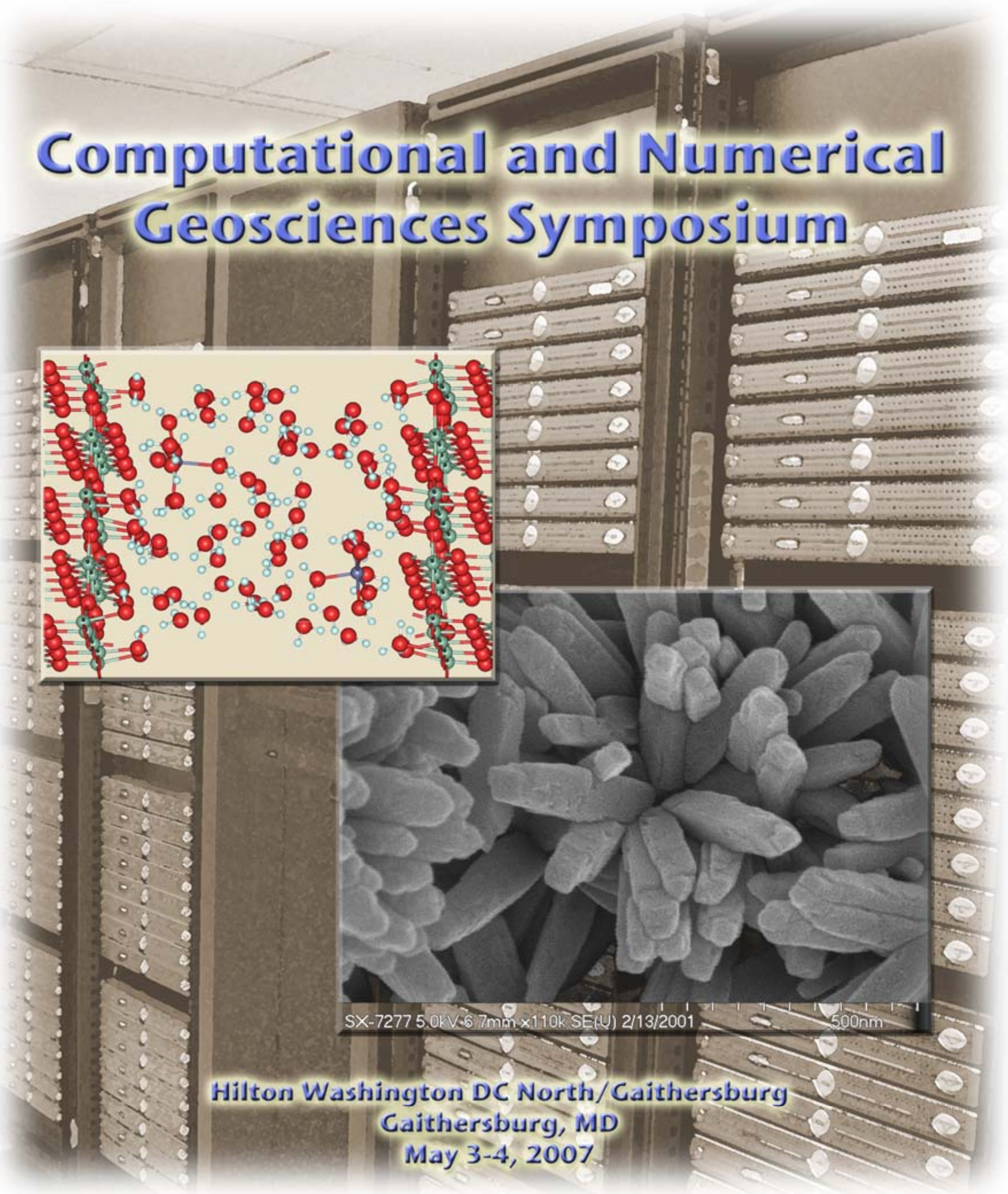
Computational and Numerical Geosciences Symposium



Hilton Washington DC North/Gaithersburg
Gaithersburg, MD
May 3-4, 2007

FORWARD

"Computational and Numerical Geosciences" is the thirteenth in a series of Geosciences Research Program Symposia dating from 1995. These symposia are topically focused meetings for principal investigators in the program and provide opportunities for our investigators to give presentations on their Office of Basic Energy Sciences' supported research. In addition to the recognition the symposium gives to all of the investigators, we traditionally also recognize one outstanding contribution from a DOE Laboratory Project and one from a University Project. The outstanding contributions are selected by our session chairpersons. We are fortunate to have as guest session co-chairs Prof. Ken Larner from the Colorado School of Mines, Prof. David Zachmann from Colorado State University, Prof. Mary Wheeler from the University of Texas, Austin, and Prof. Mark Reed from the University of Oregon. They join our Principal Investigator co-chairs Prof. J.W. Rudnicki from Northwestern University, Prof. William Klein from Boston University, Prof. John Tossell of the University of Maryland, and Prof. Tony Ladd from the University of Florida. For their efforts on behalf of the investigators I thank them all. We are looking forward to an outstanding series of presentations.

Nicholas B. Woodward
Geosciences Research Program
Office of Basic Energy Sciences
U.S. Department of Energy

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Cover illustration by Diana Swantek (LBNL): Geophysics cluster, LBNL; model of Zn(II) adsorption dynamics onto rutile (110) surfaces (Zhang et al., 2006); rutile powders with prominent (110) surfaces. Figures courtesy of E. Majer (LBNL), J. Kubicki (PSU), and D. Wesolowski (ORNL).

Computational and Numerical Geosciences

-Agenda-

Hilton Washington DC North/Gaithersburg

Gaithersburg, MD

May 3-4, 2007

Thursday, May 3 (AM)

7:30 **Registration/Continental Breakfast**

8:35 **Introductions and Greetings**
Nicholas Woodward, Department of Energy

Session 1

Chairs: Prof. Ken Larner (CSM) and Prof. J.W. Rudnicki (Northwestern)

8:45 Lianjie Huang, Los Alamos National Laboratory
Wave-equation migration for subsalt imaging, monitoring carbon sequestration, and ultrasound cancer imaging

9:10 Steven Pride, Lawrence Berkeley National Laboratory
Numerically modeling seismic attenuation in simulated porous rocks

9:35 Don Vasco, Lawrence Berkeley National Laboratory
Using time-lapse geophysical data to resolve permeability in the subsurface

10:00 John Rundle, University of California at Davis
Failure of rock masses from nucleation and growth of microscopic defects and disorder

10:25 **Coffee/refreshments**

10:45 Gary Egbert, Oregon State University
Efficient inversion of multi-frequency and multi-source electromagnetic induction data

11:10 Jeff Roberts, Lawrence Livermore National Laboratory
Permeability and electrical resistivity in partial melts: An integrated study combining laboratory measurements, X-ray computed tomography, and computational methods

11:35 Walt Polansky, Office of Advanced Scientific Computing Research, DOE
An introduction to the research portfolio of the Advanced Scientific Computing Research Program

12:05 **Working Lunch**

Thursday, May 3 (PM)

Session 2

Chairs: Prof. David Zachmann (Colorado State) and Prof. William Klein (BU)

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High performance computing and networking facilities in the Office of Science

1:10 Greg Newman, Lawrence Berkeley National Laboratory
New solution strategies for large scale 3D electromagnetic inversion problems

1:35 Barbara Romanowicz, University of California at Berkeley
Towards regional tomography in South-East Asia using the spectral element method

2:00 Ian Bourg, Lawrence Berkeley National Laboratory
Molecular dynamics simulation of kinetic isotope fractionation during the diffusion of small inorganic solutes (alkali metal cations, chloride, magnesium, noble gases) in liquid water

2:25 John Weare, University of California at San Diego
Progress towards parameter free quantitative molecular models of fundamental geochemical processes: Application to metal ion and actinide species in solution and at interfaces

2:50 **Coffee/refreshments**

3:10 Joel Koplik, City College of New York
Transport and deposition in self-affine fractures

3:35 Hernán Makse, City College of New York
Stress-dependent acoustic propagation and dissipation in granular materials

4:00 Ronaldo Borja, Stanford University
Brittle faulting and cataclastic flow in porous rocks

4:25 John Rudnicki, Northwestern University
Formation and extension of compaction bands in porous sandstone

4:50 **Adjourn**

6:00 **Dinner** (On your own)

Friday, May 4 (AM)

7:00 **Coffee/Continental Breakfast**

Session 3

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Lagrangian simulation of heavy-tailed nonlocal transport in lab- and field-scale tests: Is there such a thing as a local scale?

8:25 Anthony Ladd, University of Florida
Parallel computation of flow and transport in rough fractures

8:50 Grant Garven, Johns Hopkins University
Geochemical observations and geohydrologic modeling of reactive fluid flow in faulted, petroleum-bearing sedimentary rocks

9:15 Brent Lindquist, Stony Brook University
Network and mineral characterization of Viking Sandstones for reactive transport modeling

9:40 Russell Detwiler, Lawrence Livermore National Laboratory
Reactive transport and aperture alteration in variable aperture fractures and discrete fracture networks

10:05 **Coffee/refreshments**

10:25 Kevin Rosso, Pacific Northwest National Laboratory
Computational molecular simulation of charge transport underlying the reductive transformation of iron oxides

10:50 Carl Steefel, Lawrence Berkeley National Laboratory
Resolving the discrepancy between laboratory and field rates: The role of reactive transport modeling

11:15 Craig Bethke, University of Illinois
Reactive transport analysis of the origin of microbiological and geochemical zoning

11:40 Edward Bolton, Yale University
Computational models of kinetic processes in subsurface reactive flows

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Friday, May 4 (PM)

Session 4

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Structure and dynamics at the mineral/water interface: Linking computational and experimental approaches at the atomic and nanometric scales

1:55 Tjerk Straatsma, Pacific Northwest National Laboratory
Molecular basis for microbial adhesion and geochemical surface reactions

2:20 James Rustad, University of California at Davis
Carbonate defects in Al-Fe oxyhydroxide minerals: structure, vibrational spectroscopy, and isotopic fractionation

2:45 Andrey Kalinichev, University of Illinois
Molecular scale structure and dynamics of geologically important aqueous fluids and mineral-fluid interfaces

3:10 **Coffee/refreshments**

3:30 James Rustad, University of California at Davis
Site-specific, size-dependent reactivity of Al-oxide nanoparticle surfaces

3:55 Jeffery Greathouse, Sandia National Laboratories
Structural and vibrational properties of clay minerals from classical and ab initio molecular dynamics simulations

4:20 Louise Criscenti, Sandia National Laboratories
A molecular dynamics investigation of alkaline earth metal complexation to aqueous chloride and the gibbsite surface

4:45 Dimitri Sverjensky, Johns Hopkins University
Molecular surface geochemistry: Integration of spectroscopic and theoretical molecular evidence with a predictive surface complexation approach

5:10 John Tossell, University of Maryland
Calculating the stability, Raman and UV spectra and acidity of As sulfides in aqueous solution

5:35 **Adjourn**

6:30 **Refreshments**

7:00 **Working Dinner/Awards Presentation**

Wave-Equation Migration for Subsalt Imaging, Monitoring Carbon Sequestration, and Ultrasound Cancer Imaging

Lianjie Huang[1], Michael Fehler[1], Ru-Shan Wu[2], and Xiao-Bi Xie[2]

[1]*Los Alamos National Laboratory, Los Alamos, NM*
[2]*University of California at Santa Cruz, Santa Cruz, CA*

High-resolution and high-fidelity imaging is extremely important for many different applications, including subsalt imaging for oil/gas exploration, monitoring geological carbon sequestration, and ultrasound cancer imaging. Due to reflection/scattering, diffraction, and attenuation in complex media, seismic/ultrasound reflection data contain complicated wave phenomena. It is a great challenge to use reflection data to image structures beneath complex salt bodies, to detect and characterize regions with precipitation and dissolution due to geochemical interactions of rocks with CO_2, and to detect tiny cancers at their earliest stages. Reflection imaging/migration with solutions of the wave equation in heterogeneous media can more accurately account for complex wave phenomena than ray-based Kirchhoff migration imaging, leading to significantly improved image resolution and quality. With support from DOE Office of Basic Energy Sciences (BES), we have developed a suite of novel wave-equation migration methods based on solutions of the one-way wave-equation and downward continuation of wavefields in the frequency-space and frequency-wavenumber domains (dual domains).

We have quantitatively studied the effects of an acquisition system and the imaging (migration) process on migration imaging resolution, and demonstrated that wave-equation migration produces higher image resolution than Kirchhoff migration. For 3D subsalt imaging, we have successfully obtained high-quality images from an ultra-deep water Gulf of Mexico dataset.

Faults in the caprock and wellbores are the two primary potential CO_2 leakage paths for geological carbon sequestration. It is critical to characterize the integrity of the caprock to ensure safe carbon sequestration. We have investigated the capability of our advanced wave-equation migration method to detect faults in the caprock. We need to study the potential applications of wave-equation migration for detecting where CO_2 moves. To detect CO_2 saturation and fingering, and characterize precipitation and dissolution, we have to further improve imaging resolution and develop novel approaches for quantifying small changes in geophysical properties.

One out of seven women in the U.S. will develop breast cancer during their lifetime, and breast-cancer mortality has changed little since 1930's. The key to reducing cancer mortality is early detection. We investigate the capability of our advanced wave-equation migration methods for ultrasound breast-cancer imaging. Our preliminary results show that wave-equation migration has great potential to dramatically improve ultrasound image resolution for early breast-cancer detection and diagnosis.

Numerically Modeling Seismic Attenuation in Simulated Porous Rocks

Steve Pride

Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA

Over the seismic band of frequencies (10 Hz to 1 kHz), it is difficult to measure the intrinsic seismic attenuation of rock samples in the laboratory. In an effort to help understand the nature of seismic attenuation in the seismic frequency band, we numerically model seismic attenuation on simulated porous rock samples that contain mesoscopic-scale heterogeneity in the local elastic moduli (mesoscales are larger than grain sizes, but smaller than seismic wavelengths). The approach is to numerically apply stress to the surface of a simulated heterogeneous porous rock sample, and measure the strain rate of the sample. After taking a Fourier transform, the ratio of stress rate to strain rate defines the effective complex elastic moduli of the sample (the moduli are complex if there are loss mechanisms that allow stress rate to be out of phase with strain rate) from which the seismic attenuation, as measured by Q^{-1} , can be determined . The basic loss mechanism is that the applied stress creates a heterogeneous fluid pressure response that correlates with the mesoscale heterogeneity in the elastic moduli. The fluid pressure distribution so created attempts to equilibrate in each cycle of applied stress by fluid flow (i.e., fluid pressure diffusion). The viscous flow is responsible for intrinsic seismic attenuation. The local laws controlling such response are those of poroelasticity theory (i.e., Biot theory). We have developed a time-stepping finite-difference code that stably and accurately solves Biot's equations when there is heterogeneity in the porous material properties. We will report on the various discoveries we have made about the nature of Q^{-1} associated with this mechanism. For example, we have demonstrated, both numerically and analytically, that the level of Q^{-1} is proportional to the square of the fluctuations in the local elastic moduli; i.e., the stronger the fluctuations, the stronger the attenuation. We have also shown, both numerically and analytically, that in a self-affine material having a Hurst exponent H, the relation between seismic Q and frequency f is $Q(f) = a f^{H}$. Other results concerning the nature of the frequency dependence under various circumstances will also be presented.

Using Time-Lapse Geophysical Data to Resolve Permeability in the Subsurface

D.W. Vasco

Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA

Methods for geophysical model assessment, in particular the computation of model parameter resolution, indicate the value and the limitations of time-lapse data in estimating reservoir flow properties. A trajectory-based method for computing sensitivities provides an effective means to compute model parameter resolution. We examine the common situation in which water encroaches into a reservoir from below, as due to the upward movement of an oil-water contact. Using straight-forward techniques we find that, by including reflections off the top and bottom of a reservoir tens of meters thick, we can infer reservoir permeability based upon time-lapse data. We find that, for the case of water influx from below, using multiple time-lapse 'snapshots' does not necessarily improve the resolution of reservoir permeability. An application to time-lapse data from the Norne field in the Norwegian Sea illustrates that we can resolve the permeability near a producing well using reflections from three interfaces associated with the reservoir.

Failure of Rock Masses from Nucleation and Growth of Microscopic Defects and Disorder

John B. Rundle[1] and W. Klein[2]

[1]Departments of Physics, Geology and Engineering, University of California, Davis, CA
[2]Department of Physics, Boston University, Boston, MA

Storage of nuclear waste, oil recovery and earthquakes are examples of how the structure and failure of rock masses affect processes of interest to the DOE. Each of these processes involve the multi-scale physics of geological materials at shallow depths. Observations of rock masses over a range of spatial scales indicate that the failure modes of these systems, such as fracture, demonstrate scale invariant deformation, or power law behavior, characteristic of complex non-linear systems. These are observed in both laboratory settings in acoustic emission experiments, as well as in large scale field settings associated with tectonic faults (Gutenberg-Richter magnitude-frequency relation; Omori relation for aftershocks). One important reason for this behavior is that driven threshold systems of rock masses in which defects interact with long range interactions display near mean field dynamics and ergodic behavior. This result, which was first proposed on the basis of simulations and theory, was subsequently observed in field observations on the tectonic scale.

We are investigating the failure of rock masses resulting from the complex physics of microscopic dynamical processes in rocks, as manifested in the nucleation and growth of defects, microcracks, damage, and macroscopic fracture. These processes are a result of the complex emergent dynamics of self-organizing geological materials which we will analyze using the methods of statistical physics and large scale simulations employing both molecular dynamics and Monte Carlo methods.

Fully interacting fields of defects and damage are generally not included in most current models for material deformation. Instead, defect density and damage fields are assumed to be non-interacting or dilute, implying a strictly mean field approach. We have used statistical physics methods to understand the dynamics of interacting defect and damage fields, made possible by the construction and use of statistical field theories, to greatly improve our predictive capability for the macroscopic failure of materials.

In this talk I will summarize our current understanding of rock deformation as a response to stresses driving the evolution of damage and defects within the rock mass. The important quantities to compute are the nucleation rate, or its inverse, lifetime to failure. I will also discuss applications of this research to rock deformation across a range of spatial and temporal scales.

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

Gary D. Egbert

College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR

We present a new class of more efficient algorithms for regularized inversion of multi-frequency electromagnetic (EM) data. To generate one search direction conjugate gradient (CG) methods used for penalty functional minimization require two solutions per frequency of the governing differential equations. These calculations effectively generate data sensitivities for one linear data contrast for each frequency. By saving the results of these calculations a good approximation to the full Jacobian of the penalty functional can be built up in a comparatively small number of CG steps, allowing use of approximate Gauss-Newton (GN) methods. Using this idea we develop a new hybrid algorithm combining elements of the standard CG and "Occam" minimum structure inversions, which adjust the regularization parameter for step-length control. Rather than calculate the full Jacobian, the scheme uses the Lanczos bidiagonalization of the Jacobian, separately for each frequency, to generate (and save) a series of linear data contrasts, and the corresponding data sensitivities. The bidiagonalization procedure is truncated after a small number of steps, and the saved sensitivities, and corresponding linear combinations of data (for each frequency separately) are then used in a reduced data space Occam inversion. Tests on synthetic data for a two-dimensional magnetotelluric problem show the method provides essentially the same solutions as those obtained using a GN method requiring full calculation of the Jacobian, but at a fraction of the computational cost. The new approach is also 3-5 times more efficient than the standard CG approach. We will discuss implementation of this and other algorithms for 2D MT within the context of a modular EM inversion system we are using as a test-bed for algorithm development. Progress on generalization to the three-dimensional MT inverse problem will be discussed.

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

Jeffery J. Roberts

Lawrence Livermore National Laboratory, Livermore, CA

Permeability is an important transport property in a large number of systems and applies to a wide variety of problems. Often, in the absence of direct laboratory or field measurements, electrical resistivity is used to infer permeability. These physical properties are inter-related in a complex way that can depend on a variety of factors including microstructural properties such as porosity, pore size distribution, tortuosity, and interconnectivity. Furthermore, there exist classes of materials where traditional methods of measuring permeability are impractical or virtually impossible. For these materials alternative techniques to measure permeability are x-ray computed tomography and electrical resistivity measurements. Here we focus on the use and development of these techniques to assess phase distribution and interconnectivity and permeability of a previously unmeasured system.

The system we have chosen to study is silicate partial-melts, specifically, olivine and iron-sulfide. The interconnectivity of metallic melt in contact with silicates addresses a central question in planetary science: How do metallic cores of terrestrial planets and planetesimals form? There are a number of proposed core formation models that vary in mechanism and timing. An important issue is the interconnectedness and potential migration of iron-sulfide (FeS) melts in contact with silicates at high temperature and pressure. The permeability of these systems is a key property used to determine melt extractability, which, in turn, applies to the larger questions of the timing and mechanisms of terrestrial core formation.

We will report on our progress in three main areas: 1) synthesis and characterization of texturally equilibrated olivine-sulfide partial melts; 2) x-ray microtomographic determination of the 3D structure and interconnectedness of the melt phase including lattice-Boltzmann simulations of the permeability; and 3) electrical conductivity measurements at pressure and temperature while maintaining textural equilibrium.

An Introduction to the Research Portfolio of the Advanced Scientific Computing Research Program

Walter M. Polansky

Office of Advanced Scientific Computing Research, DOE, Germantown, MD

The status of and the plans for the research program supported by the Office of Advanced Scientific Computing Research will be discussed. An overview of the base programs in applied mathematics, computer science and networks as well as the SciDAC Centers and Institutes will be presented. Accomplishments will be reviewed and candidates for emerging areas of research interest will be identified.

High Performance Computing and Networking Facilities in the Office of Science

Daniel A. Hitchcock

Office of Advanced Scientific Computing Research, DOE, Germantown, MD

This talk will describe the current status and future plans of High Performance Computing Facilities supported by the Office of Advanced Scientific Computing Research, including NERSC and the two Leadership Computing Facilities at ORNL and ANL. In addition, the existing programs for managing access and resource allocation at NERSC and through the open INCITE process will be described. Finally, the current status and future plans of ESnet and their implication for distributed science will be described.

New Solution Strategies for Solving Large Scale 3D Electromagnetic Inversion Problems

Gregory A. Newman

Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA

Large-scale controlled source electromagnetic (CSEM) 3D geophysical imaging is now receiving considerable attention for mapping complex geological systems, with emphasis of mapping fluids associated with potential oil and gas and geothermal reservoirs and subsurface contamination. When combined with established seismic methods, direct imaging of reservoir fluids is possible. While modeling in 1D is relatively easy and trial and error 3D forward modeling straight forward the need for 3D imaging is necessary in highly complex and subtle 3D geological environments. Faster 2D CSEM imaging technology has some relevance to this problem, but because of its assumption of 2D geology it cannot be relied upon for a consistent treatment of the 3D imaging problem, especially when data are acquired specifically for a 3D imaging experiment. Because of the size of the 3D CSEM imaging problem strategies are required exploiting computational parallelism and optimal meshing. Here we report on an imaging experiment, utilizing 32,768 tasks/processors on the IBM Watson Research Blue Gene/L supercomputer. Over a 24 hour period we were able to image a large scale field data set that previously required over four months of processing time on distributed clusters based on Intel or AMD processors utilizing 1024 tasks on an Infiniband fabric. Results of the Blue Gene/L experiment showed that the broadside inline component data displays a systematic bias that could not be fit to a degree which is within the anticipated noise level of the measurements; other field components were satisfactorily fit. Modeling confirms that a likely explanation for this outcome is the need to incorporate conductivity that exhibits transverse anisotropy within the 3D model. The speed at which the Blue Gene/L platform delivered this result is consistent with timeframes required by practical exploration problems.

Towards Regional Tomography in South-East Asia Using the Spectral Element Method

Barbara Romanowicz[1], Aimin Cao[1], Mark Panning[2], Federica Marone[3], Yann Capdeville[4], and Paul Cupillard[4]

[1]Berkeley Seismological Laboratory, University of California, Berkeley, CA
[2]Princeton University
[3]Paul Scherrer Institute, Switzerland
[4]Institut de Physique du Globe, Paris, France

We are developing a progressively more sophisticated waveform tomographic approach to model three dimensional shear velocity structure in the upper mantle beneath south eastern Asia. First, we assembled a large dataset of long period (> 60 sec) three component fundamental mode and overtone teleseismic waveforms and obtained a preliminary radially anisotropic 3D model of the region using our well-established normal-mode based NACT approach (non-linear asymptotic coupling theory, Li and Romanowicz, 1995) and a starting global 3D model previously developed (Panning and Romanowicz, 2006). This approach is based on a combination of the path average (PAVA) approximation and the Born approximation, treated asymptotically, which provides 2D kernels in the vertical plane containing the source and the receiver. Next, we have been implementing the complete Born approximation (without asymptotics) for the across-branch mode coupling part of the problem, which is theoretically more accurate, but significantly more computationally intensive. We discuss comparisons of the results using these two methods. In parallel, we have been developing a regional spectral element (SEM) code in spherical geometry which includes PML (perfectly matched layers) on a non-conformal grid. Issues to resolve, in particular, have been the inclusion of ellipticity and anisotropy, and an accurate and convenient way to handle the 3D crust. The code is operational and has been tested. We will discuss preliminary results, as well as our experiments in applying SEM to global tomography, in this case using a version of SEM coupled with normal modes (Capdeville et al., 2003), which significantly speeds up computations.

References:

Capdeville, Y., A. To, and B. Romanowicz (2003) Coupling spectral elements and modes in a spherical earth: an extension to the "sandwich" case. *Geophys. J. Int.* **154**(1), 44-57.

Li, X.D., and B. Romanowicz (1995) Comparison of global waveform inversions with and without considering cross-branch modal coupling. *Geophys. J. Int.* **121**(3), 695-709.

Panning, M., and B. Romanowicz (2006) A three-dimensional radially anisotropic model of shear velocity in the whole mantle. *Geophys. J. Int.* **167**(1), 361-379.

Molecular Dynamics Simulation of Kinetic Isotope Fractionation During the Diffusion of Small Inorganic Solutes (Alkali Metal Cations, Chloride, Magnesium, Noble Cases) in Liquid Water

Ian C. Bourg and Garrison Sposito

Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA

Isotopic ratios of aqueous solutes are widely used as natural ‘signatures’ of chemical, biological or transport processes. Isotopic fractionation during one such process, solute diffusion in water, is particularly relevant to isotopic distributions in porous media yet is currently poorly understood. Richter et al. (2006) showed that lithium and chloride isotopes (but not magnesium isotopes) are fractionated during diffusion in water, and hypothesized that solute self-diffusion coefficients follow an inverse power-law relation to solute isotopic mass ($D \propto m^{-\beta}$). Molecular dynamics (MD) simulations have recently corroborated the β-values measured by Richter et al. (2006) and confirmed the existence of an inverse power-law relation between solute isotopic mass and self-diffusion coefficient (Bourg and Sposito, 2007). Additional MD simulation results are reported for the noble gas series He, Ne, Ar, Xe and the alkali metal cation series Li^+, Na^+, K^+, Cs^+. All noble gases and alkali metal cations behave according to the relation $D \propto m^{-\beta}$, with $0 < \beta < 0.5$. For noble gases, β-values decrease as solute radius increases, as expected from the hydrodynamic-theory prediction that $\beta = 0$ for Brownian particles. For alkali metal cations, β-values are lowest for hydrophilically-solvated Li^+ and hydrophobically-solvated Cs^+, highest for the more weakly-solvated K^+, suggesting that the mass-dependence of solute self-diffusion coefficients is more closely related to solvation shell stability than to solvation mechanism (hydrophilic or hydrophobic).

References:

Bourg I.C. and G. Sposito (2007) Molecular dynamics simulations of kinetic isotope fractionation during the diffusion of ionic species in liquid water. *Geochim. Cosmochim. Acta*, doi:10.1016/j.gca.2007.01.021 (in press).

Richter F.M., R.A. Mendybaev, J.N. Christensen, I.W. Hutcheon, R.W. Williams, N.C. Sturchio, and A.D. Beloso, Jr. (2006) Kinetic isotopic fractionation during diffusion of ionic species in water. *Geochim. Cosmochim. Acta* **70**, 277-289.

Progress Towards Parameter Free Quantitative Molecular Models of Fundamental Geochemical Processes:
Application to Metal Ion and Actinide Species in Solution and at Interfaces

John H. Weare[1], Eric J. Bylaska[2], and Marat Valiev[2]

[1]*Chemistry and Biochemistry Department, University of California, San Diego, CA*
[2]*Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA*

New reliable quantitative modeling strategies for geochemical systems at the fundamental atomic scale are required to analyze the environmental impacts of the energy and materials production processes of the future. While the observed behavior of environmental processes is on time scales of days to thousands of years, the process that are the origin of this behavior occur on atomic time and length scales of tenths of picoseconds (10^{-13} sec) and several angstroms (10^{-8}cm). Nevertheless, these processes retain the atomic specificity (chemistry) characteristic of their position in the periodic table. The chemical complexity of the materials (e.g., the presence of highly correlated and poorly screened f and d electrons in the actinide elements which are the chief components of nuclear waste), the extreme temperature, pressure, complex mixing and pH conditions that may be encountered and the need for unbiased reliable predictions requires the development of dynamical simulation tools based on interactions calculated directly from the electronic Schrödinger equation (e.g. 1st principles methods). The critical challenge of the methods development required for a more quantitative geochemical interpretation is both:

- To predict the complex time dependant chemistry of geochemical processes on the fundamental atomic scale while retaining the specificity of the elemental chemistry,
- And to provide reliable tools to translate these behaviors to the many orders of magnitude larger scales of geological problems without loss of their fundamental atomic character.

Currently the most efficient approximations to the solution of the electronic Schrödinger equation are based on the density functional approximation. While simulations using this approximation are efficient enough for dynamical simulation and the results adequate for reliable interpretations for many systems, there are limitations to the application to important technology problems (e.g., to the actinide and transition metal elements, treatment of long range forces, etc.). In addition present methods do not scale well with respect to processor number. Without significant development 1st principles simulations methods will not be able to exploit the large increases in performance of the next generation supercomputers with many more processors.

In this talk the new technologies that we are developing to address the problems with present methods will be discussed in terms of algorithm implementation, accuracy, etc., and applications. Focus will be on development in the following areas: large scalable solvers implemented in a quantum chemistry/molecular mechanic method for simulations of very large systems with application to the structure of highly charged ions in solution; the development of a plane wave implementation of exact exchange with application to the localization of vacancy states on solid surfaces; the development of spin-orbit methods for performing relativistic calculations of actinide solutions and surface complexes with application to UO_2^{2+} sorption and structure in aqueous solutions; the development of rare event methods for up-scaling the time frame of 1st principle simulations with application to reactions in solutions (see figure below).

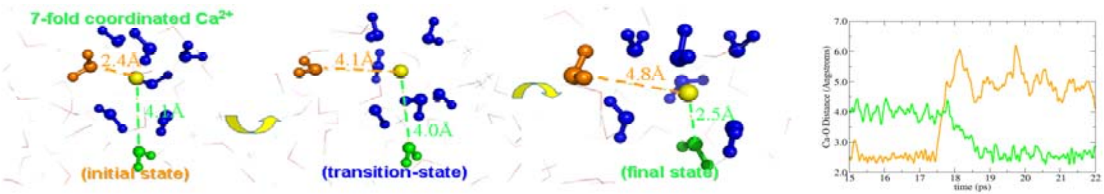

Figure: Water exchange in the hydration shell of Ca^{2+}+64H_2O first-principle simulations. Note that in the trajectories in the right panel the change in structure occurs in a few ps. Whereas the process occurs on a time scale of greater than 40 ps (i.e. an example of rare event dynamics).

Transport and Deposition in Self-affine Fractures

Joel Koplik

Levich Institute, City College of New York, New York, NY

We first review numerical computations and supporting experiments on permeability, anisotropy and dispersion in transport through geological self-affine fracture joints. We then discuss calculations in progress concerning the evolution of the fracture walls when suspended particulates deposit upon them. The calculations are largely based on the lattice Boltzmann method, supplemented by molecular dynamics simulations to determine the particle-wall interactions.

Stress-Dependent Acoustic Propagation and Dissipation in Granular Materials

Hernán Makse

Department of Physics, City College of New York, New York, NY

This project is motivated by a desire to understand acoustic propagation and dissipation in earth formations. Specifically, we study unconsolidated sediments, as those are the ones with the largest nonlinearity. The stress response and relaxation properties of granular materials confined by an external stress are enormously nonlinear and show slow relaxation dynamics in comparison with the microscopic motion of the constitutive particles. Many industrial applications depend crucially on the correct interpretation of nonlinear acoustics effects in granular materials, as exemplified by the large variation of the sound speeds or the elastic constants of the granular formation as a function of the external stress. However, a basic understanding of the physics of nonlinear granular elasticity is currently lacking.

The industrial motivation for this research derives from the fact that acoustics and nonlinear elastic methods are at the forefront of the evolving technology to help plan and optimize well location. In order to position a well correctly, the knowledge of the stress distribution around the borehole is essential. Acoustic measurements in granular materials provide the natural way to understand the distribution of stress around the borehole. The most important question is how to determine the stress from the field acoustic measurements, a method that will be the outcome of a study of elasticity of granular materials.

We study the nonlinear elastic and viscoelastic properties of cohesionless granular assemblies using computer simulations and experiments. Our experiments on the isotropic compression of a granular assembly of spheres show that the shear and bulk moduli vary with the confining pressure faster than the 1/3 power-law predicted by Hertz-Mindlin effective medium theories (EMT) of contact elasticity. Moreover, the ratio between the moduli is found to be larger than the prediction of the elastic theory by a constant value. The understanding of these discrepancies has been a longstanding question in the field of granular matter. Therefore we have performed a complete test of the applicability of elasticity theory to granular materials. We show that the elasticity theory partially describes the experimental and numerical results for a system under compressional loads. However, it drastically fails for systems under shear perturbations, particularly for unconsolidated packings with small tangential forces and friction. Our work indicates that a correct treatment should include not only the purely elastic response but also collective relaxation mechanisms related to structural disorder and non-affine motion of grains. Theories of pair-fluctuation analysis are being developed to go beyond the uniform strain approximations of the EMT.

Brittle Faulting and Cataclastic Flow in Porous Rocks

Ronaldo I. Borja

Department of Civil and Environmental Engineering, Stanford University, Stanford, CA

Under low temperature porous rocks can fail either by deformation band localization or by cataclastic flow. Deformation band localization, including compaction band, results from the coalescence of microcracks leading to a tabular zone of intense deformation, whereas cataclastic flow is characterized by grain crushing and pore collapse resulting in a severely damaged but macroscopically homogeneous compacted continuum. In this work we view the two types of instability as arising from two distinct bifurcation modes. The first mode, predicted from the singularity of the acoustic tensor, produces an indeterminate strain rate tensor with one nonzero eigenvalue and defines a deformation band. The second mode, when abruptly precipitated by pore collapse, may correspond to the singularity of the tangent constitutive operator and produces an indeterminate strain rate tensor with three nonzero eigenvalues (for 3D stress condition). After identifying the relevant bifurcation mode, we present a framework for capturing post-failure responses through constitutive branching. The post-collapse constitutive response features a cohesion softening-friction hardening applied either to an emerging fault for shear localization or to the bulk constitutive theory for pore collapse instability. The formulation is carried out under a general 3D state of stress and highlights an elastoplastic constitutive model for porous rocks that incorporates all three invariants of the stress tensor. In particular, we focus on the role of the intermediate principal stress on the triggering of deformation band localization that otherwise would not be captured with a two-invariant constitutive model. We highlight computational algorithms used for solving highly nonlinear systems of equations arising from this problem. For this presentation, we also highlight two computational finite element schemes, the first based on nonlinear contact mechanics and the second on the extended finite element method, for capturing the evolution of deformation band localization.

Formation and Extension of Compaction Bands in Porous Sandstones

John W. Rudnicki

Department of Civil and Environmental Engineering and Department of Mechanical Engineering, Northwestern University, Evanston, IL

Compaction bands are narrow, roughly planar zones of localized porosity loss. In the laboratory, the bands form perpendicular to the maximum compressive stress and are inferred to do so in the field. Although this mode of localization has been recognized only recently in porous rocks, it is common in a variety of other porous materials, e.g., cellular solids and metal foams. Both laboratory and field studies of the bands in sandstone have shown that their permeability is reduced by several orders of magnitude and that they form barriers to fluid flow across them. Consequently, their presence in subsurface formations would affect applications involving fluid injection or withdrawal, including sequestration of CO_2 to mitigate adverse effects on the climate.

This talk will briefly summarize laboratory and field observations of compaction bands and discuss theoretical results for their formation and extension. Theoretical results are roughly in accord with observations although detailed quantitative comparison is limited by the simplicity of the models and available data. More elaborate models and detailed numerical simulations are inhibited by a need for a better understanding of the evolution of inelastic behavior in these materials and its relation to microstructural deformation mechanisms. There are as yet few observations of the effects of coupling of fluid flow with deformation on the formation and extension of the bands although there is evidence that the bands observed in the field formed under saturated conditions.

Lagrangian Simulation of Heavy-Tailed Nonlocal Transport in Lab- and Field-Scale Tests: Is There Such a Thing as a Local Scale?

David Benson

Department of Geology and Geological Engineering, Colorado School of Mines, Golden, CO

It has long been hoped that predictions of the movement of dissolved pollutants through groundwater could, in theory, be made with any level of accuracy. The only impediment to a perfect, deterministic prediction was gathering enough data about the aquifer and the pollutant. For a conservative solute, the transport problem is reduced to identifying the hydraulic conductivity (*K*) and porosity at enough points. This view assumes that 1) either the aquifer as a whole or its statistical properties can be adequately described by "enough" points, and that 2) the physics of transport are well known on some smallest scale (say, the hand-specimen or lab column sample). The first assumption is often violated by the presence of either long-range dependence, nonstationary aquifer properties, or heavy-tailed data. The second assumption requires that the *local* advection-dispersion equation (ADE) is a valid model of the concentration at the small scale. Recent re-examinations of laboratory experiments indicate that this may not be valid even in relatively homogeneous material at very small scales. The core and lab-scale data indicate that the governing equation is non-local in space and/or time. This simple observation changes the way that solute transport must be simulated or predicted. A random *K* field, no matter how well characterized or finely discretized, cannot capture the nonlocality. Nor can a nonlocal model of ensemble transport (CTRW, fractional-order ADEs, etc.) be applied without local conditioning. We provide the link between the two approaches by defining a nonlocal transport model that allows conditioning of by measured data at any and all points. We also develop a novel fractal model of random fields that allows different scaling in different directions (Fig. 1) and completely user-defined correlation structures (including none) in any directions (Fig. 2). The two approaches may be combined to discern the interplay between nonlocality and discretization.

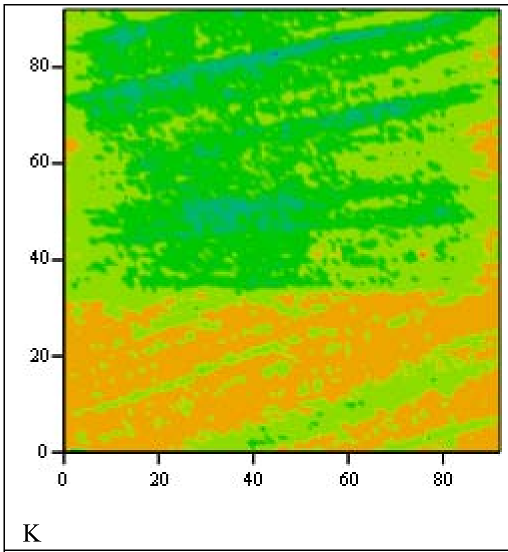

Figure 1. Massillon Sandstone *K*.

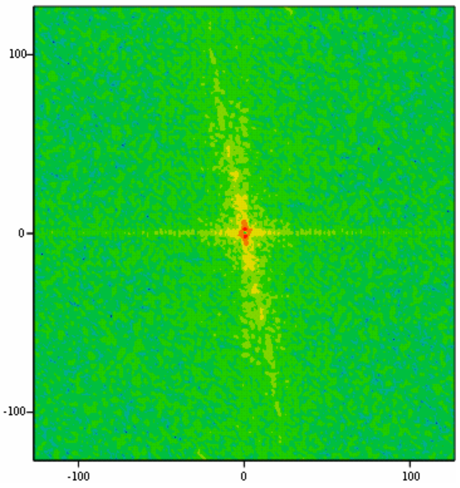

Figure 2. Spectrum of Massillon Sandstone.

Parallel Computation of Flow and Transport in Rough Fractures

A.J.C. Ladd

Chemical Engineering Department, University of Florida, Gainesville, FL

During dissolution in porous or fractured rock, a positive feedback between fluid transport and chemical reactions at the mineral surfaces may lead to the formation of pronounced, wormhole-like channels. As the dissolution proceeds the channels interact, competing for the available flow, and eventually the growth of the shorter ones ceases. Thus the number of channels decreases with time while the characteristic distance between them increases, which leads to a scale-invariant, power-law distribution of channel lengths. Eventually the leading channel penetrates to a space of much larger volume (breakthrough) and then all the flow is carried by this one channel.

A three-dimensional numerical model was constructed, in which the fluid velocity field was calculated with an implicit lattice-Boltzmann method, and the transport of dissolved species was modeled by an innovative random walk algorithm that incorporates the chemical kinetics at the solid surfaces. The model contains no free parameters or semi-empirical mass-transfer coefficients. The simulated morphological changes in a complex fracture were compared with laboratory experiments with the same initial topography (Szymczak and Ladd, 2004). A simple network model of the evolution of dissolving channels was developed and its properties studied. The results were compared with pore-scale simulations of fracture dissolution using the full three-dimensional numerical model. Despite its simplicity, the network model was found to retain the essential features of the nonlinear interaction between the channels (Szymczak and Ladd, 2006).

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

In this talk I will briefly summarize previous results and then explain the theoretical and computational aspects of the newer algorithms. I will also discuss our experiences in building a medium-size Beowulf cluster (192 nodes) and the performance that is possible with a careful selection of hardware and software. I will report benchmarks that illustrate the importance of a well-designed switch in obtaining good parallel scaling and show with a variety of applications that a highly optimized Gigabit network can match the performance of much more expensive interconnects for at least 100 processors.

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Chun, B., and A.J.C. Ladd (submitted 2006) An interpolated boundary condition for lattice-Boltzmann simulations of flows in narrow gaps. *Phys. Rev. E.*

Geochemical Observations and Geohydrologic Modeling of Reactive Fluid Flow in Faulted, Petroleum-Bearing Sedimentary Rocks

Grant Garven[1] and James R. Boles[2]

[1]*Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD*
[2]*Department of Earth Science, University of California, Santa Barbara, CA*

We are studying active faults and young petroleum fields in southern California, including the Refugio Fault in the Transverse Ranges, Ellwood Fault in the Santa Barbara Channel, and the Newport-Inglewood Fault in the Los Angeles Basin. Subsurface core samples, outcrop samples, well logs, reservoir properties, pore pressures, fluid compositions and published structural-seismic sections are being studied to characterize the geohydrologic/geochemical/geothermal history and degree of compartmentalization for these known fault networks in a transpressional tectonic setting. We are also investigating the geochemical signatures in carbonate that characterize rapid CO_2 degassing. These data provide constraints for geohydrologic models that are being developed to predict fluid pressures, flow patterns, rates and patterns of deformation, subsurface temperatures and geothermal heat flow, and geochemistry associated with large fault systems. For example, we simulated reactions associated with the transport of aqueous methane and complex mixing with meteoric groundwater in faulted, submarine reservoirs, which are partially uplifted along coastal Santa Barbara. In the model, oxidizing meteoric water enters steeply dipping aquifers outcropping in the Santa Ynez Mountains, displacing methane-bearing formational fluids and producing weak calcite mineralization along the mixing front. The greatest concentrations of calcite is precipitated in the upper levels of the Refugio-Carneros Fault due to the higher magnitude and duration of methane flux into the fault, because of its high permeability and intersection of multiple methane-rich strata. Furthermore, faults were shown to be important conduits for heat transport and likely petroleum transport. The high heat flow in the basin and rapid ascent velocities driven by buoyancy and/or overpressuring allow model temperatures in the Refugio-Carneros Fault to exceed fluid inclusion homogenization temperatures at depths within a few hundred meters of the ground surface, further contributing to calcite mineralization by locally increasing temperature. Applications of the discrete element deformation modeling are underway, and we are currently developing new reactive flow application for the Newport-Inglewood Fault system in the Los Angeles Basin, where an igneous body acts as a reservoir seal and local geothermal heat source for hydrothermal alteration of the reservoir rocks. If time permits in the presentation, additional applications of modeling reactive transport and hydrothermal mineralization in faults will be discussed for petroleum-bearing source rocks in northern Alaska, a tectonic setting characterized by extension and rifting along an ancient continental margin and platform. Fault-controlled fluid mixing in this extensional setting resulted in formation of the world's largest accumulation of metal sulfide ore.

Network and Mineral Characterization of Viking Sandstones for Reactive Transport Modeling

Catherine A. Peters[1], Marissa L. Maier[1], Michael A. Celia[1], Daesang Kim[2], and W. Brent Lindquist[2]

[1]*Civil and Environmental Engineering, Princeton University, Princeton, NJ*
[2]*Applied Mathematics and Statistics, Stony Brook University, Stony Brook, NY*

Reactive transport modeling for sedimentary materials relies on accurate estimates of the available surface areas of reactive minerals. Such estimates are frequently based on measurements of bulk mineral abundances which may or may not be representative of surface areas in pore fluids. To examine spatial patterns of reactive minerals in sandstone cores, we have employed: 1) backscatter electron (BSE) imaging and energy dispersive X-ray (EDX) analysis on thin sections and 2) X-ray computed tomography (XCT) on bulk samples. The sandstone cores are from the Viking Formation in the Alberta sedimentary basin, which has been a site for petroleum recovery, and is a potential aquifer for geological sequestration of carbon dioxide.

XCT is used to characterize the physical pore network. XCT, BSE and EDX are used to provide mineral identification. For XCT and BSE images, processing algorithms categorize minerals into three types, and statistically characterize the sizes, shapes and interfaces of mineral grains and pores. EDX is used to provide accurate determination of the mineral components in each category.

We present results of our analysis on the physical pore network and mineral distributions for 9 core samples. A typical pore in a Viking sandstone has surface area that is 1.6 to 1.9 times greater than that expected of a sphere of equivalent volume. In general 40-60% of the pores are “ball-shaped”, 30-40% are ellipsoidal-shaped, and 10-20% are crack-shaped. Kaolinite was found to cement quartz grains and line pore spaces, decreasing primary porosity and obscuring contact between pore fluids and reactive minerals. Minerals of mean atomic mass greater than quartz, which include those that are reactive under conditions that perturb fluid chemistry, occur as entire grains in sandstones and shaly sandstones. In conglomerate sandstones, these reactive minerals are typically found as inclusions, thus limiting their contact with pore fluids. Sandstone and shaly sandstone have ~5% reactive minerals, and conglomerate sandstone has ~1% reactive minerals. Mineral abundance overestimates surface area of reactive minerals by as much as a factor of five. The results are being used to support pore-scale network modeling of reactive transport in sedimentary rocks.

Reactive Transport and Aperture Alteration in Variable Aperture Fractures and Discrete Fracture Networks

R.L. Detwiler[1] and S.M. Ezzedine[1], and H. Rajaram[2]

[1]Lawrence Livermore National Laboratory, Livermore, CA
[2]Department of Civil, Environmental, and Architectural Engineering, University of Colorado, Boulder, CO

Water-rock interactions within variable aperture fractures can lead to dissolution of fracture surfaces and local alteration of fracture apertures, transforming the transport properties of fractures over time. Because fractures often provide dominant pathways for subsurface flow and transport, developing models that effectively quantify the role of dissolution on changing transport properties over a range of scales is critical to understanding potential impacts of natural and anthropogenic processes. Dissolution of fracture surfaces is controlled by surface reaction kinetics and transport of reactants and products to and from the fracture surfaces. We have developed a parallelized computational model of reactive fluid flow through discrete fracture networks consisting of interconnected variable aperture fractures. The model uses depth-averaged formulations of the flow and transport equations, and incorporates an effective mass transfer relationship that represents a smooth transition from reaction-limited dissolution to transport-limited dissolution. This computationally efficient model allows explicit representation of sub-millimeter-scale aperture variability in systems consisting of dozens of fractures over tens of meters. Direct comparison to systematic dissolution experiments demonstrates that this model effectively simulates the experimentally observed behavior over a range of the dimensionless Peclet and Damkohler numbers (Pe=advective/diffusive transport and Da=surface reaction rate/advective transport).

We designed a systematic series of simulations in single fractures and simple fracture networks to explore the influence of reaction-induced fracture alteration over a range of Pe, Da and spatial scales. The location within Pe-Da parameter space significantly influences the fracture alteration process, with results ranging from relatively uniform dissolution over the entire fracture (low Da, high Pe) to the formation of distinct dissolution fingers (high Da, low Pe). In fracture networks, individual fractures reside in different regions of the Pe-Da parameter space leading to varied behavior throughout the network. Furthermore, preferential flow paths induced by dissolution can lead to pressure gradients along fracture intersections, which lead to enhanced flow and dissolution along intersections. These results all demonstrate that local rock-water interactions can significantly influence the transport properties of individual fractures and networks of fractures over a range of scales. This highlights the importance of developing new approaches for effectively representing these processes in continuum models of reactive fluid flow through fractured rock, and provides an efficient tool for quantitatively evaluating new continuum approaches.

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Computational Molecular Simulation of Charge Transport Underlying the Reductive Transformation of Iron Oxides

K.M. Rosso[1], S. Kerisit[1], S.V.Yanina[1], and P. Meakin[2]

[1]*Pacific Northwest National Laboratory, Richland, WA*
[2]*Idaho National Laboratory, Idaho Falls, ID*

Reductive transformation of Fe(III)-oxides such as α-Fe_2O_3 (hematite) by aqueous dissolution/re-precipitation is a central part of the natural biogeochemical iron cycle in the environment. The transformation involves conversion of surface Fe(III) to Fe(II) by electron transfer from adsorbed reductant molecules followed by Fe(II) solubilization and precipitation of new phases. The process can enter an autocatalytic stage when released Fe(II) re-encounters and reduces the hematite surface. Some Fe(III)-oxides such as hematite are semiconductors with a propensity for fast charge redistribution and limited electron diffusion by solid-state electron transport. Microscopic evidence suggests that sites of Fe(II) release are coupled to a process of mobile charge segregation through the surface to specific crystallographic regions. Specifically, atomic force microscopy shows that the acidic reductive dissolution of hematite single crystals proceeds by etching on all surfaces except (001) which undergoes homoepitaxial growth of additional hematite islands. This (001) growth process only occurs when other facets such as (012) or (113) on the same single crystal are simultaneously exposed to solution, suggesting a coupled solution and solid-state circuit for the flux of ions and electron equivalents, respectively.

Because the growth of hematite islands on (001) requires the conversion of adsorbed Fe(II) into Fe(III) hematite 'building blocks', interfacial electron transfer and solid-state charge transport appear to be relevant. At room temperature charge carrier mobility depends on the formation and diffusion of small polarons occurring by Fe(II/III) valence interchange and the presence of traps and defects. We developed a theory approach that combines molecular dynamics (MD) simulations based on an empirical potential model and *ab initio* calculations to calculate rates of small polaron hopping in the hematite bulk and at (001) and (012) surfaces in vacuum and in equilibrium with an overlying bulk water phase. An umbrella sampling method is used to compute the free energy surfaces. *Ab initio* electronic coupling calculations demonstrate the importance of superexchange via bridging oxygen atoms. The MD/*ab initio* calculation results were used to parameterize a kinetic Monte Carlo (KMC) model, from which we determined the self-diffusion coefficient for small polarons in hematite as a function of their concentration, interaction with a variety of fixed attractive and repulsive lattice defects, and crystallographic direction. The temperature dependence and anisotropic behavior of the electrical conductivity as predicted by our model are in good agreement with experimental data on hematite single crystals. Interaction potentials between charge carriers and fixed defects determined from MD simulations show little deviation from the Coulombic interaction energy. Integration of these potentials in the KMC simulations allowed us to determine small polaron diffusion coefficients and the density and residence time of small polarons around defect sites as a function of their type and concentration.

The model supports the experimentally evident transformation mechanism for the reductive dissolution of hematite involving surface-specific Fe(II/III) valence cycling via oxidative Fe(II) adsorption and solid-state electron migration. We propose that island growth of hematite (001) occurs by preferential re-adsorption of solution phase Fe(II) onto the surface, where it re-oxidizes and is incorporated back into the hematite structure. The emerging picture for hematite transformation has important implications for our understanding of the natural iron cycle in the environment.

Resolving the Discrepancy between Laboratory and Field Rates: The Role of Reactive Transport Modeling

Carl I. Steefel

Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA

One of the key uncertainties in evaluating field-scale reaction rates involves the determination of the physically and hydrologically accessible reactive surface area (Maher et al., 2006). The lack of available reactive surface area is one of the possible explanations for the oft-cited discrepancy between laboratory and field rates, but its value in low permeability crystalline rocks is typically poorly known. It is clear that the value of the reactive surface area depends on the texture of the porous material, and specifically the geometry of the pores through which flow or diffusion of reactive solutes take place. Fortunately, modern X-ray microtomographic techniques now make it possible to resolve quantitatively the detailed pore structure of the reactive material down to the scale of about a micron. These data can then be used directly in non-reactive and reactive transport simulations to quantify both the transport properties and the geometric reactive surface area of the porous medium.

For the purpose of understanding the rates of weathering rind advance in basaltic clasts from Costa Rica (Sak et al., 2004), we have undertaken X-ray microtomographic imaging of the reaction interface separating weathered from fresh rock. The microtomography carried out on Berkeley Laboratory Advanced Light Source Beamline 8.3.2 indicates that weathering results in the formation of sinuous dissolution channels or "micro-wormholes" that enhance both the porosity and its connectivity. This has been confirmed by analyzing the data with the code Percolate, which employs a "burning algorithm" to map pore connectivity in three dimensional samples. The data indicate that there is almost no pore connectivity in the porosity range of 3% to about 16% bulk porosity, while between about 16-18% porosity, a dramatic increase in pore connectivity occurs. 3D non-reactive diffusion simulations were carried out using the pore geometry determined with the X-ray microtomography—pixels that correspond to pores (fluid only) were given a tortuosity of 1, while pixels that correspond to matrix were given a tortuosity determined from tracer experiments in unweathered basalt. The simulations were then compared with diffusion experiments on the same sample using a bromide tracer imaged with μ-XRF at the Advanced Light Source. The good agreement between the position of the bromide front and the tracer front computed using the microtomographic data suggests that the latter may be useful in estimating effective diffusion coefficients where the pores are sufficiently large that they can be resolved with current X-ray synchrotron techniques. The same approach is used with 3D reactive transport simulations to determine an effective or "upscaled" reactive surface area that incorporates the detailed geometry of the pore structure created as a result of weathering. These upscaled geometric reactive surface areas are then used in 1D simulations of the weathering rind advance.

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Reactive Transport Analysis of the Origin of Microbiological and Geochemical Zoning

Craig Bethke, Robert Sanford, Theodore Flynn, Dong Ding, Matt Kirk, Jungho Park and
Qusheng Jin

Department of Geology, University of Illinois, Urbana, IL

Geochemists have long been aware of the extensive influence microbes have on groundwater composition, but they are just beginning to appreciate the extent to which the complexity of the distribution of groundwater chemistry results from the development in the subsurface of zoned microbiological communities. The erratic distribution of natural arsenic contamination in young glacial and deltaic aquifers, for example, results from the zoning of subsurface populations of sulfate reducing bacteria. In zones where the bacteria are active, arsenic is not observed, but where they are not, arsenic builds up to levels far in excess of health standards. Iron-rich groundwater, as a more direct example, results from zones containing active populations of iron reducing bacteria.

Evaluating the factors that control microbiological zoning is central to understanding the composition of fluids in the Earth's crust. Previous studies have attributed zones to either thermodynamic or kinetic effects. By the thermodynamic interpretation, a functional group of microbes comes to dominate a zone by maintaining substrate concentrations at levels too small to provide energy for other functional groups. In the kinetic theory, a functional group of microbes excludes other groups by metabolizing the substrate quickly. We find full support for neither interpretation in observations from the field. In the Middendorf aquifer of South Carolina, for example, energy levels are sufficient for methanogens to live, although they appear to be completely excluded from much of the aquifer.

We use reactive transport modeling techniques to see how microbiological zones develop within groundwater flows. The models account for the transport of reactant species to, and product species from microbial populations, the rates at which various functional groups metabolize their substrates, and microbial growth and decay. The results show rich and varied patterns of interaction, as the functional groups compete for substrate even as they exhibit mutualistic behavior.

Sulfate reducing bacteria can hold substrate concentrations at levels where acetoclastic methanogens cannot reproduce quickly enough to offset predation. Even though the methanogens have sufficient energy to grow, their population falls to zero. Iron reducing and sulfate reducing bacteria develop mutualistic communities in which their reaction products precipitate as sulfide minerals, avoiding reactant inhibition. Iron-rich groundwater can develop in these communities, even when dominated by sulfate reducers.

Computational Models of Kinetic Processes in Subsurface Reactive Flows

Edward W. Bolton

Department of Geology and Geophysics, Yale University, New Haven, CT

Numerical models our group has developed for understanding the role of kinetic processes during fluid-rock interaction will be released free to the public. We will also present results that highlight the importance of kinetic processes. These codes will be useful as teaching and research tools. The codes may be run on current generation personal computers. I am preparing manuals describing the numerical methods used, as well as "how-to" guides for using the models. The release will include input files, full in-line code documentation of the FORTRAN source code, and instructions for use of model output for visualization and analysis. The aqueous phase (weathering) and supercritical (mixed-volatile metamorphic) fluid flow and reaction models for porous media will be released separately. Although other codes are available for attacking some of the problems we address, unique aspects of our codes include sub-grid-scale grain models to track grain size changes, as well as fully dynamic porosity and permeability. Also, as the flow field can change significantly over the course of the simulation, efficient solution methods have been developed for the repeated solution of Poisson-type equations that arise from Darcy's law. These include sparse-matrix methods as well as the even more efficient spectral-transform technique. Results will be presented for kinetic control of reaction pathways and for heterogeneous media. Codes and documentation for modeling intra-grain diffusion of trace elements and isotopes, and exchange of these between grains and moving fluids will also be released. The unique aspect of this model is that it includes concurrent diffusion and grain growth or dissolution for multiple mineral types (low-diffusion regridding has been developed to deal with the moving-boundary problem at the fluid/mineral interface). Additional code and documentation will be released for modeling diffusion and consumption of oxygen by ancient organic matter and pyrite in an eroding shale soil, as relevant for understanding an important boundary condition for the long-term evolution of Earth's atmosphere. Results indicate that ancient organic matter is normally oxidized before eroding except for rapid erosion rates. The source codes can be readily modified for use in other reactive-transport models or for individual use. Application of the KINFLOW code shows that spatial heterogeneity of the permeability field can explain much of the so-called "lab-field kinetic-rate discrepancy". This work complements the work of Lichtner on subgridscale diffusive exchange due to heterogeneities (Computational Subsurface Sciences Workshop, Jan. 2007), and Li Li's work (with Peters and Celia) on chemical heterogeneities. I will highlight 1) the influence of heterogeneous permeability, 2) the importance of spatial variations in the deviation from equilibrium, and 3) how lab rates vs. field rate differences in 'bulk' reaction rates can naturally arise from heterogeneous permeability. I will also highlight computational techniques that easily accommodate long-term permeability changes.

Structure and Dynamics at the Mineral/Water Interface: Linking Computational and Experimental Approaches at the Atomic and Nanometric Scales

J. Kubicki[1], A. Bandura[2], J. Sofo[3], L. Vlcek[4], P. Cummings[4], M. Machesky[5], P. Fenter[6], Z. Zhang[6], and D. Wesolowski[7]

[1]Department of Geosciences, Penn State University, University Park, PA
[2]St. Petersburg State University, St. Petersburg, Russia
[3]Materials Research Institute, Penn State University, University Park, PA
[4]Department of Chemical Engineering, Vanderbilt University, Nashville TN
[5]Illinois State Water Survey, Champaign, IL
[6]Chemistry Division, Argonne National Laboratory, Argonne, IL
[7]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN

Periodic density functional theory (DFT) calculations using VASP were carried out for H_2O and various ions in contact with the (110) and (100) surfaces of isostructural rutile (TiO_2) and cassiterite (SnO_2), which differ in their unit cell dimensions (~10%) and bulk dielectric constants (120 vs 9). DFT-MD simulations were conducted with periodic DFT methods to examine the relative energetic stability of a variety of configurations. In order to more completely sample configuration space, interatomic force fields were developed for the H_2O-oxide interfaces using the program GULP. The force field reproduces structures calculated with DFT reasonably well and the relative energies of configurations are similar between the two methods. The DFT surface structures and charge distributions were used as input for large-scale classical MD simulations of the interfaces with bulk SPC/E water ± dissolved ions, as well as site-complexation modeling using the MUSIC model to predict proton affinities of bridging and terminal oxygens at the (110) surface of both oxides (Fig. 1). The calculations show excellent agreement with SHG measurements on rutile and X-ray standing wave (XSW) and crystal truncation rod (CTR) studies of both oxides at Argonne's APS for water in contact with the (110) surfaces. XSW, polarized EXAFS spectroscopy, and plane-wave periodic DFT–calculations were used to study the details of Zn(II) adsorption onto the rutile (110) surface. The XSW data reveal that Zn(II) adsorbs as an inner-sphere complex at two sites: a monodentate site above a bridging oxygen atom and a site between two terminal oxygen atoms. EXAFS results indicate a reduction of the Zn coordination number from six in the aqueous phase to either 4- or 5-fold upon adsorption. Decreasing pH from 8 to 6 does not change the structure of the surface complexes, but it does change the relative stability of the sites. The monodentate site is dominant at pH 8, but the two sites have approximately equal concentrations at pH 6. DFT calculations were used

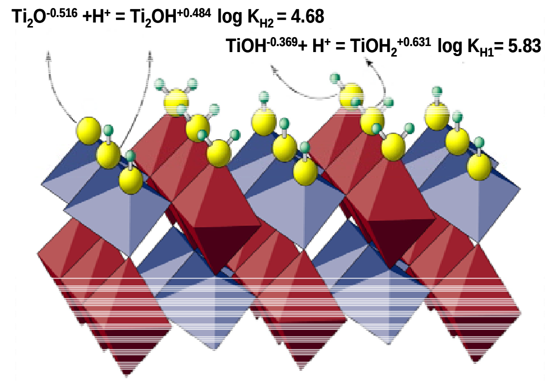

Fig. 1 – MUSIC model predictions of rutile (110) pKa's based on DFT structures.

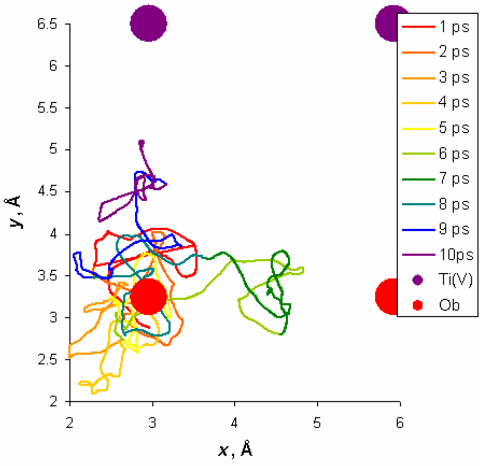

Fig. 2 – DFT-MD simulation of Zn(II) on the (110) surface of rutile.

as a basis for models of the polarized EXAFS spectra and to help interpret the XSW results. In addition, the hydrolysis of Zn(II) at the surface was predicted to be the driving force for the reduced coordination change. DFT-MD simulations were used to test the relative stability and exchange among various potential adsorption sites (Fig. 2). DFT-MD simulations of up to three H_2O layers sorbed on rutile and cassiterite (110) show excellent agreement with the rotational and translational dynamics of outer layer H_2O sorbed on rutile and cassiterite nanoparticles (110 surface predominant), obtained from quasielastic neutron scattering studies at NIST. We are now conducting DFT MD simulations of rutile and cassiterite (110) surfaces at the same level of hydration, which indicate vibrational and librational densities of state of inner H_2O layers that are in qualitative agreement with inelastic neutron scattering studies conducted by collaborators at Argonne's IPNS. The classical and DFT-MD studies, and neutron scattering results indicate that water structure and dynamics are significantly different on these isostructural mineral surfaces. DFT-MD also gives insight into proton transfer dynamics and the degree of dissociation of first-layer water on these surfaces.

Molecular Basis for Microbial Adhesion and Geochemical Surface Reactions

T.P. Straatsma

Computational Biology and Bioinformatics, Pacific Northwest National Lab, Richland, WA

Heavy metal environmental contaminants cannot be destroyed but require containment, preferably in concentrated form, in a solid or immobile form for recycling or final disposal. Microorganisms are able to take up and deposit high levels of contaminant metals, including radioactive metals such as uranium and plutonium, into their cell wall. Consequently, these microbial systems are of great interest as the basis for potential environmental bioremediation technologies. The outer membranes of Gram-negative microbes are highly non-symmetric and exhibit a significant electrostatic potential gradient across the membrane. This gradient has a significant effect on the uptake and transport of charged and dipolar compounds. To aid in the design of microbial remediation technologies, knowledge of the factors that determine the affinity of a particular bacterial outer membrane for the most common ionic species found in contaminated soils and groundwater is of great importance. Using our previously developed model for the lipopolysaccharide (LPS) membrane of Pseudomonas aeruginosa, this work presents the potentials of mean force as the estimate of the free energy profile for uptake of sodium, calcium, chloride, uranyl ions and a water molecule by the bacterial LPS membrane. Our results show that the uptake of uranyl is, energetically, a favorable process relative to the other ions studied. At neutral and basic pHs, the nuclide is shown to be retained on the surface of the LPS membrane through chelation with the carboxyl and hydroxyl groups located in the outer core.

Carbonate Defects in Al-Fe Oxyhydroxide Minerals: Structure, Vibrational Spectroscopy, and Isotopic Fractionation

James R. Rustad[1], Jean-Francois Boily[2], and David A. Dixon[3]

[1]Department of Geology, University of California, Davis, CA
[2]Pacific Northwest National Lab, Richland, WA
[3] Department of Chemistry, University of Alabama, Tuscaloosa, AL

The isotopic signature of carbonate occluded in insoluble soil minerals is potentially useful for reconstructing the composition of the Earth's atmosphere over long time scales. For example it has been suggested that the $Fe(CO_3)OH$ component of goethite indicates that the CO_2 content of the atmosphere in the geologic past has been as much as ten times the CO_2 contents recorded in the Holocene (Yapp and Poths, 1992). To help improve the potential accuracy of the $Fe(CO_3)OH$ paleoproxy, we are using a combined computational and experimental investigation of the structure, vibrational spectroscopy, and isotopic fractionation of the carbonate component of goethite (FeOOH) and diaspore (AlOOH). We begin using first-principles molecular dynamics calculations of the structure of a C^{4+} defect in diaspore, where C is substituted in the lattice for Al and H. We find that the C^{4+} ion fits almost perfectly into the face of the octahedron forming the coordination polyhedron of the replaced Al^{3+} ion. First principles MD calculations are then used to calculate the vibrational spectrum of carbonate in this type of defect within diaspore. As a benchmark for interpretation of the vibrational spectrum, we also carried out a thorough first principles study of the vibrational spectroscopy of carbonate and bicarbonate in aqueous solution and in sodium bicarbonate and calcite. We find that, relative to the carbonate ion in solution, there is a red-shift of one of the asymmetric stretch vibrations by about 50 cm^{-1} and the C inversion vibration by about 20 cm^{-1}. The large separation between the asymmetric stretching bands appears to be consistent with our IR measurements and may be diagnostic for the presence of this defect in oxyhydroxide minerals. The difference between the ^{13}C and ^{12}C frequencies is also diminished in these modes relative to aqueous carbonate, making the C isotopic signature heavier in the defect than in aqueous carbonate by about 10 per mil. Because the fractionation factor between CO_2 in goethite and CO_2 gas has not been previously estimated and is assumed to be ~1, our results suggest that the $Fe(CO_3)OH$ paleoproxy may require modification.

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Molecular Scale Structure and Dynamics of Geologically Important Aqueous Fluids and Mineral-Fluid Interfaces

Andrey G. Kalinichev, R. James Kirkpatrick, Padma Kumar P., and Ivan S. Ufimtsev

Department of Geology, University of Illinois, Urbana, IL

Molecular scale knowledge about the structure, dynamics, and energetics of aqueous solutions and their interfaces with mineral surfaces and other substrates is essential to understanding the fundamental chemistry of a wide range of geochemical and environmental processes, including sorption, mineral precipitation and dissolution, and geochemical transport. Our research focuses on the continued development of relevant molecular scale computational approaches, application of these approaches to important geochemical questions, relevant experimental studies, and application of computational modeling methods to understanding the experimental results. The combination of computational modeling and experiment is proving highly effective in addressing these problems.

At hydroxylated mineral-solution interfaces, individual water molecules and hydrated ions simultaneously participate in multiple dynamic processes which can be characterized by different, but equally important time- and length- scales. Most of these processes can be effectively studied by classical molecular dynamics simulations in a single MD run. On a relatively long time scale (~10-100 ps), we are able to quantify the diffusional processes related to reformation of the entire interfacial H-bonding network and surface adsorption/desorption of H_2O molecules and ions. Interfacial dynamics on the intermediate time scale (~1-10 ps) is dominated by molecular librational and re-orientational motions. The libration (hindered rotation) of surface hydroxyls also occurs at this time scale. These motions are responsible for the reformation and breaking of individual hydrogen bonds, and the strength of these individual bonds can be directly correlated with the intra-molecular O–H vibrations on the shortest, sub-ps time scale. Our MD simulation results are in good quantitative agreement with spectroscopic data for H_2O molecules associated with mineral surfaces.

Our new computational directions are focused on the modeling of proton exchange reactions in aqueous systems using *ab initio* molecular dynamics (AIMD), metadynamics and multi-state empirical valence bond (MS-EVB) approaches. OH^- ion plays a central role in many reactions but is difficult to model. We have developed an MS-EVB force field to study the solvation and dynamics of hydrated OH^- ions and the dynamics of the process in which H_2O molecules exchange a proton hole. The empirical parameters of the MS-EVB Hamiltonian matrix elements are fitted to reproduce the potential energy surface of the $H_3O_2^-$ dimer obtained from quantum mechanical calculations as well as geometries and energies of small hydrated $(H_2O)_nOH^-$ clusters. As part of this work, we developed a novel "charged-ring" model of OH^-(aq) for classical MD simulations. Carbonate minerals and solution carbonate species also play many key geochemical roles, but little is known about their molecular scale reactivity. We have investigated the dissociation reaction pathways of carbonic acid (H_2CO_3) and the corresponding energy barriers using AIMD and metadynamics computer simulations. Significant rearrangements in the H_2CO_3 hydration shell during its conformational changes require a cooperative mechanism that involves larger energy barriers relative to the gas-phase. H_2CO_3 makes strong H-bonds with H_2O molecules with occasional proton exchanges between them. This behavior indicates its natural tendency to form bicarbonate ion under ambient conditions.

More broadly, the MS-EVB, AIMD, and metadynamics methods hold great potential in addressing solution state and mineral surface reactivity but are computationally much more demanding than classical MD simulations. However, the development of effective ways to incorporate proton exchange reactions is essential for a comprehensive understanding of mineral surface reactivity, which is critically coupled to the structural and dynamic characteristics of the interfacial H-bonding network. The availability of petascale supercomputing capabilities in the near future will be important in effectively bringing these approaches into geochemistry.

Site-Specific, Size-Dependent Reactivity of Al-oxide Nanoparticle Surfaces

James R. Rustad[1], William H. Casey[1,2], and J. Wang[2]

[1]Department of Geology, University of California, Davis, CA
[2]Department of Chemistry, University of California, Davis, CA

Water-exchange rates have long been used as key indicators of chemical reactivity in aqueous coordination compounds. Rates of surface complexation reactions in environments characteristic of large aqueous polyoxocations and solid-water interfaces are intimately involved in diverse phenomena such as adsorption, electron transfer, and surface charging. There is no doubt that water-exchange rates are as fundamental to the reactivity of these systems as they are to coordination compounds, but, thus far, experimental determination of rates has been possible only for the simplest polynuclear systems.

We use molecular dynamics calculations to estimate water-exchange rates for a series of aluminum (oxy)hydroxide compounds. These include the $Al(H_2O)_6^{3+}$ monomer; the ε-Keggin ion $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+/8+}$ (Al_{13}); the $[Al_2O_8Al_{28}(OH)_{56}(H_2O)_{26}]^{18+}$ (Al_{30}) aqueous polyoxocation; the surfaces of Al-oxyhydroxide minerals boehmite (AlOOH) and gibbsite ($Al(OH)_3$); and the aluminosilicate mineral kaolinite ($Al_2Si_2O_5(OH)_4$). Like the minerals, the nanometer-sized polyoxocations (Al_{13} and A_{30}) have waters bound at active sites that are separated by sets of relatively rigid hydroxyl bridges. In contrast to the mineral surfaces, the polyoxocations have active sites whose arrangements are known from x-ray diffraction studies on hydrated salts of these ions (Rowsell and Nazar, 2000). The structural data can be used in conjunction with rate data from ^{17}O NMR studies (Casey, 2006) to test predictions of reactivity trends at a site-specific level. The molecular dynamics calculations here tie these structurally diverse systems together into a simple structure-reactivity trend based on Al-water bond lengths, and highlight the role of the Al_{13} and Al_{30} ions in systematically bridging the structural gap between the hexaaquo ion and the oxide surfaces.

Water-exchange rates were calculated for each species using the reactive-flux method (Bennett, 1975). In this method, an arbitrary reaction coordinate is expressed between the outgoing/incoming water molecule and the aluminum site to which it is attached. The potential-of-mean-force along the reaction coordinate, *W(r)*, was calculated using umbrella sampling, with 20-30 windows and a harmonic biasing potential. The rate constant is taken as $k=kk_{TST}$ where k_{TST} is the transition state rate constant and *k* is the transmission coefficient, computed by starting ~10,000 trajectories from the top of *W(r)*, integrating forward and backward in time, can computing the fraction of successful barrier crossings. κ is highly variable across the spectrum of reactive sites, ranging from 0.1 to 0.001.

Overall, the estimates of τ^{298} for the aluminous minerals are surprisingly short, falling within the range of ~10^{-8}-10^{-10} s, close to those for alkali and alkaline-earth metal ions. Waters bound at the edges of the minerals will exchange rapidly with bulk waters and with other ligands. The fast rates for these surface sites are consistent with the long Al-water bond lengths and also follow the general trend that rates increase, and $DH^{\ddagger}$ values decrease, with increasing size and decreasing charge/Al ion of the complex.

This framework provides, for the first time, a means for estimating kinetic parameters for individual sites at aqueous polynuclear ions and oxyhydroxide surfaces. This result is enormously important for environmental chemistry where treatment of reactions at the aqueous-mineral interface is a long-standing problem. The structure-reactivity relation presented here places the ligand-exchange properties of extended interfacial systems on a new site-specific, quantitative footing.

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Structural and Vibrational Properties of Clay Minerals from Classical and *Ab Initio* Molecular Dynamics Simulations

Jeffery A. Greathouse, James P. Larentzos, and Randall T. Cygan

Geochemistry Department, Sandia National Laboratories, Albuquerque, NM

The structural and vibrational properties of talc and pyrophyllite are investigated through classical and *ab initio* molecular dynamics (AIMD) simulations. The AIMD simulations are based on density functional theory (DFT), which is sufficiently accurate to predict the structural and vibrational properties of these clays. However, to understand the nature of adsorption and diffusion in these clays, treatment of these systems in a fully quantum mechanical manner becomes difficult due to the computational burden. The CLAYFF force field is a viable alternative, where it has been shown to faithfully reproduce the crystal structures with relatively simple analytical models that include only non-bonded interactions. Comparison of the *ab initio* and classical MD structure provides a detailed understanding of the important physics that must be included in future refinements of the empirical force field.

In particular, the geometrical arrangement of the hydroxyl group is critical in understanding the adsorptive properties of clays, both at the basal surface and at protonated edge sites. Signature spectroscopic peaks that are characteristic of the hydroxyl group vibrations and bends are easily identified experimentally. With the assistance of molecular simulations, the relationship between hydroxyl group spectroscopy and the molecular-scale structure is explored. The orientation of the hydroxyl group is closely monitored to understand the vacancy effects on these uncharged clays. While the talc hydroxyl orientation is essentially perpendicular to the **ab** plane and has a relatively narrow angle distribution, the presence of vacancies in pyrophyllite significantly alters the behavior into a very broad distribution, as shown in Figure 1. The simulations are in agreement for talc. However, the hydroxyl group orientation in pyrophyllite differs between the *ab initio* and classical MD simulations. The overall impact of the hydroxyl group on the clay properties will be discussed.

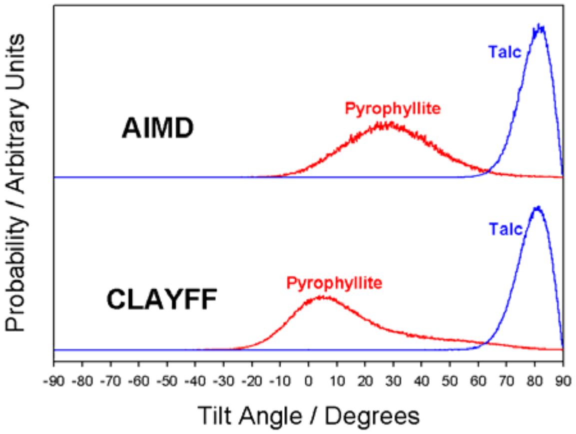

Figure 1. Distribution of the AIMD and CLAYFF hydroxyl angles relative to the **ab** plane.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

A Molecular Dynamics Investigation of Alkaline Earth Metal Complexation to Aqueous Chloride and the Gibbsite Surface

Louise J. Criscenti

Geochemistry Department, Sandia National Laboratories, Albuquerque, NM

The adsorption of contaminant metals onto oxide and clay minerals is a critical process that affects the extent of contaminant migration in ground water. Surface complexation models suggest that metal-anion pairs such as $SrOH^+$ and $PbCl^+$ form on mineral surfaces. Because these surface complexes are very difficult to identify using spectroscopic techniques, molecular dynamics (MD) simulations are used to assess the potential for different metal species to be present at mineral surfaces. We started our investigation by examining the relative stability of alkaline earth metals ($M^{2+} = Mg^{2+}$, Ca^{2+}, Sr^{2+}, and Ba^{2+}) and their chloride complexes in both aqueous solution and at the gibbsite (001) surface using the CLAYFF force field with a flexible SPC water model.

For each metal in aqueous solution, the free energy profile between a metal cation and a chloride anion was calculated via potential of mean force simulations. Three types of ion pairs can be identified: a contact ion pair with no water molecules between M^{2+} and Cl^-, a solvent-shared ion pair with one shared water molecule between M^{2+} and Cl^-, and a solvent-separated ion pair in which each ion retains one full hydration shell. The calculated association constants for MCl^+ suggest that the ion pair stability decreases with ionic radius, consistent with association constants derived from bulk thermodynamic data. In addition, the simulations provide more detailed information regarding the relative stability of the different types of metal-chloride pairs. The preference for contact ion pair formation increases with increasing ionic radii and is directly related to the metal hydration energies.

Surface potential of mean force curves suggest that the alkaline earth metals prefer to adsorb as outer-sphere complexes, where one water molecule is located between the metal and the gibbsite surface. Large activation barriers associated with removing water from the first solvation shell make it difficult for ions to adsorb as inner sphere complexes. However, inner sphere complexes are more likely to occur for larger ions such as Ba^{2+}, due to weaker metal-water interactions. For both the aqueous metal-chloride system and metal adsorption onto the gibbsite surface, the most dramatic variance in the free energy profiles is associated with the release of water from the solvation shell between the metal and the ligand involved - either the chloride ion or the gibbsite surface.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administrator under contract DE-AC04-94AL85000.

Molecular Surface Geochemistry: Integration of Spectroscopic and Theoretical Molecular Evidence with a Predictive Surface Complexation Approach

Dimitri Sverjensky

Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD

Prediction of the interactions between natural waters and solids in natural and in polluted environments depends on a thorough understanding of the solid-water-electrolyte adsorbate interface. From the synthesis of prebiotic organic molecules, to weathering reactions at the earth's surface and diagenetic reactions in reservoirs, to the migration of toxic species in aquifers, to metal implants in the human body, the interactions of aqueous inorganic and organic species with mineral surfaces in electrolyte solutions play a critical role. The interfacial chemical reactions involved determine the responses to perturbations in environmental conditions, such as variations in pH, electrolyte type, ionic strength, and surface coverage.

Recent *in situ* ATR-FTIR spectroscopic studies and X-ray studies have defined important aspects of the surface speciation of a number of cations and oxyanions (including inorganic and organic species) that typically involve multiple surface species (e.g. inner- and outer-sphere and H-bonded species). These results must be integrated with a surface complexation model (SCM) in order to predict surface speciation under environmental conditions. A predictive surface complexation model approach has been developed in the present study over a period of years by integrating available experimental data from a wide range of studies with crystal chemical and Born solvation theory. Starting with surface protonation, and then 1:1 electrolyte adsorption, followed by the addition of 2:1 electrolyte adsorption (i.e. the alkaline earths), and transition and heavy metals, the basis of a predictive approach to surface complexation has been developed. For applicability to natural waters, 1:2 electrolytes (i.e. including the sulfate, carbonate, silicate and borate ions) are also vital and incorporation of a predictive approach for these is now well underway. For these oxyanions, SCMs have often had difficulty using the spectroscopically defined surface species to fit macroscopic adsorption data. Even when this is possible, the models have not been able to predict the correct speciation trends with environmental parameters such as pH, ionic strength, and surface loading defined by the spectroscopic studies. The present study describes a new approach to this problem for oxyanions.

Inner-sphere anion adsorption by the ligand exchange mechanism with surface functional groups on metal oxides is thought to involve desorption of water dipoles chemisorbed to the surface metal ions. The electrostatic work associated with the desorption of the water dipoles from a charged surface has traditionally been neglected in SCMs. Taking this effect into account in the extended triple-layer model of surface complexation (ETLM) permits close quantitative description of anion adsorption data using a combination of inner- and outer-sphere (or H-bonded) species identified by spectroscopic studies. Furthermore, the model anion surface speciation predicted as a function of pH, ionic strength and surface coverage is in agreement with qualitative trends from *in situ* ATR-FTIR and X-ray results. Finally, when expressed relative to site-occupancy standard states, variations in the model equilibrium constants for anion adsorption from one metal oxide to another can be explained with the aid of Born solvation theory. This will enable prediction of the equilibrium constants of adsorbed inorganic and organic oxyanions on oxides. In summary, the new approach for oxyanions brings the overall predictive SCM effort closer to applicability to the chemistry of many natural and polluted waters.

Calculating the Stability, Raman and UV Spectra and Acidity of As Sulfides in Aqueous Solution

J. A. Tossell, M. D. Zimmermann and G. R. Helz

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD

Since the chemical and biological reactivity of As sulfides depends strongly upon their speciation, it is important to determine exactly what species are present within a given environment. Spectral probes such as Raman and UV can give partial information about speciation, but uncertainties and ambiguities generally remain. We are engaged in a program to perform state-of-the-art quantum mechanical studies of the structures, stabilities, spectra (Raman and UV) and acidity of As sulfide species in aqueous solution. We typically use very high level methods, such as CCSD with triple zeta, doubly polarized basis sets for the gas phase part of the calculation, and a lower-level polarizable continuum or nanocluster approach to simulate the effect of hydration. Anharmonic vibrational effects are calculated using 2nd order perturbation theory within a HF – DFT hybrid method. Using this approach we can accurately reproduce the Raman spectra of thioarsenious acid, $As(SH)_3$ and its conjugate bases. The Raman spectra of $As(OH)_3$ is also reproduced with errors of less than 10 cm^{-1} and the As-O(H) distances with errors of only 0.02 Å Such calculations establish that the neutral species in arsenious acid solutions is indeed $As(OH)_3$ rather than $HAsO_2$. This assignment is also supported by our calculated UV spectra. However, accurate calculation of the Raman spectra of the conjugate bases of $As(OH)_3$ requires the inclusion of both explicit waters and counterions. Trends in the acidity of As acids with changing oxidation state, ligand and degree of protonation are well reproduced, but accurate absolute vaues for the oxidic species are elusive. Possible reasons for the overestimation of pKAs for the oxidic species are presented. We have established computationally that the conjugate bases of $As(OH)_3$ are susceptible to sulfidation by H_2S, while As(III) sulfides such as $AsS(SH)_2^-$ are susceptible to oxidation to As(V) by elemental sulfur or polysulfides. By contrast the addition of H_2S to $AsS(SH)_2^-$ to form $As(SH)_4^-$ is calculated to be unfavorable. We can thus generate a comprehensive picture of speciation based upon direct quantum mechanical calculation of a number of properties for possible candidate species.

Participants:
David Benson, Colorado School of Mines
Craig Bethke, University of Illinois
Jean-Francois Boily, Pacific Northwest National Laboratory
Marsha Bollinger, US DOE Office of Basic Energy Sciences
Edward Bolton, Yale University
Ronaldo Borja, Stanford University
Ian Bourg, Lawrence Berkeley National Laboratory
Eric Bylaska, Pacific Northwest National Laboratory
Louise Criscenti, Sandia National Laboratories
Russell Detwiler, Lawrence Livermore National Laboratory
Dave Dixon, University of Alabama
Patrick Dobson, US DOE Office of Basic Energy Sciences
Gary Egbert, Oregon State University
Paul Fenter, Argonne National Laboratory
Grant Garven, Johns Hopkins University
Jeffery A. Greathouse, Sandia National Laboratories
Daniel Hitchcock, US DOE Office of Advanced Scientific Computing Research
Lianjie Huang, Los Alamos National Laboratory
Dave Janecky, Los Alamos National Laboratory
Allan Jelasic, US DOE Office of Energy Efficiency and Renewable Energy
Andrey G. Kalinichev, University of Illinois
John Kinney, Lawrence Livermore National Laboratory
R. James Kirkpatrick, University of Illinois
William Klein, Boston University
Kate Klise, Sandia National Laboratories
Joel Koplik, City College of New York
James Kubicki, The Pennsylvania State University
Anthony Ladd, University of Florida
Ken Larner, Colorado School of Mines
David Lesmes, US DOE Office of Basic Energy Sciences
Brent Lindquist, Stony Brook University
Hernán Makse, City College of New York
John Miller, US DOE Office of Basic Energy Sciences
Gregory Newman, Lawrence Berkeley National Laboratory
Catherine Peters, Princeton University
Walter Polansky, US DOE Office of Advanced Scientific Computing Research
Steven Pride, Lawrence Berkeley National Laboratory
Mark Reed, University of Oregon
Jeff Roberts, Lawrence Livermore National Laboratory
Barbara Romanowicz, University of California, Berkeley
Kevin Rosso, Pacific Northwest National Laboratory
John Rudnicki, Northwestern University
John Rundle, University of California, Davis
James Rustad, University of California, Davis
Jorge Sofo, The Pennsylvania State University

Carl Steefel, Lawrence Berkeley National Laboratory
Tjerk Straatsma, Pacific Northwest National Laboratory
Dimitri Sverjensky, Johns Hopkins University
John Tossell, University of Maryland
Donald Vasco, Lawrence Berkeley National Laboratory
Lukas Vlcek, Vanderbilt University
John H. Weare, University of California, San Diego
David Wesolowski, Oak Ridge National Laboratory
Mary Wheeler, University of Texas, Austin
Nicholas B. Woodward, US DOE Office of Basic Energy Sciences
Ru-Shan Wu, University of California, Santa Cruz
John Zachmann, Colorado State University
Merle Zimmermann, University of Maryland

Not Presented at the Symposium:

Thermodynamic and Transport Properties of Molten and Glassy Geomaterials at Elevated Temperatures and Pressures by Molecular Dynamics Simulation

Frank J. Spera[1], Dean Nevins[1], Ben Martin[1] and Mark Ghiorso[2]

[1]Department of Earth Science, University of California, Santa Barbara, CA
[2]OFM Research – West, 7336 24th Ave NE, Seattle, WA

Molecular Dynamics (MD) simulations are performed on liquid and metastable supercooled liquid of composition $MgSiO_3$ and Mg_2SiO_4 using a Coulomb-Born-Mayer-van der Waals pair potential with parameters from Oganov (2000) and Matsui (1994), respectively. Experiments were performed with 8000 atoms and a 1 fs time step. The atomic structure (neighbor statistics), equations of state (EOS), tracer diffusion (Mg, O, Si) and shear viscosity (by Green-Kubo) are determined from atom trajectories. For liquid Mg_2SiO_4, state points along isochores are simulated every 500 K in temperature range of 2500–5000 K yielding a grid of ~ 75 simulations spanning the pressure range 0–150 GPa, appropriate for the core-mantle boundary on Earth (P_{CMB}~135 GPa). Linear scaling between the molar potential energy and $T^{3/5}$ along isochors facilitates EOS development. Atomic coordination statistics are determined by counting nearest neighbor configurations defined by the first minima of the pair correlation function. The average coordination number (CN) of O around a central Si increases from IV at 0 GPa to about VII in the highest pressure simulations, while that of Mg increases over the same range from IV to VIII. $^{[V]}$Si achieves maximal abundance at about 10 GPa. The CN of O about O varies congruently with the coordination environment of the cations up to pressures on the order of 70 GPa at which point the average O-O CN *decreases* from XV to XI over a narrow pressure interval. The CN's of the Mg and Si vary smoothly and systematically over this interval and do not mimic the O-O nearest neighbor reconfiguration at ~ 70 GPa (~ 1600 km depth on Earth). Computed values of the internal energy and density are utilized to derive the MD EOS. Interestingly, the EOS indicates the presence of a liquid-liquid phase transition in the deeply supercooled region with a critical temperature close to 1050 K and critical pressure of about 1.5 GPa. In the two-phase region two structurally distinct liquids coexist. The coexisting liquids share the same composition; however, the structure of the two liquids is distinct as reflected by differences in density. Computed tracer diffusivity of Mg, Si and O is fit to Arrhenian form with activation volume ~ 1cm^3/mol; D_O (=15×10^{-10} m^2/s) > D_{Mg} (=6×10^{-10} m^2/s) > D_{Si} (2×10^{-10} m^2/s) at 100 GPa and 3500 K. The shear viscosity of molten $MgSiO_3$ at 3500 K and 0 and 100 GPa is 0.001 Pa•s and 0.14 Pa• s, respectively. For Mg_2SiO_4 melt, first nearest neighbor coordination statistics show a continuous decrease in $^{[IV]}$Si and increase in $^{[V]}$Si and $^{[VII]}$Si with increasing pressure along an isotherm. In distinction, the abundance of $^{[I]}$O (O with one nearest Si neighbor) is roughly constant at about 70%, with $^{[0]}$O and $^{[II]}$O both at about 15% as pressure increases along an isotherm. Oxygen tracer diffusivity is ~6.7×10^{-9} m^2/s at 10 GPa and 3100 K. Mg and Si tracer diffusivities are 1.7 and 0.8 that of oxygen, respectively. Using the Stokes-Einstein and Eyring relations between shear viscosity and oxygen tracer diffusivity, a viscosity of ~2.1×10^{-3} Pa• s is estimated for molten Mg_2SiO_4 at 10 GPa and 3100 K, about a factor of ten less than for $MgSiO_3$. Liquid density computed by MD compares very well with those inferred from Clapeyron slope of the laboratory fusion curve of forsterite. The purpose of the project is to compute properties of molten silicate geomaterials pertinent to the mantle and crust in the system MgO-Al_2O_3-CaO-

FeO-SiO_2.

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