Research 39 (13) doi:10.1029/2002WR001542, 2003)

Parametric studies of the influence of fracture properties on satiated phase structure, and associated flow and transport properties are ongoing. The areal saturation (S_f) of the flowing phase at saturation is shown to depend on the ratio of two dimensionless parameters related to the fracture properties (C/δ , where the curvature number C , representing the mean influence of in-plane curvature, is the ratio of the mean aperture to the correlation length, and δ is the coefficient of variation of the aperture field). As C/δ goes to zero, behavior is as in standard invasion percolation within a correlated field, and $S_f \sim$

0.37. As C/δ increases above ~ 0.1 , S_f increases, approaching 1 for large $C/\delta \sim 10$. (Physical Review E 68, 061110, 2003)

We have also investigated infiltration in meso-scale laboratory fracture-matrix networks, demonstrating the occurrence of dynamic preferential pathways. (Water Resources Research, 38(12), 1281, doi:10.1029/2001WR001002, 2002).

Laboratory Investigation of Constitutive Property Upscaling

Vince Tidwell, vctidwe@sandia.gov

Rarely can petrophysical data be acquired at the desired scale of analysis. The resulting disparity between the scale at which data are measured and the desired scale of analysis necessitates the application of averaging or upscaling models. The goal of this research is to enhance fundamental understanding of upscaling processes through systematic physical and numerical experimentation. To challenge our understanding, laboratory experiments involving the collection of over 200,000 permeability values (with a gas mini-permeameter) from six different heterogeneous blocks of rock using six different scales of measurement were conducted.

Over the last year numerical experiments have been performed to explore the coupled effects of media heterogeneity/anisotropy and non-uniform flow (i.e., instrument characteristics) on permeability upscaling. Tests are designed to mimic the laboratory upscaling experiments; that is, the numerical experiments simulate flow from a mini-permeameter through media with heterogeneous characteristics similar to that of the sampled rocks. Simulations assume fully three-dimensional steady state, single-phase flow under isothermal, Darcian flow conditions. A stripped-down finite difference flow code developed at New Mexico Tech is being used. These simulations are performed on three-dimensional, single- and multi-scale Gaussian random fields with statistical properties taken from the sampled rocks. These heterogeneous permeability fields are being generated with the GSLIB family of geostatistical tools.

To date, efforts have largely focused on developing and verifying the computational framework to be used for the simulations. Numerous simulations have been performed to refine the resolution of the computational grid and the size of the sample domain, while striking a balance between model accuracy and computational burden. We have achieved numerical results within 0.3% of the analytical solution (mass flow and pressure) on grids of approximately 7M nodes. Using this grid, numerical experiments reproducing upscaling data acquired from various sandstone rock samples are being conducted.

These experiments will help develop confidence in the modeling by comparing the results of the numerical upscaling studies with that physically measured. Once confidence is gained we will turn our attention to other instruments like linear core tests and radial flow pump/slug tests. Effort to code and test these other flow geometries is currently underway.

PART II: OFF-SITE

AMERICAN CHEMICAL SOCIETY

1155 Sixteenth Street, NW
Washington, DC 20036

Grant: DE-FG02-04ER15518

Interfacial Phenomena: Linking Atomistic and Molecular Level Processes - Symposium March 28 - April 1, 2004

Jay Brandes, brandes@utmsi.utexas.edu

Drs. David J. Wesolowski of Oak Ridge National Laboratory and Gordon E. Brown of Stanford University co-chaired a symposium entitled “Interfacial Phenomena: Linking Atomistic and Molecular-Level Processes” at the ACS Annual Meeting in Anaheim, CA, March, 28 - April 1, 2004. Dr. Jay Brandes, Treasurer of the ACS Division of Geochemistry assisted in organizing the symposium and distributing funds. The symposium featured keynote talks by 9 international experts in surface science, and 5 student grants were awarded on a competitive basis. This DOE grant supported 5 of the keynote speakers and one student. The titles and authorship of their talks are listed below, and are referenced as “Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, USA, March 28 - April 1, 2004”. Over 40 speakers participated in the two-day symposium. The DOE-supported talks were: “Size Dependent Reactivity of Iron Oxyhydroxide Nanoparticles” (A.J. Anschutz, L.R. Penn), “Phase Transitions and Chemical Reactions at the Nano-scale: Effects of Confinement” (B. Coasne, K.E. Gubbins, F. Hung, E. Santiso, M. Sliwinska-Bartkowiak). “Cooperative Interactions in Chemisorption Oxides” (W.F. Schneider), “Structure and Bonding of Water on Metal Surfaces” (A. Nilsson, L.G.M. Pettersen, H. Ogasawara), “Viscosity and Hydrophobicity of Interfacial Water” (S. Granick), and “Heterogeneous Reactions of Carbonate Minerals with Trace Atmospheric Gases” (V.H. Grassian).

UNIVERSITY OF ARIZONA

Department of Agricultural and Biosystems Engineering
Tucson, AZ 85721

Grant: DE-FG02-04ER15608

Seismic Absorption and Modulus Measurements in Porous Rocks in Lab and Field: Physical and Chemical Effects of Fluids

Robert Roth, bobroth@ag.arizona.edu

We are exploring a new technology that is based on using low-frequency seismic attenuation data to monitor changes in fluid saturation conditions in two-fluid phase porous materials. The seismic attenuation mechanism is related to the loss of energy due to the hysteresis of resistance to 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 the (1) onset of contaminant leakage at buried waste sites, (2) progress of contaminant remediation, and (3) progress of water flooding or steam injection during enhanced petroleum recovery.

Last year marked the initial phase of our feasibility study in the field, where we seek to detect changes in recorded strain signals (attenuation) in response to local changes in the fluid saturation conditions in the vadose zone. Rather than employing manmade sources, which are very expensive and invasive, we are exploring the use of natural sources of strain and seismic waves, specifically Earth tides and globally-recorded, natural microseisms, respectively. The field site is operated by the University of Arizona, and has sophisticated facilities for controlled water irrigation and a comprehensive, dense array of instruments used for measuring water saturations and flow. We plan to change the saturation conditions by irrigating at the site with water in October '03, with water plus a biosurfactant in late spring '04 and again with water late in '04. First background data over a 9 months period from three tiltmeters and 3 seismometers are encouraging.

We measured the wettability hystereses of clean and diesel-coated quartz crystals by water, diesel, and oil-reducing bacteria solution. The purpose of this work was to see if there are differences in the wettability hystereses, which result in differences in low-frequency seismic attenuation. When the diesel-coated quartz was dipped in and out of the bacterial solution, we observed significant changes in hystereses that did not occur with the other fluid constituents. These results suggest that we ought to be able to monitor bioremediation progress using low-frequency seismic attenuation data.

ARIZONA STATE UNIVERSITY

Department of Geological Sciences
Tempe, AZ 85287

Grant: DE-FG02-02ER15361

Development of an Experimental Data Base and Theories for Prediction of Thermodynamic Properties of Aqueous Electrolytes and Nonelectrolytes of Geochemical Significance at Supercritical Temperatures and Pressures

Everett Shock, eshock@asu.edu

Reactions of aqueous solutions with rocks control the generation, migration, and accumulation of fossil fuels as well as many other geochemical processes. Analogous interactions determine the movement of metals, hydrocarbons and other toxic compounds in aquifers, tailings piles from mining landfills, nuclear waste repositories, and contaminated sites. This diversity of geochemical processes involving aqueous solutions is suited for study with theoretical models that employ thermodynamic data. The objective of this research is to combine new experimental measurements with theoretical equations of state and with first principles quantum mechanical predictions to supply the necessary thermodynamic data. Our use of experimental conductance measurements to get equilibrium association constants for a variety of aqueous electrolytes at high temperature has been going very well. We have measured association of the ions in the following salts: sodium acetate, sodium chloride, potassium chloride, sulfuric acid, hydrochloric acid, sodium sulfate, and sodium hydrogen sulfate. Methods for predicting second cross virial coefficients for interactions involving water have been developed. These predictions are needed in our new equation of state. Progress has been made in developing equations of state for salt solutions at high temperatures. We have collaborated in the construction of a new heat capacity calorimeter at the University Blaise Pascal in France so that measurements on this important property can be continued. In order to expand our thermodynamic database to cover temperatures and pressures where measurements are impossible, we have further developed our new method of predicting free energies of hydration. This method uses molecular dynamic simulation and *ab initio* quantum mechanics to make the predictions. The free energy of hydration of water at extremes of temperature and pressures has been predicted using this new method. We have also shown that our new method can predict hydration free energies of ions at high temperatures with good accuracy. It seems clear that using this new method we can now predict free energies of hydration with an accuracy of about 5 kJ/mole for any reasonably simple solute containing elements as heavy as chlorine at temperatures to about 3000 K and pressures to about 300,000 atmospheres.

ARIZONA STATE UNIVERSITY

Department of Geological Sciences
Tempe, AZ 85287

Grant: DE-FG03-94ER14414

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

Lynda B. Williams, Lynda.Williams@asu.edu

The objective of this research program has been to use chemical and isotopic variations of diagenetic minerals and organic compounds in hydrocarbon bearing sedimentary basins in order to address the chemical dynamics (changes and movement over time) of fluids interacting with host rocks. We focus on trace elements and their isotopes as they are released from maturing hydrocarbon sources and fractionated during incorporation into authigenic clays and other mineral cements. In 2004 we studied Li isotopes as a monitor of hydrocarbon related fluids. We have 1) tested Li-isotope standards and SIMS protocol for Li-isotope ratio measurements, 2) conducted hydrothermal experiments to determine the equilibrium Li-isotope fractionation between illite and water and 3) tested the effect of crystal growth on isotope ratio measurements. Furthermore, in preparation for a comparison of experimental isotope fractionation results to field areas with different reaction kinetics, a variety of field areas were sampled. These include a contact metamorphosed bentonite, Salton Sea cores, the Geysers, and hydrothermal deposits from Yellowstone National Park. These samples are currently being prepared and analyzed for bulk and clay mineral composition. A select group of the samples will be used for our study of Li and B isotope variations in illite formed in open and closed geologic systems at a various temperatures. The results of the hydrothermal reaction of clay mineral SWy-1 smectite to illite in sealed Au-capsules with water containing -67‰ $\delta^7\text{Li}$, 0‰ $\delta^{11}\text{B}$ (300°C , 100 MPa) showed similar isotopic trends. This is important because it shows that tetrahedral (containing B) and octahedral (containing Li) sites of the illite re-equilibrate simultaneously. By separating the reaction products into fine (<0.2) medium (0.2 to 2.0) and coarse (>2.0) size fractions and studying the isotopic trends we have concluded that: 1) Small crystals reflect earliest precipitation in metastable equilibrium with fluid. 2) Larger illite crystals approach isotopic equilibrium faster than small crystals as smectite dissolves and illite grows. 3) Illite grows in equilibrium with the fluid in a matrix of smectite that is out of equilibrium. 4) The Li isotope fractionation between illite and water at 300°C is approximately -11‰ .

BOSTON UNIVERSITY

Department of Physics and Center for Computational Science
Boston MA 02215

Grant: DE-FG02-95ER14498

Collaborative Research: Analysis and Interpretation of Multi-Scale Phenomena in Crustal Deformation Processes: Using Numerical Simulations of Complex Nonlinear Earth Systems

W. Klein, (617) 353-2188, klein@bu.edu

Critical energy facilities face a variety of hazards and risks from tectonic instabilities in the complex earth system, including primarily earthquakes, but also including volcanic eruptions and landslides. Understanding these hazards and forecasting these risks has been the motivating rationale for our work under this project. We have pioneered a large array of modeling and numerical simulation techniques to develop a deep understanding of the basic physical processes associated with strong space-time simulations during the last three years. Our work has been a joint effort of model development, theoretical understanding and testing with observed data. We have now successfully formulated and tested a class of forecast algorithms that are significantly more effective at forecasting observed large earthquakes than a corresponding random data set from which all the space-time structure has been removed by randomly re-shuffling the data in time. Of the last 8 earthquakes larger than magnitude 5.0 that have occurred in southern-central California since the forecast period began, 7 fell within 1 standard deviation (± 11 km) of a forecasted location. We are also developing new applications of topologically realistic earthquake fault system models of the space-time dynamics for use in forecasting. Data to which we apply our methods include GPS and Synthetic Aperture Radar Interferometry data, which give us new information about crustal deformation. In our work we have also determined that 1) statistical field theory techniques based on supersymmetric considerations indicate that the evolution of earthquake seismicity can be described by a linear theory over short times, since the nonlinear clusters in the patterns have very small amplitude; 2) there are at least 4 distinct classes of earthquakes, each with a distinct set of scaling exponents; 3) the non-equilibrium driven, mean-field earthquake fault system in southern California has many characteristics of equilibrium systems; and 4) new models with threshold weakening can be shown to generate aftershocks and foreshocks. The scaling properties of the Gutenberg-Richter relation are strongly affected by the time scale of the threshold weakening, indicating the appearance of a new scaling field.

CALIFORNIA INSTITUTE OF TECHNOLOGY

Division of Geological and Planetary Sciences
Pasadena CA 91125

Grant: DE-FG02-85ER13445

Infrared Spectroscopy and Stable Isotope Geochemistry of Hydrous Silicate Glasses

E. Stolper, (626) 395-6504, fax (626) 568-0935, ems@expet.gps.caltech.edu

Objectives: This project focuses on applications of experimental petrology and stable isotope geochemistry to study of volatile components dissolved in silicate melts and glasses and CO₂ in the atmosphere.

Project Description: *Parts 1 and 3* involve equilibration of volatiles with silicate melts to determine fractionations and/or diffusion rates: CO₂ in *Part 1* and H₂O in *Part 3*. *Part 2* involves equilibrating forsteritic olivine with basaltic liquid at 1 atm as a function of temperature to determine olivine-melt oxygen isotope fractionation factors for a wide range of melt compositions. *Part 4* is our study of CO₂ in the atmosphere of the Los Angeles basin, especially as it relates to sources of pollution and changes through time.

Results: *Part 1:* We published our work on Na-melilitic melt (Appora, I, JM Eiler, A Mathews, and EM Stolper (2003) *Experimental determination of oxygen isotope fractionations between CO₂ vapor and soda-melilite melt. Geochim. Cosmochim. Acta 67: 459-471*).

Part 2: We published a related paper on mineral/melt partitioning of trace elements (Gaetani, GA, AJR Kent, TL Grove, ID Hutcheon, and EM Stolper (2003) *Mineral/melt partitioning of trace elements during hydrous peridotite partial melting. Contrib. Mineral. Petrol 145: 391-405*).

Part 3: We prepared large rhyolitic samples with homogeneous water contents and diffusion couples, before working with more difficult basalts. We are preparing samples containing varying water contents but the same, homogeneous hydrogen isotopic compositions.

We are preparing a related paper that was presented at last fall's AGU meeting (KA Kelley, T Plank, S Newman, E Stolper, TL Grove, S Parman, and E Hauri (2003) *Mantle melting as a function of water content in arcs, Eos. Trans. AGU, 84(46), Fall Meet. Suppl., Abstract V41D-06*).

Part 4: Our bi-daily analyses since 1998 continue. Looking at seasonal trends compared with clean-air data for the same latitude, we have found that the local contribution to the CO₂ in the atmosphere, unlike the total CO₂ analyzed, has a seasonal cycle, being larger and lighter during the summer and autumn than during the winter and spring. Diurnal variations give different information than do daily measurements at the same time of day.

CALIFORNIA INSTITUTE OF TECHNOLOGY

Division of Geological and Planetary Sciences

Pasadena CA 91125

Grant: DE-FG02-88ER13851

Isotope Tracer Studies of Diffusion in Silicates and of Geological Transport Processes Using Actinide Elements

Gerald J. Wasserburg, isotopes@gps.caltech.edu

Three major projects were carried forward: 1) A study of Ca isotopes in calcite grown from solution. The shift in Ca isotopes ($\Delta(^{44}\text{Ca}/^{40}\text{Ca})$) in calcite crystals relative to that of the parent solutions were determined by TIMS. Alkalinity, pH and concentrations of CO_3^{2-} , HCO_3^- , and CO_2 in solution were determined. Solutions with different Ca concentrations were used. In all cases, the condition $[\text{Ca}] \gg [\text{CO}_3^{2-}]$, obtained. A wide range in $\Delta(^{44}\text{Ca}/^{40}\text{Ca})$ was found for the crystals, extending from 0 to -1.5 per mil. The results show that $\Delta(^{44}\text{Ca}/^{40}\text{Ca})$ is a linear function of the saturation index (Ω). “Rate-controlled calcium isotope fractionation in synthetic calcite” D. Lemarchand, G.J. Wasserburg, D.A. Papanastassiou (2004) GCA, in press. 2) A study of the sources of Sr in ground water in a carbonate aquifer. Major element concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured in groundwaters and bedrock from the Madison aquifer in western South Dakota in order to investigate controls on the downgradient evolution of dissolved Sr in a carbonate groundwater system. It was confirmed that the major element chemistry of groundwaters evolves according to dolomite dissolution, anhydrite dissolution, calcite precipitation, and ion-exchange with clay minerals. “Anhydrite and the Sr isotope evolution of ground water in a carbonate aquifer.” A.D. Jacobson and G.J. Wasserburg, (2004) Chemical Geology, submitted. 3) A theoretical investigation of the evolution of metals in galaxies was carried out. A proposed model appears to explain the observations on damped Lyman-alpha systems with red shifts from $z = 0.5$ to 4.5 . The model considers the onset and cessation of infall from the intergalactic medium and appears to explain the abundances found in halo stars while providing a plausible mechanism for making globular clusters. “Chemical evolution of galaxies and enrichment of the intergalactic medium” Y.-Z. Qian and G.J. Wasserburg (2004) Astrophysical Journal, in press.

UNIVERSITY OF CALIFORNIA, BERKELEY

Department of Earth and Planetary Science
Berkeley CA 94720

Grant: DE-FG03-01ER15163

Precipitation at the Microbe-Mineral Interface

Jill Banfield, 510 643 2155, jbanfield@berkeley.edu

Microbial biomineralization can dramatically modify the distribution of metals in the environment. Our goal is to investigate how microbial activity affects the nature and distribution of nanoparticulate metal sulfide biomineralization products. The first stage of research focuses on how thermodynamics control the rate of microbial sulfate reduction, and the consequences for the characteristics of nanoparticulate products. Using *Desulfovibrio desulfuricans* as an example, we found that the energy available from sulfate reduction exerts significant control on the respiration rate. As a result of thermodynamic control, significant amounts of sulfate remain at the end of experiment, where sulfate reduction ceases. Although the residual amount of sulfate, or threshold sulfate concentration, varies with initial lactate and sulfate concentrations, the free energy from lactate oxidation and sulfate reduction remains same, about -85 kJ mol^{-1} lactate, at the end of experiments. We are currently extending our experiments to the complete pathways of acetate oxidation and sulfate reduction by *Desulfobacter postgatei*. We are setting up anaerobic flow-through sand columns to use thermodynamic control to study how microbial metabolism affects the form of metal sulfide nanoparticles and their aggregates, as well as their transport through porous media. We will compare how transport of biogenic and inorganic-synthesized nanoparticles differ. The results of this work will improve understanding of the ways in which microorganisms influence the physical and chemical nature of their surroundings.

UNIVERSITY OF CALIFORNIA, BERKELEY

Department of Earth and Planetary Science

Berkeley CA 94720

Grant: DE-FG02-01ER15218

Experimental, Theoretical, and Model-Based Studies of Crystallographically Controlled Self-Assembly During Nanocrystal Growth

Jill Banfield, 510 643 2155, jbanfield@berkeley.edu

The growth of ZnS nanoparticles with both water and mercaptoethanol was found to occur predominantly via crystallographically-specific oriented attachment (OA). The growth mechanism determines particle morphology and microstructure. Twins and stacking faults form in the coarsened mercaptoethanol-capped ZnS, whereas more complex, closely spaced twins, stacking faults, and polytypic intergrowths form in coarsened water-ZnS. At long reaction times, diffusion-controlled growth removes surface irregularities arising from OA to yield rounded particles with complex internal structures. The character of the surface ligands affects both phase transformation pathway and temperature of phase transformation. Methanol desorption and rewetting, and water binding cause structural changes, reversible in the case of methanol ligands. Aggregation and disaggregation also cause reversible structural modification. Dispersed nanoparticles in suspension have a more distorted internal structure than aggregated nanoparticles of the same size. Reversible switching between distorted and crystalline structures can be induced by changing the aggregation state at room temperature, implying a low activation energy for the transformation. The results are believed to be the first surface-driven room temperature transitions observed in nanoparticles. The results indicate that nanoparticle structure is not kinetically trapped, but responsive to environmental changes. The growth of goethite nanoparticles was explored with a variety of synthesis methods, including a flash annealing technique to create nanoparticles in the range from 5-80 nm with differing crystallinity, habit and surface properties. TEM characterization shows aggregation in the more equant particles that is suggestive of initial face-to-edge impingement. This mode of aggregation was further suggested in large scale 10,000 atom MD simulations that showed positive charge buildup at the edges of goethite nanoparticles and negative charge buildup in the centers of the faces. We thus infer a possible mechanism for OA in these nanoparticles that mitigates the problem of particle-particle electrostatic repulsion. Other work has measured the growth of goethite nanoparticles in real time via synchrotron-based wide and small angle x-ray scattering (WAXS and SAXS, respectively). As with ZnS there is evidence for a change of mechanism with nanoparticle size in the tens of nm regime, possibly from OA to diffusion-controlled growth.

UNIVERSITY OF CALIFORNIA, BERKELEY

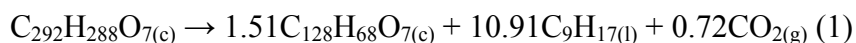
Department of Earth and Planetary Science
Berkeley CA 94720

Grant: DE-FG02-03ER15418

Diffusion/Dispersion Transport of Chemically Reacting Species

Harold C. Helgeson, brogie@berkeley.edu

It has been demonstrated (see Program Summary Book, 2002) that incongruent melting at 150°C and 830 bars of an immature type-II reactant kerogen represented by $C_{292}H_{288}O_{7(c)}$ to produce a mature (oxidized) kerogen corresponding to $C_{128}H_{68}O_{7(c)}$, crude oil with an average composition of $C_9H_{17(l)}$, and CO_2 gas can be described by writing



in which oxygen and hydrogen are conserved. Consideration of the stoichiometries of incongruent melting reactions analogous to Reaction (1) for reactant kerogens with different atomic hydrogen to carbon ratios ((H/C)s) and/or (O/C)s permits calculation of the volume of oil (mole of reactant organic carbon (ROC))⁻¹ that can be generated in, as well as the minimum volume of oil (mol ROC)⁻¹ that must be expelled from hydrocarbon source rocks as a function of the H/C and O/C of the reactant kerogen. It can be deduced from Reaction (1) that nearly 11 moles of crude oil are produced from one mole of the reactant kerogen, which increases to 39.5 moles with increasing C and H/C in the reactant kerogen to $C_{415}H_{698}O_{22(c)}$. The secondary porosities created in source rocks by Reaction (1) and others like it are of the order of 75-80 volume percent of the oil generated, which requires expulsion of the remainder. This minimal volume of expelled crude oil is comparable to, or exceeds the oil produced and in proven reserves in major oil fields such as the North Sea, the Paris and Los Angeles Basins, and those in Kuwait, Saudi Arabia, and elsewhere in the Middle East. For example, taking account of the average weight percent organic carbon in the immature kerogen (~1.68) with an average H/C of ~ 1.16 in the Early Cretaceous source rocks in Kuwait, which have an average aggregate thickness of ~210 meters, it can be shown that all of the oil produced and in proven reserves in Kuwait (121×10^9 bbls or 6.8×10^6 bbls km⁻²) can be accounted for by minimal expulsion from the source rocks of oil generated at 150°C and 830 bars solely by the incongruent melting process.

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

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 the jarosite – alunite series of hydrated sulfates, iron oxyhydroxides, other phases related to acid mine drainage, uranyl minerals, phosphates, arsenates, and selenium minerals. New calorimetric approaches to the energetics of sulfide minerals are being developed.

UNIVERSITY OF CALIFORNIA, DAVIS

Department of Geology

Davis CA 95616

Grant: DE-FG02-04ER15498

Size and Shape Effects on Surface Charging and Energetics of Goethite Nanoparticles

James R. Rustad, 530-754-6021, jrrustad@ucdavis.edu

Objectives: It is generally thought that surface reactivity at mineral-water interfaces is determined by variations in local coordination structures in stable terminations of protonated oxide surfaces. Solvent accessibility, global minimization of electrostatic potential, and edge effects also make some contribution to surface reactivity. Computational investigations of structurally well-defined aqueous polynuclear systems can be used to determine the relative importance of these effects in determining reactivity at geochemically important interfaces.

Project Description: We have developed computational chemical models that allow direct investigation of complex reaction mechanisms at protonated oxide-water interfaces. The basis of these models is a polarizable, dissociating water model that is transferable from the gas-phase to condensed phases. These models have been extensively tested and benchmarked in aqueous and ultra-high vacuum environments. These models will be used to study acid-base, ligand-exchange, and electron transfer reactions in heterogeneous aqueous environments. To check the model predictions, we will use experimental studies conducted on polynuclear systems whose structure is known from x-ray studies on hydrated salts of the polynuclear ions.

UNIVERSITY OF CALIFORNIA, DAVIS

Department of Chemistry, Department of Geology
Davis CA 95616

Grant: DE-FG02-02ER15325

Tailored Crystal Growth and Impurity Control Using Nanocluster Adsorbates

William H. Casey, 916-752-3211, whcasey@ucdavis.edu

The morphologies, growth rates and properties of crystals grown from solution are dramatically affected by adsorbates that poison the highly reactive steps on surfaces. As a consequence, impurity adsorption is a central issue in pharmaceutical manufacturing, corrosion, single-crystal production, and mineralization in geochemical and biological environments. In nearly all of these processes, impurities are either an unavoidable feature of the system, or are intentionally introduced to modify the product. We are studying this problem systematically by conducting careful atomic-force microscopy (AFM) experiments on KDP (potassium dihydrogen phosphate) crystals coupled to a combination of inert and labile adsorbate complexes to affect growth. The results are complemented with *ab initio*-molecular dynamics calculations of the step energies and terrace morphologies on the growing KDP surfaces. The crystal growth rates and morphologies of KDP are extraordinarily well characterized, and in more recent work we are extending the research to calcium-oxalate minerals.

Certain trivalent metals, such as Al(III) and Cr(III), when added to the aqueous growth solution, dramatically affect the growth rates and morphologies of KDP crystals by pinning elementary steps, causing step bunching and the formation of supersteps that can consist of hundreds of elementary steps. In experimental studies we are attempting to understand this chemistry by adding inert coordination complexes of specific geometries in order to reproduce the result. The fact that a fresh solution of Rh(III) additives in trace amounts does not affect the KDP growth morphologies, but causes profound step pinning if Rh(III) is allowed to age in the KDP growth solution, indicates that the step poisons are probably phosphato complexes, but of unknown structure. Although we understand that the step-pinning complex is a metal-phosphate molecule, we have been unable to synthesize this complex and a series of Co(III)-amminophosphate and Co(III)-amminopyrophosphate complexes show no effect. Because these complexes are large relative to the unit cell of KDP, we speculate that a mix of ligands bound to the inert metal but away from the phosphate is needed. Apparently, it is important that the step-pinning molecule be able to both accept and donate hydrogen bonds in order to pin elementary steps on KDP.

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: Analysis and Interpretation of Multi-Scale Phenomena in Crustal Deformation Processes Using Numerical Simulations of Complex Nonlinear Earth Systems

John B. Rundle, (530) 752-6416, rundle@physics.cse.ucdavis.edu

Critical energy facilities face a variety of hazards and risks from tectonic instabilities in the complex earth system, including primarily earthquakes, but also including volcanic eruptions and landslides. Understanding these hazards and forecasting these risks has been the motivating rationale for our work under this project. We have pioneered a large array of modeling and numerical simulation techniques to develop a deep understanding of the basic physical processes associated with strong space-time correlations during the last three years. Our work has been a joint effort of model development, theoretical understanding, and testing with observed data. We have now successfully formulated and tested a class of forecast algorithms that are significantly more effective at forecasting observed large earthquakes than a corresponding random data set from which all the space-time structure has been removed by randomly re-shuffling the data in time. Of the last 8 earthquakes larger than magnitude 5.0 that have occurred in southern-central California since the forecast period began, 7 fell within 1 standard deviation (+/- 11 km) of a forecasted location. We are also developing new applications of topologically realistic earthquake fault system models of the space time dynamics for use in forecasting. Data to which we apply our methods include GPS and Synthetic Aperture Radar Interferometry data, which are other new types of crustal deformation data. In our work, we also have determined that 1) statistical field theory techniques based on supersymmetric considerations indicate that the evolution of earthquake seismicity patterns can be described with a linear theory over short times, since the nonlinear clusters in the patterns have very small amplitude; 2) there are at least 4 distinct classes of earthquakes, each with a distinct set of scaling exponents; 3) the non-equilibrium, driven, meanfield earthquake fault system in southern California has many characteristics of equilibrium systems; and 4) new models with threshold weakening can be shown to generate aftershocks and foreshocks. The scaling properties of the Gutenberg-Richter relation are strongly affected by the time scale of the threshold weakening, indicating the appearance of a new scaling field.

UNIVERSITY OF CALIFORNIA, DAVIS

Department of Geology

Davis CA 95616

Grant: DE-FG02-01ER15145

Electrochemical Measurements and Theoretical Predictions of the Thermodynamic Properties of Carbonate and Oxide Minerals

Peter Rock, parock@ucdavis.edu

Assessment of two of the proposed strategies for reducing the flow of carbon dioxide into the atmosphere, namely, disposal of carbon dioxide in geological media and acceleration of the carbon cycle in soil or oceans requires a detailed knowledge of the Gibbs energies of carbonate minerals. Carbonate mineral solubilities vary considerably with composition and sound thermodynamic data are the starting point for estimating the fate of carbonate in geologic strata.

We have devised a novel electrochemical double-cell technique that is used for the direct determination of the Gibbs energies of formation of metal carbonate solid solutions, mixed-metal carbonate minerals, hydroxycarbonates, and disordered metal carbonates. Electrochemical determinations of Gibbs energies of formation for Brady protodolomite, Westrich high magnesian calcites, the hematite-to-dolomite conversion, the La, Lu, Y, Tb, Nd and Pr(III)carbonates, and magnesite, hydromagnesite and artenite have been completed.

We have developed a novel theoretical method based on electrostatics for calculating lattice energies of calcite-structure metal carbonates, which we have extended to calcite-structure metal-carbonate solid solutions. The method also has been applied to M_2O_3 metal oxides with the corundum structure.

Our lattice-energy calculation model for calcite-structure metal carbonates treats the lattice energy a sum of electrostatic, polarization, and repulsive components. The electrostatic contribution is evaluated by summing the energies of all pairwise point-charge interactions throughout the crystal, while the polarization contribution is determined via computation of all ion/dipole and dipole/dipole interactions in the crystal.

Before the three components of the lattice energy can be evaluated, the parallel and perpendicular components of the oxygen polarizability in $MCO_3(s)$ must be determined along with the charge distribution of carbonate in metal carbonates. The calculation of the polarizabilities is accomplished by using the Lorentz Local Field Method which requires experimentally determined crystal refractive indices. The method does not involve adjustable parameters. We are presently extending our lattice-energy calculations to metal carbonates with the aragonite structure, which constitutes a much more difficult theoretical challenge, because of the lower lattice symmetry. Theoretical work on metal oxides with the corundum structure has been completed, except for metal-oxygen cluster calculations to determine the charge on the metal ion. We plan to publish the experimental and theoretical results together in each case.

UNIVERSITY OF CALIFORNIA, LOS ANGELES

Department of Earth and Space Sciences
Los Angeles CA 90095

Grant: DE-FG02-89ER14049

Application of $^{40}\text{Ar}/^{39}\text{Ar}$ Thermochronometry and Ion Microprobe Stable Isotope Geochemistry to the Evolution of Petroleum Reservoirs and Hydrothermal Systems

T. Mark Harrison, tmh@oro.ess.ucla.edu, (310) 825-7970

Our research is to assess the utility of thermochronologic and ion probe microscale isotope techniques in deriving fluid evolution and thermal histories in crustal environments that bear upon energy exploration, reservoir assessment, and paleoclimatology. We seek to characterize the timescales of transient heating in young geothermal systems, understand the temporal and spatial aspects of fluid/heat fractionation involved in the geothermal environment; and (3) develop high spatial and temporal resolution proxy climate records of modern and ancient speleothems. We have augmented our suite of zircon and sphene samples from 24 drillholes distributed through The Geysers geothermal field with a suite of samples from scientific drill hole SB-15-D from the Northwest Geysers field and are currently analyzing single crystals of sphene and zircon using (U-Th)-He methodology to evaluate competing models for the heat source of the Geysers plutonic complex. We have developed a model that simultaneously uses constraints from $^{40}\text{Ar}/^{39}\text{Ar}$ and (U-Th)-He dating to produce best-fit thermal history calculations for The Geysers and other areas. We have obtained a suite of samples from the 320 ka intrusive phase of the Medicine Lake geothermal field appropriate for thermochronological measurements. We are developing methods to obtain high spatial and temporal resolution proxy climate records from modern and ancient speleothems. Results from the 80 year record of Moondyne Cave, Australia, provides an excellent test of speleothem climate proxies because the regional climate and has experienced a 20% reduction of mean rainfall since 1964 and 0.8°C temperature rise since 1953. Inter-annual variations of oxygen and carbon isotopes were measured by conventional mass spectrometry whilst intra-annual $\delta^{18}\text{O}$ was measured by high spatial resolution ion microprobe. Both reveal surprising trends. $\delta^{18}\text{O}$ varies positively with temperature on both intra- and inter-annual timescales. On the inter-annual scale, $\delta^{18}\text{O}$ rises 0.3°C after 1974, 10 years after the regional rainfall decrease but synchronous with a delayed response seen in P and Mg, which otherwise vary strongly with rainfall, indicating that speleothem $\delta^{18}\text{O}$ is responding to rainfall $\delta^{18}\text{O}$. Preservation of the annual rainfall $\delta^{18}\text{O}$ signal suggests that rainfall amount is recorded by speleothems in this region.

UNIVERSITY OF CALIFORNIA, SANTA BARBARA

Department of Earth Science
Santa Barbara CA 93106

Grant: DE-FG02-96ER14620

Fluid Flow in Faults: Processes and Effects from Modern and Paleo Systems in a Transpressional Tectonic Setting, Southern California

James R. Boles, (805)893-3719, boles@geol.ucsb.edu

Objectives: This is a collaborative study to quantify basinal fluid flow, submarine methane migration and diagenetic effects within deforming faults in a transpressional setting, which is seismically active.

Project Description: We have mostly targeted active faults and young petroleum fields in southern California for study, such as the Refugio-Carneros Fault in the Transverse Ranges near Santa Barbara. Subsurface data and published structural-seismic sections were analyzed to characterize the tectonic history and diagenetic evolution for the fault. These data provide constraints for finite element models that were developed to predict fluid pressures, flow patterns, rates of deformation, temperatures, and carbonate mineralization patterns associated with large fault systems and the geochemical mixing of fluids.

Results: Our FY2004 studies have shown that the Refugio-Carneros Fault is relatively unique amongst the numerous faults in the region in being a conduit of high temperature fluid and hydrocarbon migration, suggesting hydrocarbon migration events can be short lived. We have recently documented isotopic disequilibrium during rapid calcite and aragonite crystallization following rapid CO₂ degassing, in the form of co-varying carbon and oxygen isotopes in tunnel speleothems and well tubing scale. Our goal is to develop a quantitative understanding of this phenomenon in order to interpret isotopic signatures found in fault zone cements. A study in an offshore Santa Barbara oil field has calculated a fault permeability of 20 md, a similar value to overall reservoir permeability, from the rate of seawater influx into an underpressured reservoir. We have also documented diluted formation waters in newly explored deep parts of the Los Angeles basin and are seeing changes in the Na/Ca ratio due to plagioclase albitization. A kinetic model for plagioclase albitization has been published that allows prediction of this important reaction as a function of geologic time and burial temperature. One new manuscript was submitted that characterizes fault-valve behavior and earthquake recurrence in a generic transpressional profile. In addition, a paper on reactive flow modeling has been prepared that tests the concept of CH₄-bearing fluids mixing with meteoric groundwater in faulted, submarine reservoirs along coastal Santa Barbara, replicating observed patterns of calcite mineralization.

UNIVERSITY OF CALIFORNIA, SANTA CRUZ

Institute of Geophysics and Planetary Physics
Santa Cruz CA 95064

Grant: DE-FG02-01ER15144

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

Ru-Shan Wu, 831-459-5135, wrs@pmc.ucsc.edu

The purpose of the current project is developing new methods for wave equation based imaging and extending these techniques for the estimation of subsurface model parameters. In the 2004/2005 project year, our research focuses on the following areas:

We extended the thin-slab method for elastic wave propagation from the isotropic media to the VTI media. The elastic thin-slab approximation is a dual-domain formulation for modeling wide-angle forward- and back-scattering using the De Wolf approximation. We introduced the anisotropy parameters based on the elastic perturbation theory and derived the formulation for anisotropic scattered qP and qSV waves. Numerical simulations proved the validity of the method.

We developed a wave equation based method for seismic illumination analysis. A one-way wave-equation based generalized screen propagator is used to extrapolate the wavefields from sources and receivers to the target. A local plane wave analysis is used at the target to calculate localized directional energy fluxes for both source and receiver wavefields. Using these energy fluxes, we construct an illumination matrix to quantify the target illumination conditions. The information about target geometry is used to manipulate illumination matrix and generate different types of illumination maps. Unlike illumination analyses based on ray-tracing, the wave equation based approach avoids difficulties due to the high-frequency approximation of the ray-based method. This new method is flexible and practical for illumination analysis in complex 2D and 3D velocity models with different acquisition and target geometries.

Using beamlet decomposition of the wavefield, we developed an angle-domain amplitude correction method for wave-equation based true-amplitude, true-reflection imaging. First, local image matrix and local illumination matrix are obtained. The amplitude correction is carried out in the local angle domain using common-dip-angle image gathers. With this correction, the effects from limited acquisition geometry, the path effect from propagation through complex overburden and the reflector dip angle are all considered. Numerical examples show that the image quality of subsalt structures is greatly improved and the image amplitudes are more balanced. Meanwhile, the noise and migration artifacts are effectively compressed.

UNIVERSITY OF CALIFORNIA, SAN DIEGO

Department of Chemistry and Biochemistry
San Diego CA 92093

Contract: DE-FG02-02ER15311

First Principles Simulation of the Supercritical Behavior of Ore Forming Fluids

J.H. Weare, (858) 534-3286, fax (858) 534-7244, jweare@ucsd.edu

In this program we apply advanced simulation tools to the analysis of the processes that lead to the concentration of metal species in natural waters and deposition of ore-rich formations. It is widely accepted that the chemical properties of concentrated brines at high temperatures and pressures are responsible for the transport of metals via the formation of metal ion (e.g., Fe^{3+} , Zn^{2+} , etc.) associations with highly concentrated anions (e.g., Cl^- and HS^-). To predict the properties of metal ions in hydrothermal solutions, we are developing dynamic simulation methods based on first-principles density functional calculations of the forces between atoms in solution (ab-initio molecular dynamics, AIMD). These methods accurately account for properties such as changes in forces in the water molecules due to interactions with ions or transfers of protons in acid/base reactions. These processes play an essential role in the chemistry of aqueous solutions and cannot be treated by conventional molecular dynamics. This year we worked on the analysis of the solvation properties of Al^{3+} ions. Our AIMD results agree well with the measured octahedral structure of the 1st solvation shell. The properties of the 2nd solvation shell of the ions are poorly determined. Data from X-ray measurements have been interpreted using a highly coordinated model with two water molecules in the second shell coordinating each of the six 1st shell waters. The $G(r)$ calculated from our AIMD simulations shows a second shell peak with roughly 12 water molecules hydrogen bonded to the first shell waters, which is consistent with X-ray measurements. The calculated shell radius is in excellent agreement with the measured radius of 4.02Å. However, more careful analysis of the simulations shows that there is also a liquid-like contribution in the second shell. This is the first evidence of liquid behavior in this shell. At high temperatures, and less frequently at lower temperatures, hydrolysis reactions (proton exchanges) are evident in the dynamical simulations and calculated $G(r)$. While various hydration species ($\text{Al}(\text{OH})_n(3-n)^+$) have been postulated from modeling solution solubility data, evidence of their existence at neutral pH is indirect. The AIMD method is essential to simulate such proton transfers.

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

Stephen R. Sutton, 630-252-0426, Fax 630-252-0436, sutton@cars.uchicago.edu

GeoSoilEnviroCARS is a national consortium of earth scientists whose goal is to operate, as a national user facility, synchrotron radiation beam lines at the Advanced Photon Source, Argonne National Laboratory. Instrumentation for the following techniques is open to the scientific community: (1) x-ray absorption fine structure spectroscopy; (2) fluorescence microprobe analysis; (3) microtomography; (4) powder, microcrystal and surface diffraction; (5) high-pressure crystallography with diamond anvil cells and multi-anvil presses, and (6) 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 radionuclides in contaminated sediments, redox chemistry of metals at the root-soil interface, chemical nature of hydrothermal fluids, and structures of and chemical reactions at mineral-water interfaces. Since FY1999, more than 500 beam time proposals were received, 350 outside users (25% students) have conducted experiments, and 180 publications have been produced. New results include (1) structure determination of the hydrated α -Al₂O₃ (0001) surface (Eng et al. 2000); (2) observation of partial Fe occupancy on the hydrated α -Fe₂O₃ (0001) surface explaining the large reactivity difference between α -Al₂O₃ (0001) and α -Fe₂O₃ (0001) (Trainor et al. 2002); (3) Pb speciation at the biofilm-metal oxide interface (Templeton et al. 2003); (4) observed oxidation of Mn(II) during surface reaction of rhodonite, suggesting Mn mobility retardation via precipitation and/or hydrolysis (Farquhar et al. 2002); (5) identification of chloride complexes as the Cu species in hydrothermal fluid inclusions from an ore-forming region in Australia (Mavrogenes et al. 2002); (6) confirmation of strong arsenic sequestration by iron hydroxide plaques on plant roots from a Superfund site (Keon et al. 2002); (7) observation of sharply terminated Cr diffusion fronts in soil aggregates caused by locally rapid Cr(VI) reduction by microbial activity (Tokunaga et al. 2003), (8) observation of heterogeneous incorporation of Sr into coral aragonite (Allison et al. 2001; Finch et al. 2003) and (9) evidence of dynamic effects on fluid distribution in porous media (Wildenschild et al. 2002).

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

Stephen R. Sutton, 630-252-0426, FAX 630-252-0436, sutton@cars.uchicago.edu

The project focuses on applications of the x-ray fluorescence microprobe on Beam Line X26A at the National Synchrotron Light Source (NSLS, BNL) for determinations of the compositions, structures, oxidation states, and bonding characteristics of earth and environmental materials with trace element sensitivity and micrometer spatial resolution. Research focused on actinide incorporation in minerals and sediments, biogeochemistry of metal contaminants, mineral surface site controls on metal uptake by minerals, and iron oxidation states in igneous petrogenesis. Two examples are given here. Spectroscopic and diffraction studies of arsenic-bearing tailings, soils and sediments from the Yellowknife area (Canada) were pursued to identify the mineralogical form of the arsenic and assess its stability in various geochemical environments (with S. Walker and H. Jamieson, Queen's Univ., Ontario Canada). MicroXANES results indicated that fresh flotation tailings contain only sulfide-bound arsenic (As^{-1}). Roaster-generated hematite ($\alpha\text{-Fe}_2\text{O}_3$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) in all ages of tailings (fresh to 50 years old) contain arsenic in mixed oxidation state (As^{+5} and As^{+3}). This contrasts with iron oxyhydroxides formed by weathering of pyrite (FeS_2) and arsenopyrite (FeAsS) which contain only As^{+5} . MicroXRD analyses allowed definitive identification of hematite and maghemite, minerals that are difficult to distinguish petrographically in these materials. Factors such as charge and ionic size of the impurity introduced and the crystallographic orientation of the calcite surface sites play a major role in site selectivity in trace element incorporation. E. Elzinga and R. Reeder (Stony Brook University) demonstrated that divalent Cu and Zn, which have ionic radii smaller than Ca, are preferentially incorporated into the $\langle 4\bar{4}1 \rangle^+$ steps that define one pair of symmetrically equivalent vicinal faces on polygonized growth spirals. In contrast, other divalent metals with six-fold ionic radii smaller than Ca (Co, Cd, Mn, Mg) have been shown to be preferentially incorporated into $\langle 4\bar{4}1 \rangle^-$ growth steps, which define the second pair of vicinal faces on the growth spirals. Studies by V. Alexandratos and R. Reeder (Stony Brook University) similarly demonstrated that AsO_4^{-3} anions prefer the - vicinal faces as well implying that bulk partition coefficients for As(V) depend on the availability of different calcite surface sites.

UNIVERSITY OF CHICAGO

Department of the Geophysical Sciences
Chicago IL 60637

Grant: DE-FG02-01ER15254

Kinetic Isotope Fractionation by Diffusion in Liquids

Frank M. Richter, 773-702-8118, Fax 773-915-9505, richter@geosci.uchicago.edu

The overall objective of our research is to document and quantify kinetic isotope fractionations during chemical diffusion in a variety of liquids. One set of experiments was designed to measure the isotopic fractionation of Ca and Li in annealed diffusion couples juxtaposing molten basalt and rhyolite. Very significant isotope fractionations were found and the results have been published in *Geochimica Cosmochimica Acta*. Chemical and isotopic fractionation of dissolved species by diffusion in water was also studied using small spherical chambers filled with salt solutions (KCl, LiCl, MgCl₂) connected to a much larger water-filled reservoir by a cylindrical diffusion tube. If the dissolved species diffuse through the connecting tube at different rates, the residue of salt in the smaller chamber will become progressively enriched in the more slowly diffusing species. The validity of our experimental design was confirmed by reproducing the already known ratio of the diffusion of K to that of Li. In the case of MgCl₂ we found no measurable isotopic fractionation of Mg (<0.5 per mil for ²⁶Mg/²⁴Mg) even when less than 5% of the original Mg remained in the inner chamber. If the mass-dependence of Mg isotope diffusion in water had been similar to that in molten silicates, we would have measured a fractionation of about 25 per mil. In the case of Li, we did measure a 5 per mil fractionation of ⁷Li/⁶Li when 5% of the Li remained in the inner chamber, but again this is very significantly less than the fractionation that would have occurred under similar circumstances in a molten silicate liquid. We also found a small but measurable fractionation of Cl isotopes. We interpret the much-diminished isotopic fractionation associated with diffusion in water relative to that in molten silicate liquids as being due to the hydration of the dissolved ions. We have recently developed a new capability for high precision Fe isotope measurements using a multi collector plasma source mass spectrometer, and will use this to determine the degree to which diffusion can fractionate Fe isotopes.

CLARK UNIVERSITY

Department of Physics
Worcester MA 01610

Grant: DE-FG02-02ER15367

Physics of Channelization: Theory, Experiment, and Observation

Arshad Kudrolli, (508) 793 7752, akudrolli@clarku.edu

Our project seeks to better characterize the physical processes that erode landscapes, with emphasis on the formation of drainage channels and channel networks. Our approach consists of tightly coupled theoretical and experimental studies augmented by field observations. The work is performed in collaboration with Prof. Daniel Rothman of MIT. The group at Clark is primarily responsible for experiments while the group at MIT is primarily responsible for theory.

Fluvial erosion in natural systems can be induced by either surficial, overland flows or subsurface, seepage flows. The latter process constitutes the present focus of our project. Using modern laser-aided data-acquisition and digital imaging techniques, we obtain detailed time-dependent two-dimensional topographic data. Our objective is to understand the evolution of the topography as fully as possible.

We have thus far focused three problems. First, we have shown that our experiment yields a characteristic channel spacing that depends on slope and pressure gradient, and have proposed theoretical explanations for this choice of length scale. Second, we have defined, both theoretically and experimentally, the particular values of control parameters that determine the qualitative quasi-stationary features exhibited in our experiment. The third focus of our work has been on the dynamics of channel evolution. We have discovered that the problem may be usefully portrayed as a trajectory in a two-dimensional phase space. Commonalities in all such trajectories indicate surprisingly that the growth of individual channels is at least to some extent independent of other channels in the channel network, in a manner that is determined by the geometry of the subsurface water flow.

The laboratory-scale component of this project is performed so that at least one manifestation of channelization may be completely understood. To better understand where our theories and experiments apply in the natural world, we also perform simple observational studies of natural channels found on beaches.

COLORADO SCHOOL OF MINES

Center for Wave Phenomena
Green Center
Golden CO 80401

Grant: DE-FG02-98ER14908

Inversion of Multicomponent Seismic Data and Rock-Physics Interpretation for Evaluating Lithology, Fracture and Fluid Distribution in Heterogeneous Anisotropic Reservoirs

Ilya Tsvankin, 303-988-0461, fax 303-273-3478, ilya@mines.edu

Objectives: The goal of the CSM group is to develop a methodology for characterizing heterogeneous fractured reservoirs using 3-D multicomponent seismic data. The results are applied to evaluation of the position, orientation, spatial density and connectivity of fractures and other reservoir heterogeneities.

Project description: CSM investigators are working on inversion and processing of wide-azimuth PP and PS (mode-converted) reflection data for azimuthally anisotropic media. Anisotropic velocity analysis followed by multicomponent depth imaging produces an accurate heterogeneous model of the reservoir. Interpretation of the anisotropic parameters in terms of the physical properties of natural fractures is the main focus of collaborative research of CSM, LLNL and Stanford University within the framework of this project.

Project results: Stacking-velocity tomography for orthorhombic media. Our tomographic method originally devised for transverse isotropy was extended to orthorhombic models typical for fractured reservoirs. The algorithm estimates the anisotropic parameters and azimuths of the vertical symmetry planes of layered orthorhombic media using normal-moveout ellipses of wide-azimuth PP and split SS reflections.

Azimuthal velocity analysis of long-spread data. We developed a semblance-based methodology for inverting long-spread (nonhyperbolic), multiazimuth P-wave moveout recorded over azimuthally anisotropic media and successfully applied it to the reflection from the top of a fractured reservoir at Weyburn field.

Modeling and analysis of anisotropic geometrical spreading. The geometrical-spreading factor of reflected waves for horizontally layered anisotropic media was expressed as a function of the spatial derivatives of reflection travel times and used to evaluate anisotropy-induced amplitude distortions of wide-azimuth data for typical fractured models.

Seismic characterization of dipping fracture sets. Employing the linear-slip theory, we studied the effective medium produced by a system of obliquely dipping rotationally invariant fractures embedded in a VTI matrix and developed a complete fracture-characterization procedure for this model based on multicomponent seismic data.

COLORADO SCHOOL OF MINES

Department of Geophysics
Golden CO 80401

Grant: DE-FG02-03ER15390

Optical Measurement of Seismic-Frequency Attenuation and Velocity Dispersion at In-Situ Conditions

Michael Batzle, mbatzle@mines.edu

We have developed a fiber-optic strainmeter to estimate moduli and seismic wave attenuation at low frequencies (10-3000 Hz) in a stress-strain experiment. The system follows a Mach-Zehnder interferometer setup from which phase lags (attenuation) and deformations (moduli) are estimated from the fringe pattern. By using interferometry high sensitivity to deformations (picometers) and phase lags (microradians) is achieved. Stress-strain measurements using strain gages or ultrasonic wave propagation sample only part of the core sample, the fiber-optic strainmeter would analyze the rock sample response to an applied stress as a whole.

UNIVERSITY OF COLORADO

CIRES/Geological Sciences
Boulder CO 80309

Grant: DE-FG02-94ER14419

Seismic Absorption and Modulus Measurements in Porous Rocks in Lab and Field: Physical and Chemical Effects of Fluids

Hartmut Spetzler, spetzler@colorado.edu, 303-492-6715

We are exploring a new technology that is based on using low-frequency seismic attenuation data to monitor changes in fluid saturation conditions in two-fluid phase porous materials. The seismic attenuation mechanism is related to the loss of energy due to the hysteresis of resistance to 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 the (1) onset of contaminant leakage at buried waste sites, (2) progress of contaminant remediation, and (3) progress of water flooding or steam injection during enhanced petroleum recovery.

Last year marked the initial phase of our feasibility study in the field, where we seek to detect changes in recorded strain signals (attenuation) in response to local changes in the fluid saturation conditions in the vadose zone. Rather than employing manmade sources, which are very expensive and invasive, we are exploring the use of natural sources of strain and seismic waves, specifically Earth tides and globally-recorded, natural microseisms, respectively. The field site is operated by the University of Arizona, and has sophisticated facilities for controlled water irrigation and a comprehensive, dense array of instruments used for measuring water saturations and flow. We plan to change the saturation conditions by irrigating at the site with water in October '03, with water plus a biosurfactant in late spring '04 and again with water late in '04. First background data over a 9 months period from three tiltmeters and 3 seismometers are encouraging.

We measured the wettability hystereses of clean and diesel-coated quartz crystals by water, diesel, and oil-reducing bacteria solution. The purpose of this work was to see if there are differences in the wettability hystereses, which result in differences in low-frequency seismic attenuation. When the diesel-coated quartz was dipped in and out of the bacterial solution, we observed significant changes in hystereses that did not occur with the other fluid constituents. These results suggest that we ought to be able to monitor bioremediation progress using low-frequency seismic attenuation data.

UNIVERSITY OF COLORADO

Department of Civil, Environmental, and Architectural Engineering
Boulder CO 80309

Grant: DE-FG02-02ER14590

The Physics of Two-Phase Immiscible Fluid Flow in Single Fractures and Fractured Rock

Harihar Rajaram, hari@colorado.edu

The objective of this research is to develop quantitative understanding of the critical processes controlling two-phase flow and transport in rock fractures, with potential applications in radioactive waste isolation, CO₂ sequestration and petroleum engineering. Our previous research identified the importance of phase structure in controlling system behavior. We have developed experimental systems to create and measure a wide range of phase structures, and flow and transport through them. Current efforts focus on models of phase structure, parametric relationships for flow, transport and inter-phase transfer, and behavior in fracture-matrix networks.

Our previous experimental studies have demonstrated two important classes of phase structures in variable aperture fractures: satiated structures, wherein the invading phase fully entraps the defending phase, and fingered structures resulting from gravity destabilization. Both classes are accurately modeled using modified invasion percolation (MIP) algorithms that account for the influence of gravity, in-plane curvature and simultaneous invasion-reinvasion of two phases.

The MIP algorithm with simultaneous invasion-reinvasion of two fluids was shown to reproduce the dynamics of gravity-driven wetting fingers in variable-aperture fractures. Fragmentation behind the fingertip, pulsating flow and the stop-and-go dynamic of fingers were simulated, closely following experimental observations. Average finger widths are within 20% of experimental measurements. (Water Resources Research 39(3) doi:10.1029/2002WR001542, 2003)

Parametric studies of the influence of fracture properties on satiated phase structure, and associated flow and transport properties are ongoing. The areal saturation (S_f) of the flowing phase at satiation is shown to depend on the ratio of two dimensionless parameters related to the fracture properties (C/δ , where the curvature number C , representing the mean influence of in-plane curvature, is the ratio of the mean aperture to the correlation length, and δ is the coefficient of variation of the aperture field). As C/δ goes to zero, behavior is as in standard invasion percolation within a correlated field, and $S_f \sim 0.37$. As C/δ increases above ~ 0.1 , S_f increases, approaching 1 for very large $C/\delta \sim 10$. (Physical Review E 68, 061110, 2003)

We have also investigated infiltration in meso-scale laboratory fracture-matrix networks, demonstrating the occurrence of dynamic preferential pathways. (Water Resources Research, 38(12), 1281, doi:10.1029/2001WR001002, 2002).

UNIVERSITY OF CONNECTICUT

Department of Marine Sciences
1080 Shennecossett Road
Groton CT 06340

Grant: DE-FG02-95ER14528

Air-Derived Noble Gases in Sediments: Implications for Basin Scale Hydrology

Thomas Torgersen, 860 405 9094, thomas.torgersen@uconn.edu

The goal of this project is to isolate and identify the various air-derived noble gas components in sediments, particularly, but not exclusively, those sediments associated with hydrocarbons. The project is designed to address how noble gas elemental patterns are acquired and retained, how they are transferred to basin fluids in which they have been measured, and to improve the application of noble gas isotope studies to multiphase fluid processes in the Earth's crust.

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 smooth mass dependent abundance patterns have led to adsorption hypotheses, three observations argue against single stage 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) Laboratory heating experiments suggests the enriched component is tightly bound, counterintuitive to a simple adsorption history. And (3) many sedimentary rocks (~half) and some oil field gases contain excess Ne in conjunction with excess Xe.

We are examining diffusive filling and emptying of angstrom-scale half-spaces in lithic grains as an explanation for the observed absolute and relative abundances sedimentary rocks. Since physical properties of the noble gases are strong functions of atomic mass, the individual diffusion coefficients, adsorption coefficients and atomic diameters combine to impede heavy noble gas transport relative to the lighter noble gases. Filling of lithic grains/half-spaces thus produces Ne enrichments in the early and middle stages of the filling process, emptying lithic grains/half-spaces produces a Xe-enriched residual in the late stages of the process, and both Ne and Xe enrichments can be produced by incomplete emptying of the half-spaces followed by incomplete filling. A system of labyrinths-with-constrictions when combined with simple adsorption results in stronger diffusive separation and non-steady-state enrichments that persist for longer times. Laboratory work is currently underway to better evaluate noble gas absolute and relative abundances in sediments by isolating and identifying carrier phases and trapping mechanisms.

UNIVERSITY OF DELAWARE

Department of Chemistry and Biochemistry
Newark, DE 19716

Grant: DE-FG02-89ER14080

Development of an Experimental Data Base and Theories for Prediction of Thermodynamic Properties of Aqueous Electrolytes and Nonelectrolytes of Geochemical Significance at Supercritical Temperatures and Pressures

Robert Wood, rwood@brahms.udel.edu

Reactions of aqueous solutions with rocks control the generation, migration, and accumulation of fossil fuels as well as many other geochemical processes. Analogous interactions determine the movement of metals, hydrocarbons and other toxic compounds in aquifers, tailings piles from mining landfills, nuclear waste repositories, and contaminated sites. This diversity of geochemical processes involving aqueous solutions is suited for study with theoretical models that employ thermodynamic data. The objective of this research is to combine new experimental measurements with theoretical equations of state and with first principles quantum mechanical predictions to supply the necessary thermodynamic data.

Our use of experimental conductance measurements to get equilibrium association constants for a variety of aqueous electrolytes at high temperature has been going very well. We are writing up measurements of the association of the ions in the following salts: sulfuric acid, hydrochloric acid, sodium sulfate, sodium hydrogen sulfate, lithium sulfate, and potassium sulfate. Methods for predicting second, cross, virial, coefficients for interactions involving water have been published. These predictions are needed in our new equation of state. Progress has been made in developing equations of state for salt solutions at high temperatures. We have collaborated in the construction of a new heat capacity calorimeter at the University Blaise Pascal in France so that measurements on this important property can be continued.

In order to expand our thermodynamic database to cover temperatures and pressures where measurements are impossible, we have further developed our new method of predicting free energies of hydration. This method uses molecular dynamic simulation and *ab initio* quantum mechanics to make the predictions. We have shown that our new method can predict hydration free energies of ions at high temperatures with good accuracy and used the method to predict sodium and chloride ions at many high temperature state points. It seems clear that using this new method we can now predict free energies of hydration with an accuracy of about 5 kJ/mole for any reasonably simple solute containing elements as heavy as chlorine at temperatures to about 3000 K and pressures to about 300,000 atmospheres.

UNIVERSITY OF FLORIDA
Chemical Engineering Department
PO Box 116005
Gainesville FL 32611

Grant: DE-FG02-98ER14853

Evolution of Surface Morphology During Dissolution of a Rough Fracture

Anthony J.C. Ladd, 352-392-6509, Fax: 352-392-9513, ladd@che.ufl.edu

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, CO₂ 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. The foundation of our investigation is a very efficient numerical simulation of fluid flow in irregular geometries. Since the evolving surface morphology modifies the fluid flow, it is necessary to run the flow solver many times over during a single calculation of the dissolution or deposition process. The flow solver was developed under our previous DOE grant, and is more than two orders of magnitude faster than conventional lattice-Boltzmann methods. We have also implemented and tested a stochastic model for the transport of reactants in porous media, and used it to model chemical erosion in a rough fracture.

The numerical simulation algorithm has been applied to the dissolution of a rough fracture of known topography, for which experimental dissolution patterns were available. At high Peclet numbers the under-saturated fluid penetrates deep inside the fracture and the dissolution tends to be uniform throughout the sample, but at lower flow rates the erosion is slower and much more inhomogeneous, with a clearly visible dissolution front. This front becomes unstable with respect to fingering instabilities, since an increase in permeability within a channel enhances solute transport, leading to faster growth of the channel. As the dissolution proceeds, the channels compete for flow and the growth of the shorter channels eventually ceases. At the end of the experiment, the flow is focused in a few main channels while most of the pore space is bypassed. The simulation results are in semi-quantitative agreement with experimental measurements on the same initial fracture topography.

This work supports Geosciences objectives aimed at developing a fundamental understanding of transport and reactive processes in rock-fluid systems, and specifically aids the goals of the CO₂ sequestration initiative by providing numerical algorithms for a reactive flow and transport model.

GEORGE WASHINGTON UNIVERSITY

Department of Chemistry
725 21st St., NW
Corcoran Hall
Washington, DC 20052

Grant: DE-FG02-02ER15366

A Comparative Study of Dissolution Processes on Growth/Cleavage Surfaces and at Near/Far-from Equilibrium Conditions

H. Henry Teng, 202-994-0112, hteng@gwu.edu

Direction-specific behavior is a fundamental property of anisotropic materials. Extensive studies have documented this unique property for various materials. Despite these efforts, a fundamental question remains to be answered regarding the direction-dependence of solubility. Thermodynamics dictates that chemical potential necessary to maintain crystal growth differs amongst faces with different surface energies. This leads to the conclusion that multiple solubilities exist for crystals that have faces unrelated by symmetry operations. Yet, little is found in the literature to experimentally verify the face specific solubility for any crystal systems. This study investigates the crystallographic direction-specific behavior of the {10-14} cleavage faces of calcite, a well known anisotropic mineral, at near equilibrium conditions and explores the possible solubility difference between the $\langle -441 \rangle_+$ (obtuse) and the $\langle -441 \rangle_-$ (acute) steps. Experimental results reveal no dissolution in either direction when the ionic activity product (IAP) of Ca^{2+} and CO_3^{2-} in the solution is greater than $10^{-8.41}$, whereas retreat is observed in both steps when IAP is smaller than $10^{-8.51}$. Furthermore, when $10^{-8.26} > \text{IAP} > 10^{-8.45}$, dissolution is seen in the obtuse steps, but not in the acute steps: while the acute steps continue to advance at a rate of 0.06 nm/s, obtuse steps become serrated and start to retreat with an average rate 0.03 nm/s at $\text{IAP} = 10^{-8.45}$. Additionally, growth in the acute steps remains measurable until IAP was reduced to $10^{-8.47}$. Further decrease in IAP to $10^{-8.51}$ finally led to dissolution at all steps.

The above AFM observations suggest the obtuse and acute steps have different thermodynamic stabilities. Putting the observed simultaneous growth and dissolution into the classic thermodynamic framework, we show that these results may indicate the two steps have different solubility constants. Experimental measurements demonstrate that the obtuse steps are 5% more soluble than the acute steps. This may have provided the first crystallographic direction dependent solubility constant for any crystals. These results further suggest that the current thermodynamic database may need significant addition to reflect the anisotropy of crystalline materials.

GEORGIA STATE UNIVERSITY

Department of Geosciences
Atlanta, GA 30303

Grant: DE-FG02-02ER15365

Development and Application of a Paleomagnetic/Geochemical Method for Constraining the Timing of Burial Diagenetic Events

W. Crawford Elliott, wcelliot@gsu.edu

The proposed work tests a hypothesis that chemical remnant magnetization (CRM) is concordant with the timing of potassic diagenetic processes in argillaceous rocks caused by thrust sheet, progressive burial, and/or migration of heat and fluids due to contact metamorphism. This hypothesis is tested by comparing the timing of chemical remnant magnetization (CRM) recorded by authigenic magnetic minerals to the measured K-Ar dates of diagenetic illite at specific settings (Disturbed Belt, Montana; the timing of CRM in relation to progressive burial and maturation of organic matter in the Mississippian Desert Limestone, and magnetization associated with heat and fluids accompanying through marls adjacent to Tertiary intrusions in the Isle of Skye). The results describing the work on the Isle of Skye are detailed below.

Previous results on the study of the clay mineralogy of the Jurassic sedimentary rocks of Skye, Scotland showed a hypothetical connection between the smectite-to-illite conversion and magnetite authigenesis/remagnetization. A presence-absence test and the timing of acquisition of a dual polarity early Tertiary (50-60 Ma) CRM suggests that magnetite authigenesis is related to the smectite-to-illite conversion. A modified version of Illite Age Analysis is used to derive the age of diagenetic illite in these marls that contain both detrital and diagenetic illite. The measured K-Ar dates of illite and percentage of 2M1 illite both decrease with clay size fraction from 160-213 Ma (1-2 micron) to 101-105 Ma (< 0.25 micron) from three marls. The age of diagenetic illite is derived by a non-linear extrapolation of measured K-Ar dates to 0% 2M1 illite and these extrapolated ages (40- 67 Ma) are concordant or slightly younger than the age of remagnetization and Tertiary intrusions.

The results from this study and combined with data from other diagenetic settings (such as thrust sheet burial, burial metamorphism, maturation of hydrocarbons and the movement of fluids and heat due to contact metamorphism) provide information about the formation of authigenic magnetic minerals and diagenetic illite in relation to prominent geologic processes and, in turn, increase our knowledge of the diagenetic processes marking the time-temperature window for the generation of oil and gas.

GORDON RESEARCH CONFERENCES

West Kingston RI 02892

Grant: DE-FG02-04ER15609

Rock Deformation Conference

Andreas Kronenberg, a-kronenberg@tamu.edu

The presentations and discussions at this conference emphasized the chemical and physical roles of aqueous fluids in deformation, the sources and transport of fluids in deforming rock bodies and faults of the crust and mantle, and the importance of fluid-rock interactions to tectonics. The conference, which was held at Mount Holyoke College, South Hadley, MA, from Aug. 8-13, 2004, focused on the role of water on rock deformation. Presentations and discussions were grouped in the following sessions:

- Rheological structure of the lithosphere and water weakening
- Surface hydration, fluid films, solute transport and deformation
- Fluids and deformation at collisional boundaries
- Fluids, diagenesis and deformation of sediments
- Fluids and deformation in fault zones
- Water weakening and creep in the middle to lower crust
- Water weakening and creep in the mantle

Two poster sessions also accompanied the conference. The posters were organized into two sessions:

- The sources, distribution and character of fluids, fluid transport, and hydrous defects
- The coupling of fluids with fracture, friction and flow of rocks

HARVARD UNIVERSITY

School of Engineering and Applied Sciences
Cambridge MA 02138

Grant: DE-FG02-03ER15384

Dissolution Mechanisms of the Carbonate Minerals

Scot T. Martin, scot_martin@harvard.edu, (617) 495-7620

Oxide and carbonate minerals are central in regulating the chemical composition of environmental aqueous systems. Dissolution and precipitation of iron and manganese oxides, calcite, and other carbonates control pH, alkalinity and contaminant mobility. Thus, a detailed, mechanistic understanding of these reactions is essential for reliable quantitative modeling. Our approach examines the relationship between macroscopic and microscopic observations of mineral dissolution and precipitation. Collectively we find that macroscopic phenomenon (such as aqueous iron or manganese and associated heavy metal pollutants such as chromium, arsenic, or lead) released per square meter per second can be linked to microscopic processes of surface complexation, step retreat, and film precipitation. Study of carbonate group mineral dissolution kinetics using scanning probe microscopy and bulk solution flow reactors revealed a complex association between microscopic and macroscopic behavior. Geometric models employing microscopic step retreat velocities measured on CaCO_3 and MnCO_3 proved to be accurate predictors of the absolute macroscopic dissolution over a wide range of pH values. The same is true for FeCO_3 and MgCO_3 only at $\text{pH} < 4$. In other cases, microscopic and macroscopic carbonate dissolution rates differed by an order of magnitude.

Applied in conjunction with our experimental observations, we showed that molecular modeling was an especially valuable tool for understanding the mechanisms of surface reactions. In particular, calculated bulk and surface energies were useful in predicting microscopic and macroscopic rates for carbonates. A log-linear relationship between calculated lattice energies and measured macroscopic dissolution rates was established. The rigid ion model was further applied to simulate the microscopic processes active in dissolution. For larger pits, we showed that ion pair translation energies predict experimentally observed step velocities.

Scaling microscopic phenomenon to macroscopic observations is integral to the construction of quantitative and predictive models, which can be further linked from macroscopic to field scale dimensions. When accomplished, this combined model can be employed to provide rational and effective solutions to problems of environmental contamination and remediation.

UNIVERSITY OF ILLINOIS

Department of Geology
1301 W. Green St.
Urbana IL 61801

Grant: DE-FG02-00ER15028

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

R. James Kirkpatrick, kirkpat@uiuc.edu

The overall objectives of our research are to advance understanding of molecular-scale behavior of water and aqueous solutes at mineral-solution interfaces, in interlayer galleries and in nano-spaces. Our research approach involves a unique combination of computational molecular modeling and experimental spectroscopy and addresses key, fundamental geochemical questions related to the effects of solid substrates on the structure, dynamics, and energetics of interfacial aqueous fluids.

During 2003, research was focused on 1) computational molecular dynamics (MD) modeling of the effects of mineral composition and surface structure on the structure, dynamics and energetics of near-surface water and dissolved species, 2) experimental far-infrared spectroscopy and MD modeling of the structure and low-frequency vibrational dynamic behavior of hydrated mineral interlayers, 3) experimental nuclear magnetic resonance (NMR) and computational MD study of the interaction of natural organic matter (NOM) and solute species, and 4) initiation of a combined experimental NMR and computational MD project to study the chemical interaction of amino acids with minerals.

Some of the principal findings of this work include new insight into the structural transition between surface-adsorbed and bulk water, the molecular scale origin of the experimentally observed differences between the interaction of dissolved species with silicate mineral surfaces and NOM, and the structural and chemical controls of the interactions of a wide variety of dissolved anionic species with layered double hydroxide phases. In addition, the effective calculation of the low frequency vibrational spectra of hydrated mineral interlayers provided a stringent test of the effectiveness of the CLAYFF MD force field, developed by R. T. Cygan of the Sandia National Laboratories in collaboration with us.

Published papers based on this research include:

X.Hou et al., *Am. Mineral.*, **88**, 167, 2003.

J.Wang, et al., *Am. Mineral.*, **88**, 398, 2003.

R.T.Cygan et al., *J. Phys. Chem. B*, **108**, 1255-1266, 2004.

J.Wang et al., *Earth and Planetary Science Letters*, **222**, 517, 2004.

J.Wang et al., *Geochim. Cosmochim. Acta*, **68**, 3351, 2004.

R.J.Kirkpatrick et al., in T.Kloprogge, ed., *The Application of Vibrational Spectroscopy to Clay Minerals and Layered Double Hydroxides*, The Clay Minerals Society, CMS Workshop Lectures, Vol. 13, pp. 239-285, 2004.

UNIVERSITY OF ILLINOIS

Department of Geology

1301 W. Green St.

Urbana IL 61801

Grant: DE-FG02-02ER15317

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

Craig Bethke, (217) 333-3369, bethke@uiuc.edu

We use quantitative modeling techniques to better understand how physical transport, chemical reaction, and microbiological activity work together to control the chemical composition of groundwater in the Middendorf aquifer, a mostly confined aquifer of the Atlantic Coastal Plain province, in South Carolina. Historically, geochemists called first on equilibrium thermodynamics and then geochemical kinetics to explain how groundwater evolves in composition as it flows through the subsurface. These attempts have fallen short, however, and there is a general consensus currently that microbial life exerts a dominant influence on groundwater chemistry, although an influence that has proved difficult to quantify. We are sampling groundwater from an array of wells across the aquifer and analyzing it chemical and microbiologically. The chemical analyses include assays of the oxidized and reduced species that serve as electron-donating and electron-accepting species for respiring organisms. We are analyzing biomass filtered from the water in various ways, including MPN, T-RFLP, MPN-PCR, and real-time PCR. We will integrate the results of these analyses into a reactive transport model to attempt to explain the distribution of chemical reaction and microbial activity in the aquifer.

UNIVERSITY OF ILLINOIS AT CHICAGO

Department of Earth and Environmental Sciences
Chicago IL 60607

Grant: DE-FG0203ER15381

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

Neil C. Sturchio, 312-355-1182, fax 312-413-2279, sturchio@uic.edu

In this collaborative program with Paul Fenter (Argonne National Laboratory) and others, we continue the development and application of synchrotron X-ray scattering techniques for in situ studies of mineral-fluid interfaces, taking advantage of the major increases in temporal and spatial resolution afforded by the high X-ray brilliance and energy available at the Advanced Photon Source (APS). These experiments will help bridge the gap between real-space and reciprocal-space techniques, will further define kinetics and reaction mechanisms at the atomic scale in key mineral-fluid systems, and will constrain the continued development of theory pertinent to processes at mineral-fluid interfaces. Advances in these fundamental areas will yield significant benefits in terms of DOE mission-related applications, such as energy resource exploration and utilization, environmental restoration and waste management, and materials.

Structure and bonding at the mineral-fluid interface are just beginning to be understood for the most simple minerals, and further progress is limited by the development of new experimental and computational techniques capable of elucidating the atomic realm. A particularly powerful set of techniques for *in situ* studies of mineral-water interfaces arises from X-ray scattering effects. This set of techniques is practical only at high-intensity synchrotron radiation sources. We have performed such experiments at the APS since 1997. These experiments demonstrated the first uses of low-angle X-ray reflectivity, thin-film diffraction, X-ray standing waves, crystal truncation rod measurements, and resonant anomalous X-ray reflectivity for in situ studies of mineral-fluid interfaces in static and dynamic mineral-fluid systems. We are focusing our efforts in several experimental thrusts, each corresponding to a major area of scientific need in mineral-fluid interface studies. Progress during the past year included further investigations of a broad range of mineral-water interface structures, processes (molecular adsorption and mineral dissolution), and reaction kinetics, for a variety of mineral-water systems (carbonates, silicates, and oxides).

UNIVERSITY OF ILLINOIS AT CHICAGO

Department of Earth and Environmental Sciences

845 W. Taylor St., MC-186

Chicago IL 60607

Grant: DE-FG02-02ER15364

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

Kathryn Nagy, klnagy@uic.edu, (312) 355-3276

We seek to acquire mechanistic understanding of processes at the mineral-water interface that explain macroscopic observations and that can be applied to problems such as the distribution and reactivity of environmental contaminants as well as the chemically-reactive behavior of ground water flow in porous media. We are addressing two specific questions regarding rates and mechanisms of sorption, dissolution, and growth, raised by our previous research. First, what is the nanoscale/molecular scale structure of the interface between micas or clays (phyllosilicate minerals) with aqueous solutions and how does that structure relate to the processes of sorption and secondary mineral nucleation and growth? Second, what systematics control the aging kinetics of nanoparticles of iron-oxides and aluminosilicate clays and the simultaneous incorporation of chemical components such as contaminant ions and organic molecules?

The basal surface of phyllosilicates is a primary sorbent of environmental contaminants, natural organic matter, and life-sustaining nutrients. Micas are also superb atomically-flat substrates used in materials science and surface physics applications. Despite the interdisciplinary importance of phyllosilicate basal surfaces, a full molecular-scale description of the crystal-solution interface structure is not yet available. Our recent application of X-ray scattering techniques using high brilliance synchrotron radiation coupled with atomic force microscopy (AFM) has revealed molecular-scale details of the interface structure such as relaxation of atoms in the crystal, surface roughness, and properties of the electrical double layer in the contacting aqueous solution (containing water, cations, anions, and organic molecules). Parameterization of the data provides subnanometer-scale resolution of the relaxation of the solid, structure of the overlying solution including positions of sorbed ions, and structure of the sorbed organic films.

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 aging Fe-oxides and phyllosilicate clays in the presence of selected cations, anions, and organic molecules, and quantifying the effects of surface area, morphology, and phase proportions on the aging process.

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

Arndt Schimmelmann, (812) 855-7645, aschimme@indiana.edu

Isotopically labile organic hydrogen in fossil fuels occupies chemical positions that participate in isotopic exchange and in chemical reactions during thermal maturation. We monitor changes in the H-isotopic exchangeability and stable isotope D/H ratio in oil and maturing kerogens in source rocks to evaluate paleoenvironmental and diagenetic influences. In 2004 we advanced three sub-projects. First, our study of stable hydrogen isotopes in terrestrial petroleum systems was published (Schimmelmann, A., A.L. Sessions, C.J. Boreham, D.S. Edwards, G.A. Logan, and R.E. Summons, 2004. D/H ratios in terrestrially-sourced petroleum systems. *Organic Geochemistry* **35**, 1169-1195; <http://dx.doi.org/10.1016/j.orggeochem.2004.05.006>). In brief, D/H ratios of terrestrially-sourced whole oils and their respective saturated, aromatic, and polar fractions, individual *n*-alkanes, formation waters and non-exchangeable hydrogen in kerogen were measured from source rocks from seven Australian petroleum basins. δD_{oil} and $\delta D_{saturated}$ show no evidence for H-exchange with formation water under reservoir conditions at temperatures up to 150°C. Acyclic isoprenoids and *n*-alkanes show essentially indistinguishable δD , indicating that primary isotopic differences from biosynthesis have been erased. Overall, extensive exchange of C-bound H in petroleum with other hydrogen is apparent, but seems to have affected most hydrocarbons only during their chemical genesis from precursor molecules. In a second sub-project, stable isotope ratios of non-exchangeable hydrogen (δD_n) and of carbon were measured in type-II kerogens from two suites of Late Devonian to Early Mississippian black shale. δD_n values increase with maturation up to a vitrinite reflectance of R_o 1.5 %, then level out. Increasing δD_n values suggest isotopic exchange of organic hydrogen with water-derived deuterium and/or preferential loss of 1H -enriched chemical moieties from kerogen during maturation. The resulting changes in δD_n values are obscuring the original hydrogen isotopic paleoenvironmental signal in kerogen, albeit in a systematic fashion. A manuscript was submitted (Lis, Schimmelmann, Mastalerz; D/H ratios and hydrogen exchangeability of type-II kerogens with increasing maturity. *Organic Geochemistry*, in review). An unexpected sub-project arose in 2004 when we were asked to write a review article about "Hydrogen isotopic (D/H) composition of organic matter during diagenesis and thermal maturation" for the prestigious *Annual Review of Earth and Planetary Sciences* (Schimmelmann, Sessions, Mastalerz; in review).

JOHNS HOPKINS UNIVERSITY

Department of Earth and Planetary Sciences
Baltimore MD 21218

Grant: DE-FG02-96ER14619

Fluid Flow in Faults: Processes and Effects from Modern and Paleo Systems in a Transpressional Tectonic Setting, Southern California

Grant Garven, garven@jhu.edu

Objectives: This is a collaborative study to quantify basinal fluid flow, submarine methane migration and diagenetic effects within deforming faults in a transpressional setting, which is seismically active.

Project Description: We have mostly targeted active faults and young petroleum fields in southern California for study, such as the Refugio-Carneros Fault in the Transverse Ranges near Santa Barbara. Subsurface data and published structural-seismic sections were analyzed to characterize the tectonic history and diagenetic evolution for the fault. These data provide constraints for finite element models that were developed to predict fluid pressures, flow patterns, rates of deformation, temperatures, and carbonate mineralization patterns associated with large fault systems and the geochemical mixing of fluids.

Results: Our FY2004 studies have shown that the Refugio-Carneros Fault is relatively unique amongst the numerous faults in the region in being a conduit of high temperature fluid and hydrocarbon migration, suggesting hydrocarbon migration events can be short lived. We have recently documented isotopic disequilibrium during rapid calcite and aragonite crystallization following rapid CO₂ degassing, in the form of co-varying carbon and oxygen isotopes in tunnel speleothems and well tubing scale. Our goal is to develop a quantitative understanding of this phenomenon in order to interpret isotopic signatures found in fault zone cements. A study in an offshore Santa Barbara oil field has calculated a fault permeability of 20 md, a similar value to overall reservoir permeability, from the rate of seawater influx into an underpressured reservoir. We have also documented diluted formation waters in newly explored deep parts of the Los Angeles basin and are seeing changes in the Na/Ca ratio due to plagioclase albitization. A kinetic model for plagioclase albitization has been published that allows prediction of this important reaction as a function of geologic time and burial temperature. One new manuscript was submitted that characterizes fault-valve behavior and earthquake recurrence in a generic transpressional profile. In addition, a paper on reactive flow modeling has been prepared that tests the concept of CH₄-bearing fluids mixing with meteoric groundwater in faulted, submarine reservoirs along coastal Santa Barbara, replicating observed patterns of calcite mineralization.

JOHNS HOPKINS UNIVERSITY

Department of Earth and Planetary Sciences
Baltimore MD 21218

Grant: DE-FG02-89ER14074

Reactions and Transport of Toxic Metals in Rock-Forming Silicates at 25°C

David R. Veblen, (410) 516-5049, dveblen@jhu.edu

This project is an investigation of reactions between silicate minerals and toxic metal-bearing aqueous fluids. We are specifically exploring mechanisms of oxidation-reduction reactions at the mineral-fluid interface involving reductants structurally bound in minerals and sorbed to mineral surfaces. The project has three main components: experimental investigation of U reduction and sorption by phyllosilicates; transmission electron microscopy (TEM) characterization of reaction products; and development of new characterization techniques. Technique development includes X-ray photoelectron spectroscopy (XPS) and atomistic-scale TEM methodologies to probe sorption behavior and redox reactions. Experiment design and sample characterization is aimed at elucidating crystallographic and solution controls on heterogeneous electron transfer between phyllosilicates and multivalent metals in the environment.

The research has focused on heterogeneous reduction of uranyl by Fe(II)-bearing micas (Ilton et al., 2004). The valence state of uranium strongly influences its solubility and sorption behavior thereby determining its mobility in environmental systems. Recent results include: differentiation of reactivity of basal surfaces, edges, and interlayer regions; identification of effects of alkali cations in solution on heterogeneous reduction of uranyl by micas; and the unexpected discovery that heterogeneous reduction of uranyl on Fe(II)-mica surfaces produces pentavalent uranium as a major sorbed species. Pentavalent U has been ignored for most aqueous systems because U(V) has only a small stability field in water and rapidly disproportionates. Previous work, however, did not consider the role of mineral surfaces in stabilizing U(V). Our research suggests that pentavalent U may play an important, but hitherto unrecognized, role in the U geochemical cycles. One of the long range goals of this project is to determine whether other mineral surfaces can stabilize U(V).

This project has utilized electron microscopy, x-ray photoelectron spectroscopy (XPS), and x-ray absorption spectroscopy (XAS) in order to determine the valence state and location of metals sorbed to phyllosilicates. In this regard, we have been developing strictly ab initio theoretical models to better interpret the fine structures in the 2p, 3s, and 3p XPS of transition metals (Bagus et al., 2004a and 2004b). Our long-range goal is to be able to simulate complex bonding environments that represent sorption at surfaces and nanosized particles.

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

Research efforts this year have focused on finalizing a quantitative characterization of the development of proton surface charge on the surfaces of minerals. This is necessary for a fundamental understanding of reactions between solids and aqueous electrolyte solutions. Despite many experimental studies of charge development, few attempts have been made to integrate the results with a theoretical framework that permits prediction. In the present study, 53 sets of proton surface charge data referring to wide ranges of ionic strengths, types of electrolyte and oxide were analyzed with the aid of the triple-layer model of surface complexation. The application of crystal chemical, electrostatic and thermodynamic theory to the results enables prediction of all the surface complexation parameters needed to calculate proton surface charge for any oxide in 1:1 electrolyte solutions. Asymmetric binding of electrolyte ions is built into these predictions. Predicted trends of electrolyte cation binding and surface charge for high dielectric constant solids (e.g. rutile) are opposite to those on low dielectric constant solids (e.g. amorphous silica). The results are described in Sverjensky, D. A. (2004, *Geochimica et Cosmochimica Acta*, in press) "Prediction of surface charge on oxides in salt solutions: revisions for 1:1 (M+L-) electrolytes". Research is also continuing on the adsorption of divalent and higher valence metals onto mineral surfaces, elucidating changes in surface speciation with solution chemistry and surface coverage. The overall objective is prediction of the acquisition of metals by fluids circulating through aquifers in the earth's crust.

LOUISIANA STATE UNIVERSITY

Department of Geology and Geophysics
Baton Rouge, LA 70803

Grant: DE-FG02-01ER15167

3D Sedimentological and Geophysical Studies of Clastic Reservoir Analogs: Facies Architecture, Reservoir Properties, and Flow Behavior within Delta Front Facies Elements of the Cretaceous Wall Creek Member, Frontier Formation, Wyoming

Christopher White, cdwhite@lsu.edu

Deltaic reservoirs comprise a major proportion of oil and gas reservoirs, aquifers, storage, and sequestration candidates. These reservoirs exhibit stratigraphic, lithologic, and petrophysical complexity that affects flow: in the United States, 15 billion barrels of mobile oil remain unrecovered in such reservoirs.

An integrated study focuses on the Wall Creek Member (Cretaceous Frontier Formation, Wyoming). The goals are to improve models of delta architecture, formulate quantitative models for property distributions, assess the effects of features on flow, and formulate methods for large-scale simulation models.

A regional study reveals the large-scale facies associations and variability within this top-truncated mixed-influence delta. Studies at several localities use digital photomosaics, measured sections, global positioning, and surveys to create geospatial models of bedding geometry and facies distribution. At the Raptor Ridge locality these data are augmented by ground-penetrating radar, core analysis, permeametry, and petrologic analyses.

Two- and three-dimensional radar surveys are calibrated using core, and interpreted based on adjacent near-strike and near-dip outcrop exposures. The results include a 3D stratigraphic framework. The data volume is 80 x 30 x ~12 (thick) m (77 x 106 data locations). Cluster analysis of core and radar data guides lithofacies classification.

The radar data are combined with facies trends and autocovariances computed from the outcrop exposures. The geostatistical model uses the proportion trends as a prior to estimate facies occurrence probabilities using truncated Gaussian simulation. These results are updated using cluster-derived facies classifications with Bayes' rule. These estimates integrate the geologic prior, geospatial data from the outcrop and wells, and radar attributes.

The flow behavior of these models is examined using flow models selected by experimental design, testing the importance of different data types – e.g., the impact of proportion curves vis-à-vis radar attributes. Finally, the best geostatistical models are used to derive response models for upscaled properties for field flow modeling. The responses include effective permeability, displacement endpoints, and shock velocities; the models depend on facies proportions, concretion occurrence, intrinsic rock properties, and engineering parameters including mean flow velocity.

UNIVERSITY OF MARYLAND

Department of Chemistry and Biochemistry
College Park MD 20742

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

Our research group utilizes the techniques of computational quantum chemistry to study the structures, energetics and properties of various metal species in solution, as components of mineral glasses, or absorbed on mineral surfaces. In Fiscal Year 2003 we have extended our studies on the UV-vis spectra of species in solution to As and Sb oxidation state III and V sulfides and to polysulfides Sn^{-2} , $n=2-6$, the bisulfide anion, SH^- , hydrogen sulfide, H_2S and the sulfanes, SnH_2 , $n=2-5$. We correctly reproduce the general trends observed experimentally, with absorption energies increasing from polysulfides to As, Sb sulfides to SH^- to H_2S . As and Sb (V) species, both monomers and dimers, also absorb at characteristically higher energies than do analog As and Sb (III) species. There is also a small reduction in absorption energy from monomeric to dimeric species, for both As and Sb III and V. Our results indicate that for the As and Sb sulfides, the oxidation state, degree of protonation and degree of oligomerization can all be determined from the visible-UV absorption spectrum. We have also calculated the aqueous phase energetics for the reaction of S_8 with SH^- to produce the polysulfides, SnH^{-1} , $n = 2-6$. Our results are in excellent agreement with available experimental data, and support the existence of a S_6 species. Recently the removal of gas-phase elemental Hg has been observed by several research groups after polar sunrise in the boundary layer in Arctic regions. At the same time Hg compounds are observed to accumulate in the polar snowpack. Several different oxidation reactions involving gas-phase Br and BrO have been hypothesized to explain this process. Molecular quantum mechanical methods are here applied to evaluate the energetics for such reactions, in both the gas-phase and aqueous solution. The formation of HgO from the reaction of HgO and BrO in the gas phase is found to be unfavorable energetically but HgBr and HgBr₂ can form exothermically through the oxidation of HgO by either Br atom radicals or Br₂.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Earth, Atmospheric, and Planetary Sciences
Cambridge MA 02139

Grant: DE-FG02-97ER14760

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

J. Brian Evans, brievans@mit.edu

Both temporal and spatial variations of permeability are common in the Earth; such variations are driven by a diverse and complex set of processes including fracturing, diagenesis, cementation, brittle pore collapse, compaction owing to pressure solution or plastic flow, crack healing, crack sealing. Each mechanism will respond to a particular set of driving forces, including local non-hydrostatic stresses; reduction of interfacial energy; dissolution into under saturated liquids, precipitation from oversaturated fluids, or reactions between phases. To identify the dominant process, kinetics laws need to be developed for each mechanism. Some processes are more efficient in changing permeability than others. In particular, neo-mineralization and dilatant micro fracturing are capable of producing large changes in permeability with relatively small changes in total porosity, but compaction during creep is less efficient, provided that capillary forces are capable of maintaining steady-state interfacial angles. Two examples of experiments to determine rates follow: 1.) When samples of Sioux quartzite were inserted into a hydrothermal pressure vessel and heat-treated at temperatures of 300-500°C confining pressures of between 300 MPa and 125 MPa and fluid pressures from 125 MPa to 250 MPa, permeability was reduced by as much as three orders of magnitude. Reductions occur fastest at higher temperatures and higher effective pressures. 2.) During deformation at 473, 523, 573 and 673 K, at confining pressures (argon) of 70 to 200 MPa, and a constant pore pressure (distilled water) of 50 MPa, Solnhofen limestone failed by dilatancy and localized deformation. The stress required to cause dilatancy and localization increases with increasing pressure and decreasing temperature. At low pressures and temperatures, strain softening and an abrupt stress drops were observed during localization. However, at higher pressure and temperature, the localization process became progressive, with strain softening and dilatancy accumulating over large amount of axial strain (up to 6%). Following the localization model of Rudnicki and Rice (1975), we used the internal friction parameter, the dilatancy factor, and the hardening modulus to characterize the failure behavior. Both the internal friction parameter and the dilatancy factor depend on P and T.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Earth, Atmospheric, and Planetary Sciences
Cambridge MA 02139

Grant: DE-FG02-99ER15004

Physics of Channelization: Theory, Experiment, and Observation

Daniel H. Rothman, (617) 253-7861, dhr@mit.edu

Our project seeks to better characterize the physical processes that erode landscapes, with emphasis on the formation of drainage channels and channel networks. Our approach consists of tightly coupled theoretical and experimental studies augmented by field observations. The work is performed in collaboration with Prof. Arshad Kudrolli of Clark University. The group at Clark is primarily responsible for experiments while the group at MIT is primarily responsible for theory.

Fluvial erosion in natural systems can be induced by either surficial, overland flows or subsurface, seepage flows. The latter process constitutes the present focus of our project. Using modern laser-aided data-acquisition and digital imaging techniques, we obtain detailed time-dependent two-dimensional topographic data. Our objective is to understand the evolution of the topography as fully as possible.

We have thus far focused three problems. First, we have shown that our experiment yields a characteristic channel spacing that depends on slope and pressure gradient, and have proposed theoretical explanations for this choice of length scale. Second, we have defined, both theoretically and experimentally, the particular values of control parameters that determine the qualitative quasi-stationary features exhibited in our experiment. The third focus of our work has been on the dynamics of channel evolution. We have discovered that the problem may be usefully portrayed as a trajectory in a two-dimensional phase space. Commonalities in all such trajectories indicate surprisingly that the growth of individual channels is at least to some extent independent of other channels in the channel network, in a manner that is determined by the geometry of the subsurface water flow.

The laboratory-scale component of this project is performed so that at least one manifestation of channelization may be completely understood. To better understand where our theories and experiments apply in the natural world, we also perform simple observational studies of natural channels found on beaches.

MINERALOGICAL SOCIETY OF AMERICA

3635 Concorde Pkwy Ste 500
Chantilly VA 20151

Grant: DE-FG02-01ER15127

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

J. Alex Speer, (703) 652-9950, fax: (703) 652-9951, j_a_speer@minsocam.org

The project was for the support of three Mineralogical Society of America and Geochemical Society short courses and companion Reviews volumes in 2003:

[1] Zircon: experiments, isotopes and trace element investigations. April 3 and 4, 2003, Freiburg, Germany. Convenors: John M. Hanchar and Paul W. O. Hoskin. Registrations were taken by the Mineralogical Society of America and the course had 60 participants (20 students and 40 professionals). Reviews in Mineralogy and Geochemistry volume 53: Zircon: experiments, isotopes and trace element investigations (500 pp.) ISBN 093995065-0 (\$36 non-members, \$27 MSA, GS, and CMS members) - 2500 copies printed on 12/04/2003.

[2] Uranium Series Geochemistry April 3-4, 2003 on Convenors: Bernard Bourdon, S. P. Turner, Gideon M. Henderson, and Craig C. Lundstrom. Registrations were taken by The Geochemical Society and the course had 90 participants (68 students and 22 professionals).

Reviews in Mineralogy and Geochemistry volume 52: Uranium Series Geochemistry (656 pp.) ISBN 093995064-2 (\$40 non-members, \$30 MSA, GS, and CMS members) - 2500 copies printed on 03/06/2003.

[3] Biomineralization. December 6-7, 2003, Napa, California. Convenors Patricia Dove, J. J. DeYoreo and S. Weiner. Registrations were taken by the Mineralogical Society of America and the course had 101 participants (48 students and 53 professionals).

Reviews in Mineralogy and Geochemistry volume 54: Biomineralization (381 pp.) ISBN 093995066-9 (\$36 non-members, \$27 MSA, GS, and CMS members) - 2500 copies printed on 11/21/2003.

UNIVERSITY OF MINNESOTA

Department of Geology and Geophysics
Pillsbury Hall
Minneapolis MN 55455

Grant: DE-FG02-04ER15500

Rheology of Earth's Interior

D.L. Kohlstedt (612) 624-7311, fax (612) 625-3819, dlkohl@umn.edu

The overall scope of this research is to determine the high-temperature, high-pressure flow law for olivine, an essential step in understanding the dynamics of Earth's deep interior. A series of twelve deformation experiments have been conducted using the D-DIA apparatus at synchrotron radiation facilities. Polycrystalline samples were hot-pressed from powders of olivine plus 5% enstatite. Experiments were carried out at constant displacement rates of 1×10^{-5} to 4×10^{-4} /s to shortening strains of ~15% with temperatures between 1273 and 1573 K and pressures of 3 to 6 GPa. The chemical environment of the olivine samples is fixed; the oxygen fugacity is buffered by the existence of both Ni and NiO, and silica activity is set by the presence of enstatite.

Precise measurements at high pressure of stress, strain, strain rate, pressure, and temperature are a distinct feature of this study. During a deformation experiment, x-ray radiographs taken periodically of the sample column yield the change in length of the sample as a function of time, from which strain and strain rate are calculated. Pressure is determined based on the spacing of x-ray diffraction peaks from a small amount of well-characterized proxy material, MgO, inserted into the deformation column, while differential stress is obtained from the strain of various lattice planes in the sample measured as a function of orientation with respect to the stress field.

Analyses of our data yield an activation volume for creep of $4\text{-}8 \times 10^{-6}$ m³/mol. Although this result is only preliminary, because additional analyses of the microstructures as well as the water contents of our samples are still in progress, it indicates that previously reported values are a factor of two too large. These first results are very exciting, as they indicate that the D-DIA experiments have adequate resolution to determine important flow parameters such as activation volume.

The techniques used for both D-DIA experiments and x-ray diffraction measurements are breakthrough technologies compared to conventional deformation experiments. Significant effort on cell design now permits experiments to 12 GPa at 1500 K. Our software package greatly simplifies data reduction, reducing the time by a factor of ten.

NATIONAL ACADEMY OF SCIENCES

Board on Earth Sciences and Resources
500 5th Street, N.W.
Washington, DC 20001

Grant: DE-AT01-04ER15569

Board on Earth Sciences and Resources

Anthony R. de Souza, 202-334-2744, adesouza@nas.edu

The Board on Earth Sciences and Resources is the focal point of earth science activities at the National Academies. Founded in 1988, the Board provides objective advice through its mandated, requested, and self-initiated studies. Many of the Board's activities are conducted through its six standing committees. These committees are Earth Resources, Seismology and Geodynamics, Geological and Geotechnical Engineering, Geophysical and Environmental Data, Mapping Sciences, and Geographical Sciences.

NEW ENGLAND RESEARCH

White River Junction, VT 05001

Grant: DE-FG02-98ER14906

Evolution of Fracture Permeability

Stephen Brown, sbrown@ner.com

Pore fluid flow within fractured rocks is a subject of primary importance to various fields of study including hazardous waste isolation and remediation, oil and gas production, geothermal energy extraction, and formation of vein fillings and ore deposits. For these reasons, considerable effort has been directed toward the characterization and modeling of flow in fractures and fracture systems. We are investigating the complex active chemical interaction between pore fluid and fractures that causes the fluid composition and fracture surface topography of these systems to change over time.

Our experimental model consists of CaSO_4 samples pressed with a constant force against an inert textured fracture surface. Pore fluids ranging from unsaturated to supersaturated, which are at a variety of flow rates, are introduced to one end of the sample in order to actively alter the topography of the CaSO_4 surface. Using a laser profiler, we are able to quantitatively monitor the changing surface topography over time as it relates to the measured sample permeability and calcium content of the pore fluid. These methods allow us to create and analyze many features seen in natural fractures, including high-flow dissolution channels, plateaus, and caverns formed from precipitate. In addition, the laser profile of the sample surface can be used to produce a map of aperture across the sample. Using this information, we have applied numerical modeling via finite difference and lattice Boltzmann methods to calculate pore fluid flow direction and magnitude over the entire sample surface.

We find that when experimental parameters (e.g. initial surface topography, flow rate history, and total experiment time) are duplicated, the topography developed on the plaster sample is reproducible. The flow channel networks, as observed visually and through numerical simulations, evolves from a homogeneous system to one more (self) organized and complex. The permeability initially drops as the experiment begins and the surfaces settle into place, then gradually rises with several further smaller decreases as some supporting asperities are destroyed.

NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY

Department of Earth and Environmental Science
Socorro NM 87801

Grant: DE-FG02-96ER14589

A Systematic Study of Heterogeneity, Instrumentation, and Scale Using Physical and Numerical Experimentation

John Wilson, jwilson@nmt.edu

Measurements are made at a variety of scales in aquifers and petroleum reservoirs, and model numerical grids are developed for even larger scales. Upscaling synthesizes these various scales. We explore fundamental understanding of upscaling through systematic physical and numerical experimentation. Our laboratory experiments employ a computer automated gas minipermeameter that collects highly resolved permeability data at a variety of scales on rock blocks and slabs. We've measured more than 250,000 permeability values on six different heterogeneous blocks of rock using six different scales of measurement, with new measurements and upscaling analyses on several of these rocks during FY02. We completed studies on the relationship between rock permeability and digital visual images of three rocks, analogous to images you would obtain with geophysical methods, and how such information might be used in aquifer/reservoir characterization. We found no significant direct correlation between the permeability measurements and any objective measure of corresponding images, despite the obvious resemblance of the permeability maps and the images. Although images can't give permeability itself, they can be used to estimate spatial statistics and to delineate the spatial pattern of permeability, especially to locate boundaries with sharp permeability contrasts. Instrument weighting functions are primary concept in our upscaling approach, which we've measured in the lab and simulated using adjoint equations. We continued simulation studies aimed at interpreting these results, especially by understanding the physical meaning of weighting functions. In collaboration with Fred Molz of Clemson we confirmed that the explanation lies in the fluid flow energy dissipation pattern, and continued studies on how spatial weighting functions depend on heterogeneity and are therefore non-unique. We continued solute transport experiments using X-ray absorption imaging, through which we quantitatively measured porosity and visualized solute transport in an exhaustively characterized slab of cross-stratified sandstone exhibiting nested scales of heterogeneity. Solute pathways were strongly influenced by the spatial permeability/porosity patterns. Macrodispersion scaled linearly with distance when flow was oriented parallel to stratification while complex, non-linear scaling relations were encountered when flows were forced to cross the stratification. Additionally, the calculated dispersion coefficients varied spatially, and with the orientation and mode of injection.

THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK

Benjamin Levich Institute & Department of Physics
New York NY 10031

Grant: DE-FG02-93ER14327

Fluid and Particulate Transport in Self-Affine Fractures

Joel Koplik, (212) 650-8162, fax: (212) 650-6835, koplik@sci.ccny.cuny.edu

We studied the motion of a passive tracer in fluid flow in geological fractures with self-affine fractally rough walls by laboratory experiments on epoxy casts of natural fracture surfaces, coupled to numerical simulation using the lattice-Boltzmann method. The focus of this year's work was to further investigate the permeability anisotropy that results from a shear displacement between the complementary self-affine walls of a rough fracture. Experiments in which a dyed fluid radially injected into a transparent fracture displaces a transparent one showed a clear flow anisotropy in the presence of shear displacements, and allowed us to estimate the ratio of the permeabilities for flows parallel and perpendicular to the shift. A simple model which accounts for the development of channels perpendicular to the shift direction qualitatively explains these results, and predicts a permeability decreasing (increasing) linearly with the variance of the aperture field for flow parallel (perpendicular) to the shear displacement. These predictions were found to agree with the results of numerical simulations performed using a lattice-Boltzmann technique, and to the anisotropies measured in displacement experiments. In order to extend the numerical approach to the case of non-Newtonian fluid flow in fractures, we developed and tested a lattice Boltzmann code suitable for power-law fluids.

THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK

Benjamin Levich Institute & Department of Physics
New York NY 10031

Contract: DE-FG02-03ER15458

Stress-Dependent Acoustic Propagation and Dissipation in Granular Materials

*Hernan A. Makse, (212) 650-6847, fax (212) 650-6835,
hmakse@levdec.engr.ccny.cuny.edu*

This project is a joint collaboration between City College of New York (CCNY) and Schlumberger-Doll Research (SDR). The goal of the project is to combine experiments, theory and simulations to develop an understanding of the elastic and viscoelastic properties of granular materials. We focus our studies on the following projects:

(i) Nonlinear elasticity and acoustics of granular materials. We attempt to understand the elastic response of a granular assembly under loading. Our experiments reveals that elasticity theory fails to describe the elastic properties of granular assemblies. The understanding of this failure has been a longstanding question in the field. We show that a correct treatment should include the collective relaxation mechanisms related to structural disorder and nonaffine motion of grains. Next, we perform a theoretical investigation that allows for grain relaxation in collaboration with Cornell University. The incorporation of additional degrees of freedom results in predictions which are in far better agreement than previously.

We also investigate the Green (response) function of random packings of grains in order to discriminate between the different theories of stress transmission. We show that elasticity theory, while approximating qualitatively the stress profiles, breaks down by not taking into account the dynamics of grain relaxation, in analogy with our studies on the elastic moduli.

(ii) Compaction and stress relaxation. The relaxation and dissipative properties of cohesionless granular assemblies under compression are being studied both experimentally and numerically. We investigate the system's exploration of the static configurations through a novel compaction procedure at varying confining pressures. Once the system is fully compactified we study the slow relaxation dynamics under an applied strain. Computer simulations reveal that the origin of the long stress-relaxation dynamics is the collective nature of the motion of the particles.

(iii) Dissipation in granular matter. An important goal of this project is to elucidate the origin of the dissipation mechanisms in granular materials. To this end we have initiated a series of experiments, simulations and theory to calculate the effective mass of a rigid cavity filled with loose granular particles. This work is ongoing.

STATE UNIVERSITY OF NEW YORK, STONY BROOK

Department of Geosciences

Stony Brook NY 11794

Grant: DE-FG02-96ER14633

An Inter-Disciplinary Study of the Surface Reactivity of Pyrite

Martin A.A. Schoonen, 516-632-8007, mschoonen@notes.cc.sunysb.edu

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. The program integrates observations at the macroscopic level with those at the microscopic scale. It is this integration that has proven to be very useful and productive. The objective of the research has been to understand important fundamental aspects of the surface chemistry of pyrite, such as charge development, reactivity, surface stoichiometry, surface structure, and interaction with dissolved constituents (sorption). Our ultimate goal is to provide insight into the role of pyrite as reactant, sorbent, and (photo)catalyst in environmentally and geologically relevant environments. This research has recently brought forth to the scientific forefront the importance of non-stoichiometric sites or defects in controlling the reactivity of pyrite. Many fundamental questions regarding the origin, presence, electronic structure, and reactivity of these defects remain unanswered and are being addressed in our studies. We believe that we need to answer these questions in order to provide the basic science needed for the development of the next generation of techniques in the abatement of acid mine drainage, one of the most important environmental problems we face (about 1 million dollars is spent per day on this problem). We argue that by understanding the reactivity of pyrite at the molecular scale strategies can be developed that target one or more of the elementary reactions in the oxidation of pyrite. While our research is primarily motivated by a desire to understand pyrite oxidation at the molecular level, our work is also of importance to several technical problems where the surface chemistry of pyrite plays a role, such as flotation of pyrite in the mining industry, acidification of hydrocarbon reservoirs (a problem relevant to terrestrial CO₂ sequestration), and sorbent of radionuclides and other constituents (e.g. gold).

STATE UNIVERSITY OF NEW YORK, STONY BROOK

Department of Geosciences

Stony Brook NY 11794

Grant: DE-FG02-99ER14996

Microscale Processes and Macroscopic Behavior of Porous Geomaterials

Teng-fong Wong, (631) 632-8212, Teng-fong.Wong@stonybrook.edu

This project focuses on the systematic investigation of the micro-scale characteristics of natural earth materials, and how these micro-scale characteristics control the macroscopic deformation and transport behavior. The research uses an integrated approach consisting of experimental rock mechanics testing, quantitative 2D and 3D microscopy and statistical microgeometric characterization, and theoretical and numerical analyses. The objective is to enhance fundamental understanding of failure and transport processes in geologic materials, and thereby strengthen the theoretical basis for the application of laboratory results to various technological operations of importance. Specifically these topics have been investigated: (1) a comprehensive study of the phenomenology of failure in porous carbonate rocks, (2) a focused investigation of the micromechanics of failure in two porous limestone, (3) a laboratory investigation of the coupling of compaction localization and fluid transport in Bentheim sandstone, and (4) a comprehensive analysis of the effects of bedding and foliation on mechanical anisotropy, damage evolution and failure mode. Portions of the research have been presented in these publications: [A] Vajdova, V., P. Baud, and T.-f. Wong, Compaction, dilatancy and failure in porous carbonate rocks, *J. Geophys. Res.*, 109 (5), B05204, doi:10.1029/2003JB002508, 2004. [B] Wong, T.-f., C. David, and B. Menendez, Mechanical compaction, in *Mechanics of Fluid Saturated Rocks*, ed. Y. Gueguen and M. Boutca, Academic Press, 2004. [C] Baud, P., L. Louis, C. David, G. C. Rawling, and T.-f. Wong, Effects of bedding and foliation on mechanical anisotropy, damage evolution and failure mode, in *Microstructural Evolution and Physical Properties in High-Strain Zones*, ed. D. Bruhn and L. Burlini, Geological Society Special Publication, in press, 2004. [D] Vajdova, V., P. Baud, and T.-f. Wong, Permeability evolution during localized deformation in Bentheim sandstone, in press, *J. Geophys. Res.*, 2004.

STATE UNIVERSITY OF NEW YORK, STONY BROOK

Department of Applied Mathematics and Statistics
Stony Brook NY 11794

Grant: DE-FG02-92ER14261

Pore Scale Geometric and Fluid Distribution Analysis

W. Brent Lindquist, (631) 632-8361, lindquis@ams.sunysb.edu

We have focused on three dimensional (3D) pore scale medium characterization, permeability computations for throat structures, and residual fluid distribution in Berea (water wet) and polyethylene (oil wet) cores.

X-ray computed microtomography combined with X-ray attenuating dopants is used to obtain 3D images of the pore network and to resolve two phase distributions at residual fluid conditions in the pore space. Employing numerical image processing algorithms based upon computational geometry to identify individual pores, throats, and fluid “blobs”, we characterize the pore space geometry and extract water and oil distributions at the level of individual pores in both imbibition and drainage displacements. Preliminary results on fluid distribution have also been obtained for constant fractional flow conditions (i.e. injection of fixed wetting:non-wetting fluid volume ratio) in polyethylene cores.

We have results on pore characterization, including distributions for pore volume, pore surface area, throat surface area, and principal direction diameters for pores and throats. Single phase lattice Boltzmann computations are used to predict permeabilities for all individual throats reconstructed from the images. These computations use actual (digitized) geometries with no shape assumptions. These permeabilities will be used in network flow model simulations for prediction of bulk permeability.

We have results on oil and water distribution in the pore space at residual oil and water conditions. We also consider the effects on residual fluid distribution due to the injection and gelation of a water-based gel. In extensive studies of Berea cores it has been observed that introducing water-based gels in the displacement process (for example, in water shut-off treatment of production wells) reduces permeability to water more than to oil. A number of micro-scale mechanisms have been proposed for this disproportional permeability reduction. Our results provide supporting evidence for the involvement of gel compaction (dehydration) and oil trapping, while discounting gel blockage in throats, as mechanisms contributing to this effect.

UNIVERSITY OF NORTH TEXAS

Department of Chemistry

P.O. Box 305070

Denton TX 76203

Contract: DE-FG02-04ER15508

Reaction and Transport of Toxic Metals in Rock-Forming Silicates at 25°C

Paul S. Bagus, bagus@unt.edu

This project is an investigation of reactions between silicate minerals and toxic metal-bearing aqueous fluids. We are specifically exploring mechanisms of oxidation-reduction reactions at the mineral-fluid interface involving reductants structurally bound in minerals and sorbed to mineral surfaces. The project has three main components: experimental investigation of U reduction and sorption by phyllosilicates; transmission electron microscopy (TEM) characterization of reaction products; and development of new characterization techniques. Technique development includes X-ray photoelectron spectroscopy (XPS) and atomistic-scale TEM methodologies to probe sorption behavior and redox reactions. Experiment design and sample characterization is aimed at elucidating crystallographic and solution controls on heterogeneous electron transfer between phyllosilicates and multivalent metals in the environment.

The research has focused on heterogeneous reduction of uranyl by Fe(II)-bearing micas (Ilton et al., 2004). The valence state of uranium strongly influences its solubility and sorption behavior thereby determining its mobility in environmental systems. Recent results include: differentiation of reactivity of basal surfaces, edges, and interlayer regions; identification of effects of alkali cations in solution on heterogeneous reduction of uranyl by micas; and the unexpected discovery that heterogeneous reduction of uranyl on Fe(II)-mica surfaces produces pentavalent uranium as a major sorbed species. Pentavalent U has been ignored for most aqueous systems because U(V) has only a small stability field in water and rapidly disproportionates. Previous work, however, did not consider the role of mineral surfaces in stabilizing U(V). Our research suggests that pentavalent U may play an important, but hitherto unrecognized, role in the U geochemical cycles. One of the long range goals of this project is to determine whether other mineral surfaces can stabilize U(V).

This project has utilized electron microscopy, x-ray photoelectron spectroscopy (XPS), and x-ray absorption spectroscopy (XAS) in order to determine the valence state and location of metals sorbed to phyllosilicates. In this regard, we have been developing strictly ab initio theoretical models to better interpret the fine structures in the 2p, 3s, and 3p XPS of transition metals (Bagus et al., 2004a and 2004b). Our long-range goal is to be able to simulate complex bonding environments that represent sorption at surfaces and nanosized particles.

NORTHWESTERN UNIVERSITY

Department of Civil and Environmental Engineering
Evanston IL 60208

Grant: DE-FG02-93ER14344

Interactions of Propagating Compaction Fronts and Pore Fluids in Porous Rock

J.W. Rudnicki, 847-491-3411; FAX 847-491-4011, jwrudn@northwestern.edu

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 one or more 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 CO₂. 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.

Conditions for the formation of both shear and compaction localization have been addressed by determining whether the material behavior for homogeneous deformation permits a solution alternative to further homogeneous deformation, in particular, one which corresponds to localization in a planar band. This approach has shown that such solutions are indeed possible for material models of the type commonly used to describe weak porous rocks in which compaction bands have been observed. Such models involve inelastic compaction and a “cap” on the yield surface indicating a decrease in the shear stress needed to cause further inelastic deformation with increasing compressive mean stress.

A specific analysis for an elliptic yield cap applied to the standard triaxial test yields results that are consistent with experimental observations of compaction bands on relatively flat portions of the stress vs. strain curve and in a limited range of lateral confining stress. The analysis predicts that there is a particular value of the lateral confining stress at which a transition from compaction localization to shear localization occurs. As the lateral confining stress is decreased from the transition value, the predicted angle between the normal to the shear band and the maximum compression direction increases rapidly from 0° (for a compaction band) to 20 to 30°. This rapid increase provides an explanation for the infrequent observation of very low angle shear bands.

UNIVERSITY OF NOTRE DAME

Department of Civil Engineering and Geological Sciences
Notre Dame, IN 46556

Grant: DE-FG02-02ER15323

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

Patricia Maurice, pmaurice@kant.helios.nd.edu

The interactions of bacteria with metals and environmental nanoparticles can play an important role in the mobility of metals through porous media. In this first year of the study, we made significant progress on several aspects of our study. First, we made significant progress on a study of the effects of siderophores on metal adsorption to kaolinite. Siderophores are metal-complexing ligands with high affinities for Fe(III), produced by many microorganisms in Fe-deficient environments. Siderophores can also form strong complexes with other metals such as Pb and Cd; hence, siderophores may play an important role in controlling metal mobility in porous media. This study compared the effects of siderophores desferrioxamine-B (DFO-B), desferrioxamine-D (DFO-D1), desferrioxamine-E (DFO-E), as well as siderophore-like ligand acetohydroxamic acid (aHA) on Pb and Cd adsorption to kaolinite (KGa-1b) at pH 4.5 to 9, in 0.1 M NaClO₄, at 22°C, in the dark. At pH > 6.5 all of the siderophores plus aHA, inhibited Pb adsorption, with inhibition increasing in the order aHA < DFO-D1 < DFO-B.

THE OHIO STATE UNIVERSITY

Department of Chemistry

100 W. 18th Ave.

Columbus OH 43210

Grant: DE-FG02-04ER15495

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

Heather C. Allen, (614) 292-4707, allen@chemistry.ohio-state.edu

Objectives: The objective of this research is 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 and vibrational sum frequency spectroscopies (XAS, VSGS), and molecular modeling to investigate the potential formation of ternary metal-anion complexes at mineral surfaces in different solution compositions over a range of surface coverages. XAS provides data on how the metal binds to the surface (monodentate, bidentate) and VSGS will provide data on the anions adsorbed with the metals, polyatomic anion orientation in some cases, and water structure at the mineral surface. Molecular modeling will support data from both spectroscopic techniques by providing information on water structure at the surface, the surface sites for metal-binding and the orientation of any associated ions, and the relative energetics of different surface complexes. We initially focused on investigating water structure and Sr^{2+} , Co^{2+} , and Pb^{2+} adsorption from NaCl, NaNO_3 , and NaClO_4 solutions onto quartz, amorphous silica, corundum, and gibbsite.

OHIO STATE UNIVERSITY

School of Earth Sciences

Columbus OH 43210

Grant: DE-FG02-02ER15327

Nanobiogeochemistry of Microbe/Mineral Interactions: A Force Microscopy and Bioinformatics Approach

Steven Lower, lower9@osu.edu

In this second phase of research, which is a collaboration between the Ohio State University (Dr. Steven Lower) and Virginia Tech (Dr. Michael Hochella, Jr.), we used force microscopy to measure inter- and intra-molecular forces between inorganic solids (e.g., silica and goethite) and two different Gram-negative microorganisms (*Escherichia coli* and *Shewanella oneidensis*). The measured forces were compared to theoretical models that describe van der Waals, electrostatic, and steric forces between a bacterium and mineral. Different force classes were found to dominate each of the two bacterium-goethite pairs. Overall, *S. oneidensis* exhibited a preferential affinity towards goethite relative to *E. coli*. We hypothesized that this preferential affinity was due to the production of outer membrane proteins by *S. oneidensis*. Therefore, we measured forces between a mineral and a bacterium that had been genetically modified to produce a fluorescently tagged protein. Simultaneous force microscopy and confocal laser scanning microscopy measurements suggested that outer membrane proteins can indeed form a bond between a Gram negative microorganism and an inorganic surface.

THE UNIVERSITY OF OKLAHOMA

School of Geology and Geophysics

100 East Boyd Street

Norman, OK 73019

Grant: DE-FG02-96ER14643

Development and Application of a Paleomagnetic/Geochemical Method for Constraining the Timing of Burial Diagenetic Events

R. Douglas Elmore, delmore@ou.edu

Field and laboratory studies have been conducted to test the hypothesis that remanent magnetization in sedimentary rocks can be used to constrain the timing of diagenetic events. Specifically, chemical remanent magnetizations (CRMs) resulting from the authigenesis of magnetic mineral phases were compared to the Apparent Polar Wander Paths for North America and Europe to constrain the timing of alteration processes. Diagenetic processes investigated include clay diagenesis (e.g. surface catalysis, illitization), kerogen maturation, and migration of basinal fluids. Results from Jurassic rocks on Skye, Scotland and preliminary data from Mesozoic rocks in the disturbed belt, Montana, are consistent with a hypothesized relationship between remagnetization and the smectite to illite conversion. We are testing the hypothesized connection by conducting K-Ar dating of illites as an alternative method for constraining the ages of magnetic mineral phases in our field areas in collaboration with Crawford Elliott (Georgia State). Simulation experiments conducted at low temperatures (62 and 98°C) resulted in the authigenesis of fine-grained magnetite on clay mineral surfaces, supporting our field observations. Results from the Mississippian age Deseret Limestone (Utah) suggest that kerogen maturation is an alternative pathway for magnetite authigenesis and acquisition of a CRM. We are currently testing this mechanism by investigating Madison Group carbonates in the Sawtooth Mountains, Montana. In all of these field studies, isotopic analyses indicate that the authigenesis of magnetic phases was probably not related to the migration of orogenic fluids. However, multiple CRMs occur in rocks along major fault zones in Scotland (e.g. Highland Boundary fault, Moine Thrust Zone, Great Glen Fault) that, based on petrographic, isotopic and fluid inclusion analyses, appear to be related to the migration of basinal-type fluids. The timing of these events, which range from the Devonian to the early Tertiary, has been established based on comparison of the pole positions to the Apparent Polar Wander Path.

OREGON STATE UNIVERSITY

College of Oceanic and Atmospheric Sciences
Oceanography Admin Bldg 104
Corvallis OR 97331

Grant: DE-FG02-02ER15318

Efficient Inversion of Multi-Frequency and Multi-Source Electromagnetic Data

Gary D. Egbert, 541-737-2941, egbert@coas.oregonstate.edu

This research project is focused on improving efficiency and practicality of three dimensional inversion of multi-frequency and multi-source electromagnetic (EM) data. The fundamental goal of the proposed work is to develop efficient but robust non-linear inversion schemes that take advantage of aspects of conjugate gradient (CG) approaches, as well as schemes that make use of at least some approximation to the Hessian of the penalty functional. The rationale for the proposed effort derives from the observation that for each search step in a straightforward application of CG, forward modeling is required for each frequency/source pair. These calculations provide multi-dimensional information about data sensitivity that can be used more effectively than in the standard CG approach, where they are used to define only a single additional search direction in the model space. To more readily explore a range of possible strategies, and to allow the algorithms developed to be applied to a wider range of EM geophysical field techniques, we are developing the inversion system in modules, using an object oriented computer programming paradigm. With this approach the inversion methodology can be developed independently of actual details of the specific EM problem, with only the forward modeling scheme and the action of the observation functionals on modeled EM fields changing between problems. We have completed development and testing of modules for two and three-dimensional EM modeling, data functionals for MT and active source applications, and sensitivity calculations. Initial inversion of magnetotelluric data (a multiple frequency problem) using a data space OCCAM approach are underway; more novel inversion schemes will be tested in the coming year, along with tests on cross-hole EM (a multiple source problem).

PENNSYLVANIA STATE UNIVERSITY

Department of Geosciences
University Park PA 16802

Grant: DE-FG02-01ER15209

Nanoscale Characterization of Corrosion at the Microorganism-Glass Interface

Susan L. Brantley, brantley@essc.psu.edu, 814-865-1619

Experiments to investigate the characteristics of microbial corrosion of silicate and apatite glass and crystal compared with abiotic dissolution have been carried out. The effects of polymerization on dissolution of aluminosilicate glass under abiotic conditions have also been investigated to lay the groundwork for understanding controls on dissolution. Corrosion of surfaces has been investigated in the presence of several microbes: a common soil bacterium (*Bacillus* sp.), a nitrogen-fixing bacterium (*Azotobacter vinelandii*), a dissimilatory iron-reducing bacterium (DIRB, *Shewanella putrefaciens/oneidensis*), a cyanobacterium (*Anabaena*), a methanogen (*Methanothermobacter thermoautotrophicus*), and an iron-oxidizing bacterium (*Thiobacillus ferrooxidans*). For example, we have utilized atomic force microscopy (AFM), X-Ray Photoelectron Spectroscopy (XPS), and Vertical Scanning Interferometry (VSI) to investigate iron-silicate glass surfaces after incubation with the siderophore desferrioxamine mesylate (DFAM) and after incubation with the soil bacterium *Bacillus* sp. We have also observed that *M. thermoautotrophicus*, as well as its cell-free supernatant, incubated with Ni-containing silicate glass increases the rate of nickel release to solution as compared to abiotic dissolution. The enhanced nickel release in the presence of *M. thermoautotrophicus* appears to be achieved by changes in solution pH. Extraction of Mo from a silicate mineral analogue is accelerated by a high-affinity ligand (a possible “molybdophore”) secreted by a nitrogen-fixing soil bacterium when Mo-limited. Experiments with *Anabaena*, a cyanobacterium, document that this organism, when grown with no P in the medium, produces excess extracellular polymeric material. The cells can extract soluble P released from the mineral apatite to extremely low concentrations. The mechanism of this solubilization may be related to lowered pH as well as the corrosive nature of the polymer. Anaerobic incubation of the Fe oxide mineral goethite with iron-reducing *Shewanella putrefaciens* results in isotopically light Fe(II) remaining in solution relative to the goethite. Fe(II) sorbed onto goethite is isotopically heavy relative to the mineral, demonstrating the importance of adsorption in fractionation processes. The iron-oxidizer *Thiobacillus ferrooxidans* was shown to influence copper isotopic fractionation during the dissolution of the copper-sulfide mineral chalcocite. Although many bioessential elements are found in low concentrations in rocks, soils, and seawater, microbially enhanced extraction of these trace elements remains poorly understood.

PENNSYLVANIA STATE UNIVERSITY
Department of Energy and Mineral Engineering
University Park, PA 16802

Grant: DE-FG02-00ER15111

Critical Chemical-Mechanical Couplings that Define Permeability Modifications in Pressure Rock Fractures

Derek Elsworth, elsworth@psu.edu

This work is examining and quantifying the processes controlling rapid changes in the transport characteristics of natural fractures due to precipitation and dissolution mediated by coupled thermal-mechanical-chemical (TMC) effects. Water flow-through experiments are monitored for changes in fluid and mineral mass efflux and concurrently imaged by X-ray CT. These three independent measurements enable changes in fracture porosity to be monitored with the progress of dissolution, and constrain mechanistic models representing permeability change.

Tests have been completed on three rock types; Berea sandstone, Arkansas Novaculite, and Bellefonte Limestone; these specific materials were selected to observe contrasting behaviors of porous media, fractures alone, and carbonate systems, respectively.

Rapid reductions in permeability have been observed, even in silicate rocks under modest temperatures (c. 80°C) and stress levels (c. 3.5 MPa), and occur over durations as short as a month. Permeabilities have reduced by up to two orders-of-magnitude, despite continuous net removal of mineral mass from the samples. Observations are consistent with the stress-mediated dissolution of contacting asperities within the fracture, resulting in closure between opposing fracture walls. At constant stress, successive increases in temperature result in successively smaller reductions in fracture aperture as the fracture approaches a residual closure characteristic of the equilibrium temperature. This incremented closure is driven by the Arrhenius-type dependence of dissolution coefficients on temperature.

This behavior is also observed in isothermal flow tests on fractures in carbonates. Permeability first decreases as asperities are dissolved, but then rapidly increases as dissolution localizes into a single dominant flow pathway. The development of preferential flow conduits is not restricted to carbonates and is surprisingly also apparent in very long-term flow tests on silicate rocks.

For the contrasting rock types, changes in aperture are surprisingly large and rapid, even for modest changes in ambient temperatures, flowrates, or aqueous chemistry. This suggests that benign changes in the thermal, stress, or chemical environment may exert profound changes in transport characteristics of fractures.

PRINCETON UNIVERSITY

Department of Geosciences

Princeton NJ 08544

Grant: DE-FG02-02ER15063

In-Situ Evaluation of Soil Organic Molecules: Functional Group Chemistry Aggregate Structure, and Metal and Mineral Surface Complexation Using Soft X-Ray Synchrotron Methods

Satish C.B. Myneni, smyneni@princeton.edu

Organic molecules (humic substances) derived from the decomposition of plant and other biological material are ubiquitous in soil and sediment systems, and play a central role in mediating a variety of biogeochemical reactions and cycling of elements. While their role in different environmental processes is well established, underlying molecular mechanisms are not understood. Using direct X-ray spectroscopy and spectromicroscopy and conventional laboratory methods, we are correlating the structural chemistry of humics and their role in various environmental processes.

In our functional group analysis of naturally occurring organic molecules, we found a significant fraction of organohalogens associated with humic substances and in the senescent and decaying plant material. In the last year we focused our investigation on identifying the biogeochemical processes involved in the formation of organohalogens in decaying plant material. Using the haloperoxidase enzymes common in soils we could convert Cl^- present in plant leaves to organochlorines, and these reactions depended on the enzyme concentration, temperature, and pH. We are exploring whether similar reactions occur in nature at rapid rates. Further we are trying to conduct detailed speciation of organohalogens associated with decaying plant material using electrospray ionization Fourier-transform ion cyclotron resonance mass spectrometry. Preliminary studies indicate that the aromatic organochlorines, which we identified using X-ray absorption spectroscopy, are present in the form of polychlorinated flavonoids. We are also finding significant concentrations of long chain aliphatic chlorinated compounds. A field station is built in Pine Barrens and in Princeton University campus (under construction) to evaluate the rates of formation and the stability of natural organohalogens in the environment.

Like organochlorines, we are also finding organobromines at high concentrations in soils, estuarine and marine sediments, and suspended particulate matter in ocean waters. The concentration of organobromines correlates directly with organic carbon in sediments. Although such a correlation was found earlier from bulk Br measurements, the speciation of Br was not conducted before. These data sets suggest that halogenation of organic molecules may play an important role in the preservation of carbon in soils and sediments.

PURDUE UNIVERSITY

Department of Physics
West Lafayette IN 47907

Grant: DE-FG02-97ER14785

Scaling of Seismic Wave Propagation Across Fractures Subjected to Time-Dependent Processes

Laura J. Pyrak-Nolte, 765-494-3027, Fax: 765-494-0706, ljpn@physics.purdue.edu

The objective of this research is to investigate the effects of time-varying length-scales on seismic wave propagation through fractured rock. The principal focus will be on experimentally linking the frequency-dependent seismic properties of fractures with their intrinsic hydraulic scale, with the ultimate goal of predicting hydraulic behavior based on seismic characterization and scaling this relationship from the laboratory scale towards the field scale.

We performed acoustic imaging experiments on single fractures in granite to determine the effect of mineral deposition on the seismic and hydraulic properties of single fractures. For mineral precipitation from the mixing of two fluids, the initial fracture void geometry controls the amount, the time-rate of mixing and the spatial distribution of mineral deposition within the fracture. If the fracture apertures are large, the precipitates flow out of the sample and leave little mineral deposition within the fracture. If the fracture has small apertures, the volume mixing of the two chemicals is reduced and the time-rate of mixing is long. Thus, the fracture void geometry determines mineral deposition when mineral precipitation is the result of the mixing of two fluids.

The most reliable seismic indicator that mineral deposition occurred within the fracture was a narrowing of the width of the distribution of the dominant frequency. The narrowing of the distribution indicates that mineral deposition in the fracture is homogenizing the fracture stiffness. Regions of the fracture that initially exhibited high attenuation of the acoustic signal showed the largest increase in transmission after mineral deposition. Because mineral deposition mainly occurs in the dominant flow paths (i.e. large apertures - low stiffness), those regions stiffen either by a reduction in aperture or an increase in contact because of the mineral deposition. The homogenization of the fracture stiffness correlated with an observed reduction in fluid flow through the fracture.

Future work includes measurements of local and global seismic parameters for fractured samples. The data will enable the determination of the link between the seismic response and fluid flow, as well as the scaling behavior of these properties.

RENSELAER POLYTECHNIC INSTITUTE

Department of Earth and Environmental Sciences
Troy, NY 12180

Grant: DE-FG02-94ER14432

Transport Properties of Fluid-Bearing Rocks

E. B. Watson, (518) 276-8838, fax (518) 276-2012, [watsoe@rpi.edu](mailto:watson@rpi.edu)

The research supported by this grant addresses "fluid-assisted" chemical transport in the Earth's crust and upper mantle through systematic experimental investigations at appropriate high temperatures and pressures (500-900°C; 1 GPa) and can be broadly categorized into three related efforts: (1) the effect on permeability when pores are surrounded by faceted crystal faces; (2) constraining the transport rates and morphology of carbon along grain boundaries; (3) measuring the 3-D geometry of individual pores by atomic force microscopy (AFM).

Many naturally occurring materials exhibit pores bounded by rational faces (facets) instead of the curved surfaces predicted in theoretical treatments and exhibited in rocks like quartzite. Recent analyses of materials exhibiting variable degrees of faceting, from moderately faceted quartzite to highly faceted amphibolite, show that permeability is significantly affected only when pore walls are highly faceted. Highly faceted pores remain disconnected at low fluid fractions, much like pores with high dihedral angles.

The transport and morphology of elemental carbon along grain boundaries may significantly affect electrical conductivity of Earth materials. All experiments indicate that diffusion of carbon along grain boundaries is sluggish; movement may be accelerated only when grains coarsen (e.g. through diffusion of silica). The results suggest that films may only exist provided that the carbon is produced as a film from another C-bearing phase, and that the grain boundaries are stable. Grain boundary migration causes isolation of discrete grains of carbon that are connected only at high volume fractions.

The 3-D pore geometry of individual pores can be measured through a new experimental technique in which fluids are introduced along synthetic grain boundaries produced by juxtaposing oriented and polished slabs of a mineral(s) in a piston-cylinder. After the experiment, grain boundaries are separated to expose half of each fluid-filled pore on complementary slabs. Two advantages of this technique are that the: (1) 3-D pore geometry can be directly measured using AFM, and (2) solid-solid interfacial energy can be controlled by varying the amount of crystal lattice mismatch (determined by electron backscatter diffraction) between juxtaposed crystals, and thus complementary dihedral angles can be measured as a function of lattice coincidence using AFM.

RENSSELAER POLYTECHNIC INSTITUTE

Department of Earth and Environmental Sciences
Troy, NY 12180

Grant: DE-FG02-02ER15286

Application of Geophysical Tomographic Imagery to the Development of Subsurface Flow and Transport Models

Jonathan Newell, newelj@rpi.edu

Objectives: This project seeks to refine the technology for forming and interpreting electrical resistance tomographic (ERT) images and electrical impedance tomographic (EIT) images of the subsurface zone. We seek to establish the extent of the advantage of using multiple current sources over a single source in such a multiple-electrode system. We also seek to assess the added information available in the reactive component of impedance above that available with only the resistance component.

Project Description: We have built four arrays of electrodes, each having eight electrodes arranged at intervals along a straight rod 15 mm in diameter. Each electrode extends 15 mm along the rod, and the spacing between electrodes is also 15 mm. Each electrode is connected to a current source and voltmeter, allowing patterns of current to be applied, and both real and quadrature voltages to be measured simultaneously on all electrodes. We then buried each electrode array in a bed of Ottawa F-35 sand at the four corners of a square. Saline was added to the sand in varying amounts, and then drained, to assess the ability to find saturation or unsaturated sand, and to detect a plume of fluid in an unsaturated bed.

Results: In saturated sand, the resistance at all electrodes was similar and low. A strong gradient of resistance was seen from the top to the bottom of the bed after it had drained for five days. When a plume of fluid was introduced at the middle of one side of the array, after the sand had drained, it produced a large resistance decrease at the nearby electrodes within two minutes. In all studies, the quadrature voltages were not proportional to the real voltages, so capacitive effects were observed which provided more information than resistance alone. Furthermore, the sand bed exhibited hysteresis, and did not behave in the same way when being saturated as when being drained. We have extended an interpretation originally proposed by Knight et al. who studied sandstone, to model these hysteresis data at the scale of pores among sand grains.

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

Alicia Wilson, awilson@sc.edu, (803) 777-1240

Objectives: Develop quantitative estimates of mass transport and fluid residence time in a resource-rich sedimentary basin where previous geochemical and hydrogeologic estimates of residence time have contrasted sharply.

Project Description: Mass transport in deep sedimentary basins strongly affects CO₂ sequestration, ore formation, petroleum migration, and geochemical reactions that affect petroleum reservoir quality, but mass transport in this type of setting is currently poorly understood. 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, whereas past hydrogeologic models have predicted that these brines could be flushed out less than 5 My. This project will 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.

UNIVERSITY OF SOUTHERN CALIFORNIA

Department of Aerospace and Mechanical Engineering
Los Angeles, CA 90089

Grant: DE-FG03-00ER15092

Three-Dimensional Miscible Porous Media Flows with Viscosity Contrast and Gravity Override

Anthony Maxworthy, maxworth@usc.edu

An experimental investigation of miscible displacements at constant volume flow-rate under the coupled effects of mobility contrast and gravity over-ride has been performed in a Hele-Shaw cell. The main variable was the Gravity number, G , a measure of the relative importance of gravitational to viscous forces. Properties such as interfacial length and injected area as functions of time and G were recorded. Viscous fingering was enhanced by the distortion generated by the effect of gravity. Independently of the Gravity number, and Peclet number (Pe) the area grew linearly in time. The calculated thickness of the injected fluid was found to be almost constant at a value of 0.5~0.58 with only a weak dependence on Peclet number (Pe). The displacement efficiency and breakthrough time decreased with increase of G , while the longitudinal finger growth rate increased with increasing G . To further simulate the effect of a porous medium tests have been performed in a single layer of regularly packed spheres between parallel plates. Porosity and hydraulic conductivity (permeability) of the porous medium were measured. Properties such as interfacial length and injected area as functions of time, Peclet number, mobility number (M) and Gravity number were recorded. The evolution of the interfacial length, transversely averaged finger length, the displacement efficiency, breakthrough time and the longitudinal finger growth rate had similar characteristics as those of the Hele Shaw cases. The fraction volume of the displacing fluid m (or FD , the ratio of the displacing fluid volume to the pore space) was again used as a diagnostic tool. In this case too the area grew linearly in time so that m was constant in any one experiment. However it was found that this fraction m was not almost constant as it was for the Hele Shaw cell but dependent on G , M and Pe , ranging in value from 0.15 to 0.78 depending on the parameter combinations considered.

STANFORD UNIVERSITY

Department of Civil and Environmental Engineering
Stanford CA 94305

Grant: DE-FG02-03ER15454

Three-Invariant Non-Coaxial Elastoplastic Constitutive Modeling and Its Implications on the Localization Properties of Rocks

Ronaldo I. Borja, (650)723-3664, borja@stanford.edu

We investigate strain localization phenomena in granular rocks using theory of plasticity and finite element simulations. Our goals are to accurately predict the onset of strain localization and continue the numerical simulation beyond the localization point. There are four main tasks identified in the project: formulation and implementation of a three-invariant elastoplastic constitutive model, introduction of non-coaxial plasticity into the constitutive framework, implementation of a well-known phenomenological friction law in the framework of the strong discontinuity model, and analysis of test data for different rocks. A three-invariant elastoplastic constitutive law is appropriate for rocks since these materials exhibit lower yield stress in tension than compression. Lately it also has come to light that the inclusion of the third invariant can enhance the onset of strain localization. Non-coaxial plasticity is often used to represent vertex-like structure in brittle rock masses, and so we also investigate its impact on the localization properties of rocks. Once a deformation band forms in an intact rock, its overall mechanical behavior is dominated by the softening plasticity occurring inside the band. We capture the mechanical properties inside the band using a state- and slip speed-dependent friction law.

A significant component of the research involves the development of a computational model, based on nonlinear finite element method, for capturing the mechanical response of rocks prior to and beyond the onset of localization. We investigate the effects of the third invariant and non-coaxial plasticity by casting these models in conventional nonlinear finite element framework. Further, we model the evolution of the ensuing deformation band, including its propagation through the material, using a non-conventional finite element technique based on embedded strong discontinuity. The latter technique allows an accurate representation of both small-scale (deformation inside the band) and large-scale (overall deformation of rocks) phenomena without severe mesh refinement. Finally, we use the developed multi-scale modeling approach to analyze a host of test data involving strain localization in granular rocks in axisymmetric and plane strain compression. Our analysis involves prediction of the initiation of deformation bands using classical bifurcation theory, and a geometric characterization of how they advance through the material.

STANFORD UNIVERSITY

Department of Geophysics
Stanford CA 94305

Grant: DE-FG02-03ER15382

Geochemical Controls on Nuclear Magnetic Resonance Measurements

Rosemary Knight, 650-736-1487, rknight@pangea.stanford.edu

Proton nuclear magnetic resonance (NMR) has the potential to provide a wealth of information about the physical, chemical, and biological properties of geological materials. The goal of our research is to advance the fundamental understanding of the link between the NMR response and the geochemical 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 the effects of the specific mineralogic form of the iron and the distribution of the iron on NMR relaxation mechanisms. In addition the current models of NMR relaxation times 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 conducting a three-year laboratory-based study of NMR relaxation time measurements in water-saturated porous materials where sample composition, pore structure and geochemical conditions are carefully controlled or determined. NMR samples are prepared by coating pure quartz sand with minerals containing both Fe(III) and Fe(II). The surface area and porosity of each sample is determined, and the distribution of the iron-bearing mineral examined using scanning electron microscopy. We measure the NMR time constants T1 and T2 of samples at chemical equilibrium and as the chemistry of the system changes due to changing redox conditions and ongoing biological activity. We are working initially with systems that can be described as spatially homogeneous and will then investigate the role of pore-scale variability in geochemical properties in determining NMR relaxation times.

Central to this research is the recent completion of a new Environmental Geophysics Laboratory in Earth Sciences at Stanford University and the acquisition of a Maran Ultra NMR core analyzer. The Maran allows us to acquire low frequency measurements of NMR relaxation times, and to modify the internal magnetic field. With these new laboratory facilities, we can undertake an extensive experimental and theoretical study of the fundamental geochemical controls on the NMR response of geological materials.

STANFORD UNIVERSITY

Department of Geophysics
Stanford CA 94305

Grant: DE-FG02-03ER15423

Porous Reservoir Rocks with Fluid: Seismic and Transport Properties

Amos Nur, (650) 723-9526, Amos.Nur@stanford.edu

The goals of our research are to model rock physical properties in general and properties of sediments with gas hydrates and high pore pressure specifically.

1. Modeling rock properties: We discovered that the relative permeability of the non-wetting phase increases with pore pressure gradient. This increase strongly depends on the details of pore geometry. The relative permeability also exhibits a non-linear dependence on pressure gradient, surface tension and wettability. Because numerical flow simulations for two-phase fluid flow are very time consuming even with modern parallel computing power we have implemented several new optimization schemes customized for the Lattice-Boltzmann algorithm. Implementing these schemes, we were able to achieve a X12 speedup of with 14 processors, while non-optimized code gave only a factor of 4. Parallel implementations allow us to perform both single-phase and two-phase flow simulations with much greater efficiency.
2. Gas hydrates: Effective elastic medium models were developed which place the hydrate in the sediment as a pore fluid component, a load bearing sediment frame component or as an elastic cement at grain contacts. The models were used to analyze data from hydrate bearing onshore sands in the NW Canada Eileen region and hydrate-bearing ocean bottom sediments from off shore of the Southeastern United states (ODP 995). The results show methane hydrate does not act as a grain contact cement at NW Eileen. In contrast for ODP 995 the modeling results show that methane hydrate acts as contact cement. The results also suggest that a large volume of methane gas may be trapped in the sediments beneath the gas hydrate-containing interval at site 995.
3. Over pressure prediction: We measured compressional and shear wave velocities and porosity of sediments at low pressures. We found the velocities to vary with the fourth root of the effective pressure and that water saturated wave velocities and V_p/V_s ratio show large porosity dependence. A power law fit was used to describe the normalized porosity reduction that is roughly proportional to the effective pressure to the two-thirds.

STANFORD UNIVERSITY

Department of Geophysics
Stanford CA 94305

Grant: DE-FG03-94ER14462

Structural Heterogeneities and Paleo Fluid Flow in an Analogue Sandstone Reservoir

David Pollard, dpollard@pangea.stanford.edu

We are developing conceptual and quantitative mechanical models for understanding the spatial distribution of permeability in sandstone aquifers and reservoirs as determined by structural heterogeneities. To accomplish these goals we are mapping compactive deformation bands, joints, sheared joints, and faults in the Aztec Sandstone at the Valley of Fire, Nevada as an analog for active reservoirs and aquifers. Our two complementary projects involve: (1) realistic representation in flow simulations of the structural elements within and between fault zones, with a special focus on capturing continuity and intersections between structures; and (2) understanding the impact of compaction bands on permeability and the geological conditions for their formation. Our results demonstrate how a complex suite of brittle structures can evolve to affect fluid flow in a typical sandstone aquifer/reservoir at a variety of length scales.

To characterize fault structure, linkage and fluid-flow effects we are developing a statistical methodology to represent the multi-scale fault and fracture patterns between seismic-scale faults. Our approach includes integration of fracture characterizations from field studies in the Valley of Fire into a geo-statistical code to generate training images to account for the geometry and spatial relationships between faults and fractures at different scales. We also are developing a detailed characterization of slip bands and of fault rock. Our main goal is to improve the geologic and hydraulic characterization of these structural components, and to assess their influence on fluid flow.

We completed work on the impacts of outcrop-scale compaction band on permeability and tested a new method for permeability estimation from thin section. This work provides independent confirmation of the porosity and permeability reductions that render compaction bands effective baffles to fluid flow. We used an air photo-based map of compaction bands over an area of 30 acres to demonstrate their effects at scales relevant to reservoir and aquifer production: optimal alignment of an injector-producer well array with the dominant compaction band orientation can increase production efficiency by more than a third. Research was completed on the observational and theoretical foundation for the interpretation of compaction bands as Eshelby inclusions that interact as anticracks.

STANFORD UNIVERSITY

Department of Geophysics
Stanford CA 94305

Grant: DE-FG02-99ER14933

Inversion of Multicomponent Seismic Data and Rock Physics Interpretation for Evaluating Lithology, Fracture and Fluid Distribution in Heterogeneous Anisotropic Reservoirs

Gary Mavko, gary@pangea.stanford.edu

Objectives: Conduct theoretical investigations into the effects of fluids and fractures on anisotropic elastic constants, and consequent constraints on lithology that may be obtained from seismic parameters.

Project Description: In this project, we are developing theoretical models to describe anisotropy in sediments and rocks. Seismic anisotropy, now widely recognized as a common feature of most subsurface formations, may lead to significant distortions in conventional seismic processing, such as errors in velocity analysis, mispositioning of reflectors, and misinterpretation of the amplitude variation with offset (AVO). Seismic anisotropy can arise from aligned fractures, stress-induced anisotropy, depositional textures, and intrinsic rock fabric anisotropy. Furthermore, geophysical characterization of fractured reservoirs via their elastic anisotropy is an extremely important economical problem. In tight formations often the only practical means to extract fluids is by exploiting the drainage provided by fractures. It is also important to understand the similarities and differences between fracture anisotropy and stress-induced anisotropy. Stress-induced anisotropy is especially important for less consolidated sediments.

Results from last year: A major portion of our activity this year was focused on studying intrinsic seismic anisotropy resulting from stratification of poured sediments using laboratory measurement of seismic V_p . We also studied the effects of hydrostatic and non-hydrostatic stress on directional dependence of V_p in sands. Velocity anisotropy was observed even under isotropic stress revealing the importance of intrinsic, fabric-related anisotropy in the sand samples. We developed a method to determine textural anisotropy using optical images of the sand and glass bead packs. In this method we use the numerically computed spatial autocorrelation function and its variation with direction to characterize the stratification texture from images of the samples. To determine if there is a relation between V_p and the textural anisotropy, we compare laboratory measured velocity anisotropy and the estimated spatial autocorrelation function. We find that velocity anisotropy can reveal internal packing of sand deposits.

TEMPLE UNIVERSITY

Department of Chemistry
Philadelphia PA 19122

Grant: DE-FG02-96ER14644

An Inter-Disciplinary Study of the Surface Reactivity of Pyrite

Daniel R. Strongin, 215-204-7119, Fax 215-204-1532, dstrongi@temple.edu

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. The program integrates observations at the macroscopic level with those at the microscopic scale. It is this integration that has proven to be very useful and productive. The objective of the research has been to understand important fundamental aspects of the surface chemistry of pyrite, such as charge development, reactivity, surface stoichiometry, surface structure, and interaction with dissolved constituents (sorption). Our ultimate goal is to provide insight into the role of pyrite as reactant, sorbent, and (photo)catalyst in environmentally and geologically relevant environments. This research has recently brought forth to the scientific forefront the importance of non-stoichiometric sites or defects in controlling the reactivity of pyrite. Many fundamental questions regarding the origin, presence, electronic structure, and reactivity of these defects remain unanswered and are being addressed in our studies. We believe that we need to answer these questions in order to provide the basic science needed for the development of the next generation of techniques in the abatement of acid mine drainage, one of the most important environmental problems we face (about 1 million dollars is spent per day on this problem). We argue that by understanding the reactivity of pyrite at the molecular scale strategies can be developed that target one or more of the elementary reactions in the oxidation of pyrite. While our research is primarily motivated by a desire to understand pyrite oxidation at the molecular level, our work is also of importance to several technical problems where the surface chemistry of pyrite plays a role, such as flotation of pyrite in the mining industry, acidification of hydrocarbon reservoirs (a problem relevant to terrestrial CO₂ sequestration), and sorbent of radionuclides and other constituents (e.g. gold).

UNIVERSITY OF TENNESSEE
Department of Geological Sciences
Knoxville, TN 37996

Grant: DE-FG02-01ER15159

Completion of Kr-81 and Kr-85 Analysis Development for Hydrogeology and Testing its Validity by Assessing Aquifer Recharge Rates

Norbert Thonnard, nthonnar@utk.edu

Objectives: (1) Implement improvements to Kr-81 and Kr-85 RIMS analyses for hydrogeology, (2) validate with standards of known Kr-85 activity, (3) measure Kr-85 in samples from a hydrogeologically simple aquifer, and (4) apply Kr-85 to measure recharge in the outcrop region of a major confined aquifer.

Project Description: The Kr-81 and Kr-85 noble gas radioisotopes, having isotopic abundance and concentration in modern water of $\sim E-12$ and $\sim E-22$ are challenging to measure, but should lead to a better understanding of processes in the environment. Applications of Kr-81 include dating of polar ice and very old ground water, impacting long-term climate and waste-disposal studies, while Kr-85 elucidates pollution transport, recharge, and overall flow of modern groundwater. The analytical process consists of (1) collecting a groundwater sample, (2) degassing it, (3) separating Kr from the recovered gases, (4) isotopic enrichment reducing interfering isotopes by E5, (5) a second isotopic enrichment of E4, and (6) detection of the rare krypton isotope in a resonance ionization time-of-flight mass spectrometer. When fully operational, this technique will permit Kr-81 or Kr-85 measurements from 10 or 2 liter water samples.

Results: During FY2002, work focused on steps 4, 5 and 6, and completed deferred maintenance and repairs on the laser system, vacuum pumps and mass spectrometers. The First Enrichment System (step 4) gas recirculation lines were reconfigured for a miniature turbomolecular pump and reduced dead volume. Together with a redesigned gas-tight ion source, sample size for Kr-85 analyses should decrease by $\sim 4X$. The Second Enrichment System's (step 5) quadrupole filter assembly was replaced, bringing performance back to specifications. A new set of poles were fabricated with dimensions calculated for operation at 450 C, which should reduce losses and memory effects from implantation into the poles. The main Nd:YAG pump laser and associated dye lasers were brought back to spec. Although the resonance ionization time-of-flight mass spectrometer sensitivity was sufficient for Kr-85 measurements, an extremely small leak (below any leak detector limit) allows atmospheric krypton to swamp the analyte signal. Repairs have been completed, but not yet tested.

TEXAS A&M UNIVERSITY

Texas Engineering Experiment Station
College Station TX

Grant: DE-FG02-00ER15033

Experimental and Analytical Studies to Model Reaction Kinetics and Mass Transport of Carbon Dioxide Sequestration in Depleted Carbonate Reservoirs

John W. Morse, (979) 845-9630; fax (979) 845-9631, morse@ocean.tamu.edu

Sequestration of carbon dioxide in depleted gas reservoirs appears to be a viable option, with a possible economic spin-off from the recovery of significant gas reserves. Little is known regarding the kinetics of calcite dissolution, diffusion of carbon dioxide in natural gas, and displacement of natural gas by carbon dioxide under conditions to be encountered in these reservoirs. This project is conducting research to better understand these phenomena through experimental determination of the reaction kinetics for calcite dissolution, coefficient of dispersion, and displacement mechanisms in respect to supercritical carbon dioxide at temperatures and pressures typically found in reservoirs. The requisite data will be used to develop a model for mass transport and reaction kinetics for the injection and storage of carbon dioxide in carbonate or carbonate-bearing depleted gas reservoirs. Calcite dissolution rates at 1 atm under high pCO₂ have been obtained in various synthetic brines containing geologically relevant concentrations of calcium and magnesium. Rates exhibit near first-order kinetics and are largely independent of brine concentration ($n = 1.4 \pm 0.2$, $k = 0.05 \pm 0.007$ moles/m²/hr). The interpreted fitting parameters were found to be highly sensitive to errors in calculated saturation state. Current models do not adequately predict the equilibrium calcium and carbonate ion activities under these conditions. Discrepancies between the predicted and observed values were strongly correlated with increasing calcium activity. An empirical correction factor to the carbonate ion activity coefficient was derived to correct for this error. A series of gas displacement experiments (20°C to 80°C and 500 psig to 3000 psig) yielded CO₂ dispersion coefficients from 0.01 to 0.3 cm²/min. Methane recovery at carbon dioxide breakthrough is 73 % to 87 % of initial volume. 3D simulation models of one eighth of a 5-spot pattern were constructed to evaluate injection of supercritical CO₂ under typical field conditions. Results indicate a large amount of CO₂ is sequestered: about 1.2 million tons in 29 years (40-acre pattern), and 4.8 million tons in 56 years (80-acre pattern). Also, a significant amount of natural gas is produced: about 1.3 BSCF or 74% OGIP (40-acre pattern), and 4.9 BSCF or 68% OGIP (80-acre pattern).

TEXAS A&M UNIVERSITY

Texas Engineering Experiment Station
College Station TX

Grant: DE-FG02-00ER15034

Time-Lapse Seismic Monitoring and Performance Assessment of CO₂ Sequestration in Hydrocarbon Reservoirs

Akhil Datta-Gupta, 979-847-9030, datta-gupta@tamu.edu

The goal of this project is to assess the feasibility of time-lapse seismic monitoring of CO₂ sequestration using coupled fluid flow and seismic modeling in fractured reservoirs. Concurrently we want to develop a formalism for the assimilation of static and dynamic data sources in the reservoir and quantification of uncertainty in performance predictions of CO₂ sequestration, particularly for fractured hydrocarbon reservoirs. We use a dual-porosity streamline model for fluid flow simulation in fractured reservoirs by treating the fracture and matrix as separate continua that are connected through a transfer function (Al-Hutheli and Datta-Gupta, 2004). We analytically compute the sensitivities that define the relationship between the reservoir properties and the fluid production response in fractured reservoirs. The sensitivities are an integral part of our approach and can be evaluated very efficiently as 1-D integrals along streamlines. Finally, production data integration into geologic models is carried out via a generalized travel time inversion (Cheng, He and Datta-Gupta, 2005). The generalized travel time inversion shows clear potential for resolving the general trends of fracture distributions in synthetic and field data. However, the resulting reservoir models are still missing potentially important parts of the fracture systems specified in the reference model, which motivates the use of seismic data to provide additional constraints. We have therefore explored the possible sensitivity of seismic data to fracture distributions and fluids contained in them. Recently developed theories for the effective properties of rock containing aligned or isotropic fracture systems provide a useful starting point for predicting variations in seismic reflection amplitudes associated with these reservoir properties (e.g., Pointer et al., 2000). These models also take into account the interaction of fluids in the porous host rock and in the fracture system, providing a natural complement to the dual porosity models used in the production data inversions.

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

Lynn E. Katz, 512-471-4244, lynnkatz@mail.utexas.edu.

Objectives: The objective of this research is 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 and vibrational sum frequency spectroscopies (XAS, VSGS), and molecular modeling to investigate the potential formation of ternary metal-anion complexes at mineral surfaces in different solution compositions over a range of surface coverages. XAS provides data on how the metal binds to the surface (monodentate, bidentate) and VSGS will provide data on the anions adsorbed with the metals, polyatomic anion orientation in some cases, and water structure at the mineral surface. Molecular modeling will support data from both spectroscopic techniques by providing information on water structure at the surface, the surface sites for metal-binding and the orientation of any associated ions, and the relative energetics of different surface complexes. We initially focused on investigating water structure and Sr^{2+} , Co^{2+} , and Pb^{2+} adsorption from NaCl , NaNO_3 , and NaClO_4 solutions onto quartz, amorphous silica, corundum, and gibbsite.

UNIVERSITY OF TEXAS
Bureau of Economic Geology
University Station Box X
Austin TX 78713

Grant: DE-FG02-03ER15430

Predicting Fracture Porosity Evolution in Sandstone

S.E. Laubach, 512-471-6303, steve.laubach@beg.utexas.edu

The goal of this research is to develop an understanding of how fracture growth and diagenetic alteration interact to systematically create and destroy fracture porosity. Our initial objective will be to study a key link between mechanical and chemical processes in opening fractures. Specifically, a new theory of quartz cementation postulates that the rate-limiting step for quartz cementation is precipitation, with supply and transport being of secondary importance. We are testing the hypotheses that this cementation process governs evolution of (1) fracture porosity and (2) fracture growth velocity (the subcritical crack index), which, in turn, controls many aspects of fracture pattern development. Despite the important influence of fracture systems on fluid flow, our understanding of the properties of these systems and how they evolve in sedimentary basins is exceedingly meager, owing in part to formidable challenges in collecting meaningful samples of fracture patterns. A practical benefit of our fundamental research is that it will lead to predictions of linked structural and diagenetic attributes, therefore potentially increasing the range of samples that provide meaningful fracture information. High temperatures and reactive fluids in sedimentary basins dictate that interplay and feedback between mechanical and geochemical processes could significantly influence evolving rock and fracture properties. We are studying mechanical and diagenetic feedback loops using new models of cementation, improved measurement methods of key mechanical properties, advanced fracture-mechanics-based fracture growth modeling, and high-resolution cement and microstructure quantification. This cross-disciplinary research will result in a fundamental advance in our understanding of how the diversity of natural fracture patterns evolves and better predictions of fracture pattern attributes in the subsurface where sparse sampling is the rule.

UNIVERSITY OF TEXAS AT DALLAS

Department of Geosciences
800 West Campbell Road
Richardson, TX 75080-3021

Grant: DE-FG02-01ER15166

3-D Sedimentological and Geophysical Studies of Clastic Reservoir Analogs: Facies Architecture, Reservoir Properties, and Flow Behavior within Delta Front Facies Elements of the Cretaceous Wall Creek Member, Frontier Formation, Wyoming

Janok Bhattacharya, janokb@utdallas.edu

The sandstones of the Frontier Formation in the Powder River basin have been variably interpreted as being deposited as offshore bars, storm deposited prodelta sand sheets, and wave-dominated deltas. Regionally, these sandstones show a mixture of different upward coarsening facies successions associated with distinctly different overlapping sandstone bodies separated by mudstones. These are interpreted as different delta lobes. Paralic and non-marine facies are absent, reflecting high degrees of top-truncation, likely caused by the generally low-accommodation and basin-distal setting.

Several scales of facies variability within these sandstones are relevant to subsurface production issues. Variability of different sand bodies with length scales of several kilometers to tens of kilometers represents large-scale reservoir compartments. These compartments show varying internal reservoir heterogeneity, depending on the proportion of river-, tide- and wave-influence within lobes.

The Wall Creek member of the Frontier Formation is the focus of an intense 3D reservoir characterization study at the Raptor Ridge locality. Here, two 2D and two 3D GPR surveys were acquired. 10 cores were drilled within the surveys, and analyzed for porosity and permeability (mini perm, routine plug, and pulse decay). The outcrops and GPR volumes show shallow, sub-tidal fluviially-derived channelized units alternating with mud-draped tidally-reworked bar deposits within an overall upward-coarsening unit that exhibits larger-scale, southward dipping clinoforms. This suggests both river and tide influence in a prograding delta lobe. The sandstone has been mapped as lobate-shaped and passes into more bioturbated and wave-dominated facies to the northeast. There is distinct along-strike facies variability, which relates to longshore drift orientation and the position and spacing of rivers.

Much of our focus has been on 3D characterization of calcite cements. These cements form as distinct and partly interconnected nodular layers that result in up to 15% volume reduction of net porous sandstone. Petrographic and geochemical data suggest that the nodules are long-lived with the major growth phase occurring between 400 to 800 m burial depths.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

Department of Geosciences
Blacksburg VA 24061

Contract: DE-FG02-00ER15112

Investigation of the Physical Basis for Biomineralization

Patricia Dove, dove@vt.edu, (540) 231-2444

Through the process of biomineralization, living organisms use macromolecules to direct nucleation and growth of a variety of inorganic materials. This research is aimed at understanding the physical mechanisms by which inorganic and organic additives modify the thermodynamics and kinetics of calcite nucleation and growth. Our methodology consists primarily of 1) *in situ* force microscopy investigations of growth on calcite surfaces under controlled conditions of temperature and supersaturation, 2) molecular modeling of stereochemical relationships between additives and crystal surfaces that lead to growth modification and 3) X-ray and ion-beam spectroscopy tools to determine both the location of adsorbed peptides and distributions of incorporated additives. Research has shown that the soluble fraction associated with mineralizing parts of organisms is distinguished by the near universal presence of peptide chains rich in acidic amino acids, especially poly-aspartic acid (Asp), we have looked at the effects of simple amino acids, some analogues, and Asp-rich polypeptides. Because Mg^{2+} and Sr^{2+} play primary roles in regulating biomineral formation, we have also investigated their effects on calcite growth.

Our results are providing significant advances in our quantitative understanding of controls on calcite growth kinetics, morphology and habit. Our present work includes: 1) complete our work on the polypeptides and extend the understanding obtained with these “simple” systems to real protein fractions found in certain marine organisms, and 2) launch a major effort to understand thermodynamic and kinetic controls on nucleation that allow organisms and other biomediated processes to deterministically produce mineral components with specific location, crystallographic orientation, and phase. Growth studies include AFM and molecular modeling of calcite modification by: (1) Asp-rich polypeptides, and (2) protein fractions extracted from abalone. Nucleation studies include: AFM, Raman, and ellipsometry investigations of $CaCO_3$ nucleation on nanoscale chemical templates. The results will be analyzed within the framework of classical nucleation and growth theories with the expectation that, as in the past, these theories will have to be modified to accommodate our findings. This work will lead to a comprehensive picture of physical controls on calcite growth and determine the relative importance of thermodynamic drivers and kinetic factors in inducing templated nucleation.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

Department of Geosciences
Blacksburg VA 24061

Contract: DE-FG02-02ER15326

Nanobiogeochemistry of Microbe/Mineral Interactions: A Force Microscopy and Bioinformatics Approach

Michael F. Hochella, Jr., (540) 231-6227, hochella@vt.edu

In this second phase of research, which is a collaboration between the Ohio State University (Dr. Steven Lower) and Virginia Tech (Dr. Michael Hochella, Jr.), we used force microscopy to measure inter- and intra-molecular forces between inorganic solids (e.g., silica and goethite) and two different Gram-negative microorganisms (*Escherichia coli* and *Shewanella oneidensis*). The measured forces were compared to theoretical models that describe van der Waals, electrostatic, and steric forces between a bacterium and mineral. Different force classes were found to dominate each of the two bacterium-goethite pairs. Overall, *S. oneidensis* exhibited a preferential affinity towards goethite relative to *E. coli*. We hypothesized that this preferential affinity was due to the production of outer membrane proteins by *S. oneidensis*. Therefore, we measured forces between a mineral and a bacterium that had been genetically modified to produce a fluorescently tagged protein. Simultaneous force microscopy and confocal laser scanning microscopy measurements suggested that outer membrane proteins can indeed form a bond between a Gram negative microorganism and an inorganic surface.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

Department of Geosciences
Blacksburg VA 24061

Contract: DE-FG02-03ER15389

Electron Density Distributions as a Guide for Understanding the Reactivity of Silicate Earth Materials

Donald J. Rimstidt, jdr02@vt.edu

Oxygen, silicon, and aluminum are the most abundant elements in the earth's crust. Of the bonds that oxygen forms, ~85% involve either Si or Al. The objective of this project is to understand the reactivity of a wide range of reagents with the SiOSi and SiOAl bonded interactions that comprise the building blocks of silicate minerals. We have undertaken ab initio periodic and molecular orbital calculations to generate electron density distributions for the reagents and silicate structures. The Laplacian of the electron density distribution provides a unique opportunity to establish an electron density model of reactivity. By evaluating the critical point properties of the electron density distribution a spatial mapping of sites of potential electrophilic and nucleophilic attack at the surfaces and in the bulk of important silicate minerals are identified, providing mechanistic insight into how Lewis acids mount electrophilic attacks and how Lewis bases mount nucleophilic attacks on specific SiOSi and SiOAl bonds. These results are tested using high-resolution rate measurements, an approach that has proven to be highly successful in organic and inorganic chemistry. Much of our current knowledge of the reactivity of SiOSi and SiOAl bonded interactions comes from studies of weathering reactions. Our research will build upon this knowledge with the goal of extending it to include the reactivity of Lewis acids (electrophilic reagents) like H_3O^+ , H_3O_2^+ and NH_4^+ and Lewis bases (nucleophilic reagents) like OH^- , F^- , AlO_4^- , H_3SiO_4^- , $\bullet\text{OH}^-$, and OCH_3^- with SiOSi and SiOAl bonded interactions. In addition, we are investigating the reactivity of substances that can act as both Lewis acids and bases simultaneously. Our results will explain why some of these reagents react vigorously while others do not react at all. This project not only aims to develop a general understanding of which reagents will react with bonded interactions in silicates but also to establish mechanisms for how the reactions proceed. With this information we will attempt to formulate a theory of chemical reactivity based on the properties of the electron density distributions of both molecular reagents and surfaces of silicate crystals.

UNIVERSITY OF WISCONSIN

Department of Geology and Geophysics
Madison WI 53706

Grant: DE-FG02-93ER14389

Resolving Complex Hydrothermal/Magmatic Events in Caldera Environments: MicroAnalysis of Oxygen Isotope Ratios

John W. Valley, (608) 263-5659, fax (608) 262-0693, valley@geology.wisc.edu

This study focuses on samples of altered volcanic rocks from several contrasting caldera complexes. New techniques allow analysis of oxygen isotope ratio in ultra-small samples; and we have contoured $\delta^{18}\text{O}$ across single crystals. Mineral zonation patterns provide new insights into processes of water/rock and magma/rock interaction.

At Yellowstone, zircons and quartz have been analyzed from 24 units erupted over the past 2 Ma. Zircon preserves the best record of primary magmatic oxygen isotope ratio. Extreme depletions of $\delta^{18}\text{O}$ occur after caldera forming eruptions. In contrast to earlier studies, analysis of zircons reveals periods of extreme disequilibrium in oxygen isotope fractionation that correlate to the periods of isotopic depletion. Diffusion modeling of $\delta^{18}\text{O}$ -zoned zircons provides time constraints ($500 \text{ y} < t < 5000 \text{ y}$) that support a new model of wholesale melting (Bindeman and Valley 2000, 2001). Ion probe dating (U-Pb) of zircons confirm our predictions (Bindeman et al. 2001). At Long Valley, analysis of zircons and quartz from rhyolites characterize the long-lived magma chamber. Values of oxygen isotope ratio are homogeneous in Bishop tuff magmas and suggest longevity ($>100,000 \text{ y}$) and convection of magmas, similar to other large volume rhyolite magma chambers (Bindeman and Valley 2002).

At Timber Mountain/ Oasis Valley caldera complex, analysis of $\delta^{18}\text{O}$ (zircon) suggests that $\delta^{18}\text{O}$ was lowered by melting of altered wall rocks, but unlike Yellowstone, the volumes of low $\delta^{18}\text{O}$ rhyolite are large (to 1000 km^3) and the depletions are less extreme.

Zircons from Trench 14, Yucca Mtn, were analyzed from fault gouge and found to be magmatic, originating from adjacent rhyolites, supporting the hypothesis that crosscutting carbonates at Yucca Mountain are pedogenic in origin (Bindeman and Valley 2003).

Tests of the Cameca 1270 multicollector ion microprobe show precision of $\delta^{18}\text{O}$ (quartz or zircon) of 0.1 to 0.5 ‰ for sample volumes that are 100 times smaller ($<1 \text{ ng}$) than by single collector ion probe and $10^6 - 10^9$ times smaller than possible by laser fluorination/ mass-spectrometry. The first Cameca 1280 ion probe has been ordered and will be delivered to the University of Wisconsin in December 2004. It will be dedicated to stable isotope chemistry. Drs. Noriko Kita and Bin Fu have been hired to work with this instrument, which will be used in future studies of isotopic zonation in minerals such as zircon, carbonates, and quartz.

UNIVERSITY OF WISCONSIN

Department of Civil and Environmental Engineering
Madison WI 53706

Grant: DE-FG02-03ER14995

A 3D Numerical Analysis of the Grounded Electric Source, Transient Electromagnetic Geophysical Method

David Alumbaugh, alumbaugh@engr.wisc.edu

This research is emphasizing the use of recently developed 3D time domain forward and inverse modeling algorithms to analyze the grounded-electric-source transient electromagnetic (GESTEM) method for subsurface imaging. This method offers a benefit over other surface EM methods in that it produces vertical currents in the subsurface which makes it more sensitive to resistors such as oil reservoirs and injected CO₂. To better understand the fundamental physics of the GESTEM method we started with a homogenous earth model, and plotted the current distribution versus time for both grounded electric and inductive loop sources. Decomposing and plotting the diffusing wavefield in terms of horizontal and vertical components indicates that the total-current maximum a) exists directly below the source at all times, b) is composed of currents that are entirely horizontal, and c) diffuses downward more slowly than that produced by a loop source. The fact that the maximum is near to the surface at all times causes ‘static shifts’ in GESTEM data which make simple interpretation difficult. However, while the maximum horizontal component is forced to exist near the surface, the maximum of the vertical component migrates downward at 45 degrees to the surface, thus allowing it to reach greater depths at earlier times than the horizontal components produced both by the grounded electric and inductive loop source.

We next complicated the model somewhat to include conductive and resistive layers in an otherwise homogenous $\frac{1}{2}$ space. The work has shown that measuring either the magnetic field or its time derivative will detect a conductive layer at depth, but is fairly insensitive to a resistive layer. The lack of resolution of resistive layers is due to the fact that a vertical current source within the earth does not produce magnetic fields at the surface. However, the horizontal electric field at the surface is sensitive to both resistors and conductors due to charge build up at the layer interface. Thus magnetic field measurements at the surface will only be sensitive to perturbations in the horizontal currents, while the electric fields will respond to both variations in both the horizontal and vertical currents.

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

Wenlu Zhu, wzhu@whoi.edu

A fundamental understanding of the effect of stress on permeability is of importance in many fault mechanics and reservoir engineering problems. Recent laboratory measurements demonstrate that in the cataclastic flow regime, the stress-induced anisotropic permeability reduction in porous rocks can be separated into 3 different stages. The onset of shear-enhanced compaction marks the transition from stage I to stage II. Before the shear-enhanced compaction, permeability and porosity reduction in stage I are solely controlled by the effective mean stress, with negligible permeability anisotropy. Stage II starts at the onset of shear-enhanced compaction, when a critical yield stress is attained. In stage II, the deviatoric stress exerts primary control over permeability and porosity evolution. The increase in deviatoric stress results in drastic permeability and porosity reduction and considerable permeability anisotropy. A transition from stage II to stage III takes place progressively during the development of pervasive cataclastic flow. In stage III permeability and porosity reduction becomes gradual again, and permeability anisotropy diminishes. Microstructural observation on deformed samples using laser confocal microscopy reveals that stress-induced microcracking and pore collapse are the primary forms of damage during cataclastic flow. Motivated by these observations, we formulate a cumulative damage model to characterize the effect of stress on permeability and its anisotropic behavior. In our model, the effects of effective mean stress and differential stress on permeability evolution are decoupled. By introducing stress sensitivity coefficients in our model, we propose a first-order description of the dependence of permeability evolution on different loading paths. This unified model provides a quantitative measure on stress induced permeability anisotropy, and thus helps us gain new insights into the coupling of stress and permeability.

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

Factors that regulate the generation and composition of natural gas during the thermal maturation of petroleum are poorly understood. The origin of natural gas is being investigated by conducting a series of laboratory heating experiments to constrain the stability of petroleum and its degradation products in the presence of water and minerals at elevated temperatures and pressures. Experiments reacting whole oils dissolved in water with Fe-bearing minerals and anhydrite have been conducted at 325-350°C. Experimental results indicate that the stability of oil and reaction pathways responsible for its degradation is strongly dependent on redox. In the presence of mineral oxidants, stepwise oxidation of C₂₊ hydrocarbons causes rapid decomposition to produce a CH₄- and CO₂-rich gas. Similar results are obtained regardless of whether the mineral oxidant is anhydrite or Fe-bearing sulfides and oxides. Aqueous sulfur species in intermediate oxidation states are catalytically active during oxidation reactions. Under reducing conditions, thermal cracking reactions dominate and decreased rates of oil degradation are observed. Except for the production of copious CO₂ and organic acids, the chemical and isotopic composition of gaseous products generated by stepwise oxidation are indistinguishable from those produced during thermal cracking. These results suggest that oxidative degradation may represent a previously unrecognized process responsible for the generation of dry natural gas. Additional experiments investigating specific reactions responsible for the decomposition of aqueous organic acids and anions have been conducted at 225 to 325°C. Results indicate that the relative rates of acetic acid oxidation and decarboxylation are strongly influenced by the presence of catalytically active Fe-bearing minerals. Decomposition of longer chain acids proceeds through deformylation to produce alkenes and formic acid that rapidly react with water to form alkanes and CO₂. Aqueous formic acid is highly reactive at temperatures typical of petroleum producing sedimentary basins and rapidly attains a state of thermodynamic equilibrium with CO and CO₂. The experimental results are consistent with concentrations of organic acids observed in basinal brines and can be used to constrain their roles during sediment alteration and the generation of natural gas.

WOODS HOLE OCEANOGRAPHIC INSTITUTION

Department of Marine Chemistry and Geochemistry

Woods Hole MA 02543

Grant: DE-FG02-86ER13466

Organic Geochemistry of Continental Margin and Deep Ocean Sediments

Jean Whelan, jwhelan@whoi.edu

The objective of this program is to develop a better understanding of processes of hydrocarbon generation and migration in coastal and offshore sedimentary basins as an aid in predicting favorable exploration areas for oil and gas. Current research focuses on utilization of organic compounds in elucidating mechanisms, rates, and consequences of subsurface fluid flow. These processes have a strong effect on the economics of oil production, particularly with respect to where, how much, and the quality of petroleum which can be produced in a particular area. Our particular long term interest has been to better understand the role of migrating gas in these reservoirs. Past research, in collaboration with scientists at Cornell, Louisiana State University and Texas A&M, has shown that the oil gas system throughout a 200 mile north to south transect across the northern Gulf of Mexico continental shelf and slope has been very dynamic with as much as 30 volumes of gas having passed through and altered oils to the north of the transect. Modeling together with our previous geochemical data shows the source, maturity, and the degree of alteration of these oils and also that the reservoirs have only recently been charged. Furthermore, the Cornell modeling results suggest that earlier oil which entered these reservoirs was probably very efficiently flushed upward and out into the overlying water column. The total volume of gas which has been involved in gas washing decreases in moving southward along our transect so that oils in the southern-most Green Canyon wells show little or no alteration attributable to gas washing. Work this year has been focused on the best way to utilize a new technique, GCxGC, as a powerful visual correlation tool, for showing changes in all the important diagnostic compounds and the processes affecting them in a single oil at one time. Results so far show the close relationship between reservoir and biodegraded seep oils in the Gulf of Mexico Green Canyon area. For the Gulf of Mexico transect oils, the new GCxGC results compare favorably with more labor intensive and less intuitively obvious ion extraction fragmentogram procedures used previously.

WRIGHT STATE UNIVERSITY

Department of Chemistry
Dayton OH 45435

Grant: DE-FG02-03ER15379

Multiscale Reactive Transport in Processes Related to CO₂ Sequestration: Nanoscale Dynamics, Upscaling and Non-steady State Kinetics

Steven R. Higgins, 937-775-2479, steven.higgins@wright.edu

This project has focused on experimental investigations on the nanoscale chemistry and dynamics of carbonate mineral surfaces exposed to aqueous solutions. The kinetics of dissolution and growth of magnesite (MgCO₃), calcite (CaCO₃) and dolomite CaMg(CO₃)₂ from elementary step edges have been studied with *in-situ* hydrothermal Atomic Force Microscopy (AFM), revealing atomic level information on the interaction of inorganic and organic ions with specific sites on reacting surfaces. The kinetics of step edge dissolution in magnesite and dolomite were highly non-linear versus solution pH and saturation state; key evidence for large differences between cation and anion dynamics at these mineral-water interfaces. The work provides key kinetic parameters necessary to extend dissolution and growth kinetic data to non-stoichiometric solutions – conditions that are more the rule than the exception in CO₂ sequestration scenarios involving deep aquifers as well in most natural waters. Mineral growth research of carbonates provided further insight into the mineralization process at the nanometer scale through Lateral Force Microscopy (LFM). LFM revealed qualitative differences in the structure and/or composition of surface grown layers on existing dolomite and calcite substrates. The differences are attributed to differences in interfacial free energies between the native substrate-water interface and the grown layer-water interface. The free energy associated with the interface between a carbonate surface and supersaturated aqueous solution is influenced by excess interfacial strain energy that was in turn influenced by solution composition. X-ray Photoelectron Spectroscopy (XPS) investigations led to the conclusion that carbonate mineralization from even moderately oversaturated solutions often leads to highly defective and compositionally heterogeneous solid phases. Subsequent kinetic studies of the dolomite-water interface led to additional conclusions related to low-temperature formation of dolomite. These studies demonstrated that near equilibrium, dolomite growth is both thermodynamically and kinetically favored, but that as solution concentrations rise, formation of more calcium rich solid phases become kinetically favored even in the presence of dolomite seed crystals. The presence of sedimentary dolomite may therefore be intimately linked to natural water saturation state at the time of mineralization.

UNIVERSITY OF WYOMING

Department of Geology and Geophysics
Laramie WY 82071

Grant: DE-FG02-03ER14623

Multiscale Reactive Transport in Processes Related to CO₂ Sequestration: Nanoscale Dynamics, Upscaling, and Non-Steady State Kinetics

Carrick M. Eggleston, 307-766-6769; Fax: 307-766-6679, carrick@uwyo.edu

Our work has several emphasis areas. The first area recognizes the potential chemical complexities of simultaneous growth and precipitation of carbonate minerals of different composition. The second emphasis area deals with the dissolution of refractory minerals that could provide cations for precipitation of carbonates in a sequestration context. We have followed earlier work on precipitation of Sr- and Co-carbonates from solutions of varying initial Sr/Ca or Co/Ca ratios as they flow over calcite surfaces with modeling work on combined advective, diffusive, and reaction mass transfer. In our case, diffusive transport must be accounted for in order to obtain meaningful kinetic rate constants for surface reactions independent of mass transport in a flowing system. Our modeling accounts for fluid velocity distribution and diffusive transport as fluids flow over the calcite surface. Results are fit to experimental fluxes until a rate constant is determined for each of several rate expressions. The morphology of etch pits changes in response to changes in cobalt concentration, providing hints as to the key reactive sites on the mineral surface. On a second front, we have investigated the effects of pH-jumps (from near-neutral to 1) on hematite dissolution in the hydrothermal atomic force microscope at 125°C. Dissolution does not appear to take place via step retreat, but through a much more complex set of processes. Studies are on-going to confirm the temperature dependence of hematite dissolution in order to constrain the amount of step motion that would be expected under these conditions. pH oscillation can produce dissolution rates that are 2 or 3 times higher than fixed pH conditions, which may be of use in accelerating important carbon sequestration reactions. In such slow-dissolution systems, however, “parasitic” redox processes can have a large impact. We have therefore done some reductive dissolution work with AFM in order to assess its effects. Surprisingly, we find that some terraces on an originally clean surface do not appear to succumb to severe reductive dissolution that corrodes up to 30 nm of the surface elsewhere. This phenomenon may have to do with locally variable semiconducting properties of hematite.

YALE UNIVERSITY

Department of Geology and Geophysics
New Haven CT 06520

Grant: DE-FG02-01ER15173

Plants, Weathering, and the Evolution of Atmospheric Carbon Dioxide and Oxygen

Robert A. Berner, 203-432-3183, Fax 203-432-3134, robert.berner@yale.edu

During the year October 2003 to September 2004 we focused on five topics

1. A paper was published (Berner, 2003) that relates the rates of global organic matter burial, calculated from carbon isotope modeling, to the abundance of oil source rocks over Phanerozoic time.
2. A computer model was constructed for calculating the concentrations of Ca, Mg and SO₄ in seawater over Phanerozoic time (Berner, 2004). Results agree well with independent determinations by others of concentrations of these elements based on measurements of fluid inclusions in salt crystals.
3. Burning experiments were completed to test the role of varying O₂ on the intensity and spread of fires. This work was done at the fire labs at Ohio State University by Richard Wildman from Yale. Wildman did thermogravimetric analysis on the ignition of various natural forest fuels (leaves, bark, grass, peat, etc) as a function of O₂ concentration. He also followed, via elevated thermocouples, the spread of fires along a long track consisting of either pine dowels or pine needles as a function of fuel moisture content (0-61%) and O₂ concentration (8% to 35%). Results, published as Wildman et al, 2004a), indicate that, at typical moisture levels, wood and pine needles will NOT burn at 30-35% O₂ which permits the possible existence of past O₂ levels this high.
4. Critical parameters were measured on the black shale that we are studying in terms of its weathering. This includes SEM photomicrographs of the organic matter texture, permeability and porosity measurements, BET surface area, and determinations of the concentrations of organic carbon and nitrogen, and sulfur and their changes with depth. Results, published as Wildman et al (2004b), indicate that the rate of O₂ uptake by weathering of organic matter is controlled by erosion and exposure to the atmosphere and not by variations in atmospheric O₂.
5. A major paper was published (Royer et al 2004) defending the role of atmospheric CO₂ as a major driver of Phanerozoic climate by way of the atmospheric greenhouse effect.

YALE UNIVERSITY

Department of Geology and Geophysics
New Haven CT 06520

Grant: DE-FG02-01ER15216

Integrated Studies of Coupled Flow, Reaction, and Diffusion in Earth's Crust

Danny Rye, danny.rye@yale.edu

Objectives:

To improve our understanding of crustal processes of fluid / rock interaction through an integration of modeling, field observations, and laboratory analysis; to develop new conceptual and computational models of coupled fluid flow and chemical reactions of geologic environments; to collect and interpret stable isotopic and geochemical field data at many spatial scales.

Project Description:

We combined field, modeling, and laboratory isotopic and chemical measurements to quantify flow, diffusion, and reaction in Earth's crust, with a focus on fractures and flow in low-permeability rocks. We will extend our fluid/rock interaction numerical models that calculate geochemical transport of multicomponent aqueous or mixed volatile fluids, kinetic control of mineral reactions, dynamic changes of heterogeneous porosity and permeability, and thermal evolution. We will couple this to our model of isotope and trace element diffusion in grains.

Results:

Modeling of kinetically controlled metamorphic reactions in siliceous carbonate rocks in two dimensions elucidates the role of kinetics in the flow and reaction pathways. Trace element modeling indicates significant kinetic effects even for high-temperature metamorphic to igneous sequences. Field-based kinetic studies reveal morphological variations in metamorphic garnets that indicate substantial deviations from chemical equilibrium during mineral nucleation and growth. A review of flow and reaction in the deep crust integrates fundamental concepts including flow laws, porosity, permeability, reaction kinetics, and mass transport mechanisms, with a synthesis of flow regimes from field examples. Field and modeling studies of metamorphosed carbonate rocks, Connecticut, show that crustal fluids mobilize a wide variety of elements, including the rare earths. In these rocks, lithologic contacts and fractures were primary flow conduits, consistent with field-modeling results for the subduction complex on Tinos, Greece. Oxygen and carbon isotopic data from shallow-crustal rocks of the Conasauga Group indicate that fluid flow was largely confined to fractures and stratigraphic boundaries in limestones, but was pervasive in shales, illustrating how the flow regime is critically dependent on rock type. Modeling of weathering and erosion of black shales examines the feedback between atmospheric oxygen levels and oxidation of organic matter and pyrite. *Ab initio* calculations examine oxygen and hydrogen isotope exchange between water and orthosilicic acid.

DOE/OBES Geosciences Research: Historical Budget Summary
(Thousands of dollars)

ON-SITE INSTITUTION	FY00	FY01	FY02	FY03	FY04
Argonne National Laboratory	438	552	530	445	480
Brookhaven National Laboratory	870				
Idaho National Laboratory					50
Los Alamos National Laboratory	1235	1235	1189	1353	1409
Lawrence Berkeley National Laboratory	2332	2367	2570	2045	2758
Lawrence Livermore National Laboratory	1736	1784	1644	1523	1598
Oak Ridge Institute for Science and Education	155	30			
Oak Ridge National Laboratory	1145	1293	1340	1190	1250
Pacific Northwest Laboratory	815	727	822	875	920
Sandia National Laboratory	1324	1367	1470	1355	1274
total, on-site published	10050	9624	9565	8786	9739
total, off-site published	10649	10393	10487	10513	10410
total, operating published	20699	20017	20052	19299	20149
total, equipment	1340	1402	1200	1023	
Total GEOSCIENCES-published	22039	21419	21252	20322	20149
OFF-SITE INSTITUTION					
American Chemical Society (Brandes)					5
Arizona, Univ. of (Roth)					25
Arizona, Univ. of (Harpalani)	10				
Arizona State Univ. (Shock)			225		239
Arizona State Univ. (Hervig/Williams)		102	105	108	133
Boston Univ. (Klein)	116	122	127	132	126

Caltech (Stolper)	135	150	150	156	162
Caltech (Wasserburg)	325	225		225	215
Calif., Univ. of Berkeley (Banfield)		178			150
Calif., Univ. of Berkeley (Helgeson)	190	179	182	164	163
Calif., Univ. of Berkeley (Nishiizumi)	144	144			
Calif., Univ. of Berkeley (Sposito)	74	74			
Calif., Univ. of Davis (Rock)		161	163	171	
Calif., Univ. of Davis (Navrotsky)	160	166	166	198	202
Calif., Univ. of Davis (Rustad)					97
Calif., Univ. of Davis (Casey)	108	72	178	109	113
Calif., Univ. of Davis (Rundle)				141	135
Calif., Univ. of Los Angeles (Harrison/McKeegan)	126	130	132	135	148
Calif., Univ. of Santa Barbara (Meiburg)	69		68	66	
Calif., Univ. of Santa Barbara (Boles)	70	79	71	78	86
Calif., Univ. of Santa Barbara (Spera)	82				
Calif., Univ. of Santa Cruz (Wu)	251	299	308	388	306
Calif., Univ. of San Diego (Weare)			125	125	125
Chicago, Univ. of (Sutton/Rivers)	475	500	525	550	575
Chicago, Univ. of (Sutton)		148	129		143
Chicago, Univ. of (Richter)		96		99	102
Clark Univ. (Kudrolli)			45	45	47
Colorado School of Mines (Klusman)	159		161		
Colorado School of Mines (Batzle)				140	117
Colorado School of Mines (Tsvankin)	216	230		239	249
Colorado, Univ. of (Rajaram)	54	54	106	70	72
Colorado, Univ. of (Rundle)	122	130	136		
Colorado, Univ. of (Spetzler)		185	153	143	155

Colorado, Univ. of (Ge)	101	94			
Colorado, Univ. of (Nagy)	128	62			
Connecticut, Univ. of (Torgersen)			27	35	33
Delaware, Univ. of (Wood)		141		138	142
Florida, Univ. of (Ladd)	63	83	111	89	
George Washington Univ. (Teng)			143		
George Washington Univ. (IPA Lesmes)					225
Georgia State Univ. (Elliott)			26	21	
Gordon Res. Conf. (Kronenberg, Jessell)			10		10
GSY-Inc. (Mackie)		46			
Harvard Univ. (Martin)				85	83
Hawaii, Univ. of (Martel)	117	108			
Idaho, Univ. of (Nicholl)		36	54		
Idaho, Univ. of (Wood)				10	10
Illinois, Univ. of (Kirkpatrick)	395		209	233	241
Illinois, Univ. of (Bethke)			117	214	92
Illinois, Univ. of Chicago (Sturchio)				59	60
Illinois, Univ. of Chicago (Nagy)			150		148
Indiana, Univ. of (Ortoleva)	112	117	120	124	
Indiana, Univ. of (Schimmelman)		78	84	119	112
Institute for Scientific Information (Zamojcin)			10		
Johns Hopkins Univ. (Garven)	77	78	75	89	80
Johns Hopkins Univ. (Veblen)	99	150	155	160	289
Johns Hopkins Univ. (Sverjensky)	100	90	140	140	137
Lehigh Univ. (Ilton)	104	115	115		
Louisiana State Univ. (White)		41		40	46
Louisiana State Univ. (Dutrow)				9	9

Maryland, Univ. of (Lower)			20	67	
Maryland, Univ. of (Tossell)	63	59	63	79	99
Mass. Inst. Tech. (Harvey)	35	37	38		
Mass. Inst. Tech. (Toksoz)	240	240	240		
Mass. Inst. Tech. (Toksoz)	144				
Mass. Inst. Tech. (Evans)	185	194	205	209	222
Mass. Inst. Tech. (Rothman)	135	133	152	158	160
Michigan Tech Univ. (Turpening)		165	11	114	
Mineralogical Society of America (Speer)		62	40	30	20
Minnesota, Univ. of (Yuen)	90	90	90		
Minnesota, Univ. of (Kohlstedt)					38
NAS/NRC (Schiffries/DeSouza)	90	90	90		90
NAS (Wessner)			114		
Nevada, Univ. of (EPSCOR - McCall)		8	9	6	
Nevada, Univ. of (Long)	96				
New England Res. (Brown)			204	199	206
New Mexico Inst. Min. Tech. (Wilson)	65	65	94	101	108
New Mexico, Univ. of (Ingber)	71	71	71		
NY, City Univ. of CC (Koplik)	89	90	95	98	102
NY, City Univ. of CC (Makse)				85	85
NY, State Univ. of Stony Brook (Schoonen)	60	60	102	65	66
NY, State Univ. of Stony Brook (Wong)	95	95		120	124
NY, State Univ. of Stony Brook (Lindquist)		67	64	64	
NY, State Univ. of Stony Brook (Hanson)	155				
North Texas, Univ. of (Bagus)					35
Northwestern Univ. (Rudnicki)	89	88	91	120	118
Notre Dame, Univ. of (Maurice)	70	70	121	174	178

Notre Dame, Univ. of (Maurice)					6
Ohio State Univ. (Lower)					71
Ohio State Univ. (Allen)					41
Oklahoma, Univ. of (Elmore)	127	124	102	103	
Oklahoma State Univ. (Nicholl)	36				
Oregon State Univ. (Haggerty)	76	68	75		
Oregon State Univ. (Egbert)			80	89	86
Penn State Univ. (Elsworth)	109		99	98	
Penn State Univ. (Brantley)	110	147	160	145	
Penn State Univ. (Brantley)					9
Princeton Univ. (Myneni)	102	102	102		
Purdue Univ. (Pyrak-Nolte)		85	102	105	109
Rensselaer Polytech. Inst. (Newell)			44	45	47
Rensselaer Polytech. Inst. (Watson)	161	198	199	199	247
San Diego State Univ. (Jiracek)			5		
Smithsonian Institution (Sorensen)	88				
South Carolina, Univ. of (Wilson)					50
Southern California, Univ. of (Maxworthy)	85		82	84	
Stanford Univ. (Mavko)	104	104	151	149	150
Stanford Univ. (Borja)				99	
Stanford Univ (Knight)				143	139
Stanford Univ. (Nur)	200	200	200	200	208
Stanford Univ. (Nur)	135				
Stanford Univ. (Pollard/Aydin)	179	260	257	267	261
Stanford Univ. (Segall)	97	100			
Temple Univ. (Strongin)	60	60	83	87	91
Tennessee, Univ. of (Thonnard)		122	129	146	

Texas A&M Univ. (Kronenberg)			65		
Texas A&M Univ. (Morse)	259		128	130	133
Texas A&M Univ. (Datta-Gupta)	304		111	130	138
Texas, Univ. of (Katz)					71
Texas, Univ. of (Laubach)				196	
Texas, Univ. of Dallas (McMechan/Bhattacharya)	124	262		95	96
Texas Tech Univ. (Graham)	90	90	90	9	
Utah, Univ. of (Forster)	25	50	50		
Utah, Univ. of (Tripp)	73	77			
Utah State Univ. (Evans)	85	85	85		
Virginia Tech (Rimstidt)				114	118
Virginia Tech (Dove)	202		121	126	
Virginia Tech (Hochella)	159	66	88		104
Virginia Tech (Bodnar)	108				
Washington, Univ. of (Unsworth/Booker)		95			
Washington Univ., St. Louis (Shock)		196			
Wisconsin, Univ. of (Alumbaugh)	50	52		101	96
Wisconsin, Univ. of (Alumbaugh)	10				
Wisconsin, Univ. of (Haimson)	115	107	110	106	
Wisconsin, Univ. of (Valley)	336		168		204
Wisconsin, Univ. of (Banfield)	103				
Woods Hole OI (Whelan)		180	197	206	204
Woods Hole OI (Zhu)	41	43	44	46	48
Woods Hole OI (Seewald)	120	120			179
Wright State Univ. (Higgins)				70	71
Wyoming, Univ. of (Eggleston)	95	85	85	52	45
Yale Univ. (Lasaga/Rye/Bolton/Ague)	222	300	326	327	

Yale Univ. (Berner)		109	110	110	130
Other	505	559	124		
OFF-SITE TOTALS	10649	10393	10487	10513	10410