

Biogeosciences

B11A MCC: 3002 Monday 0800h

Molecular Biogeochemical Processes of Terrestrial Environments I (*joint with H, V, MR*)

Presiding: J Cervini-Silva, University of California, Berkeley; J Chorover, University of Arizona

B11A-01 0800h INVITED

Molecular Biogeochemistry of Manganese

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Molecular biogeochemistry is an emerging subfield of biogeosciences that has as its primary goal the elucidation of fundamental mechanisms for key surficial processes that determine ecosystem structure and function. The distinguishing feature of this new subfield is the application of molecular techniques, drawn from chemistry, physics, and microbiology, in order to characterize natural samples exhibiting significant heterogeneity and complexity. This approach is necessarily multidisciplinary in scope and multifaceted in execution. In this presentation an ongoing collaborative research project among the authors will be described to exemplify the kinds of issues and operational strategies that seem generic to any endeavor designed to establish the molecular mechanisms of biogeochemical phenomena. The topic to be addressed is the biogeochemistry of manganese, with emphasis on the pathways of bacterially-mediated oxidation of aqueous Mn(II), the structural chemistry of biogenic Mn(III,IV) oxides, and the metal sorption reactions these oxides engage. The dynamic interplay among microbiology, wet chemistry, spectroscopy, and ab initio molecular modeling in our studies will also be highlighted.

URL: <http://mnbiooxides.ucsd.edu>

B11A-02 0830h

Characterization of Newly-Formed Manganese (Hydr)oxides in Biofilms in Pinal Creek, Arizona

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Active, biologically mediated precipitation of manganese (hydr)oxides (Mn-oxides) in Pinal Creek, Arizona, a stream with a history of high manganese levels due to historic mining practices, was studied to determine the identity of newly formed phases and their ability to sequester other metals. Packages of crushed

grains of eight clean mineral substrates, quartz, ilmenite, microcline, rutile, magnetite, hematite and labradorite, were placed in Pinal Creek for one to three months. Glass slides were set out as well in order to characterize biofilm formation. After retrieval and drying, the coating distributions were characterized using scanning electron microscopy (SEM), energy dispersive analysis, and X-ray absorption spectroscopy. Morphologically, coating material developed on the different substrates after one month appeared similar to those developed after two and three months. Overall, the SEM images indicate poorly crystalline, aggregated particles that are small (less than a few microns in general) and lack geometric regularity, although size estimates are somewhat hindered by particle aggregation. The coatings that formed on the microscope slides are characterized as biofilms, as numerous microorganisms were observed using microscopy, both confocal and SEM. Samples were further characterized using extended x-ray absorption fine structure spectroscopy (EXAFS) on coatings that had been separated from mineral substrates. EXAFS spectra of material from rutile and quartz substrates and the biofilm were analyzed and fit, using a natural and synthetic birnessite compounds as reference spectra. This analysis suggests that the rutile, quartz, and biofilm samples are composed of a disordered Mn-oxide that is similar in local structure to a natural birnessite of low symmetry. The formation of disordered, poorly crystalline birnessite is important, as it is an extremely efficient metal scavenger and the interlayer vacancies in the birnessite structure aids in metal sequestration.

B11A-03 0845h

Adhesion of Bacterial EPS to Goethite and Silica Surfaces

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Bacterial adhesion to mineral surfaces is mediated by cell surface macromolecules including lipopolysaccharides, lipoteichoic acids, surface proteins and extracellular polymeric substances (EPS). EPS, a heterogeneous mixture of polysaccharides, proteins and nucleic acids that occur in both cell-bound (capsular) and free form, are thought to mediate cell adhesion through modification of cell surface chemistry and formation of conditioning films, but molecular-scale interactions are not well known. We isolated EPS from the exponential and stationary growth phases of *Bacillus subtilis*, a common soil bacterium, and characterized them using spectroscopy (XPS, FTIR, NMR) and high pressure size exclusion chromatography (HPSEC). Attenuated total reflectance (ATR)-FTIR was employed to probe EPS adsorption from aqueous solution to goethite and amorphous silica colloids that were coated onto a Ge internal reflectance element. Relative intensity of IR bands characteristic of protein, polysaccharides and nucleic acids were dependent on growth phase and type of EPS (free or cell-bound). Proton complexation at acidic functional groups resulted in protein conformational changes; alpha-helical conformation was observed at pH < 4 and random coil (unordered) conformation at pH > 6. The apparent molecular mass estimated by HPSEC ranged from 0.42-132 kDa and peak elution times exhibited significant dependence on aqueous chemistry reflecting changes in conformation. EPS exhibited higher affinity for goethite than for silica but sorption to both solids resulted in molecular changes that were detectable by FTIR. We observed an increase in amide II band intensity and an amide I band shift to higher wavenumbers, suggesting changes in EPS secondary structure of proteins upon adsorption. Silica-sorbed EPS exhibited weak polysaccharide bands whereas sorption to goethite showed polysaccharide fractionation. Distinct spectral features indicative of the formation of P-O-Fe bonds were observed in all the goethite-sorbed EPS spectra, suggesting that phosphates from nucleic acid constituents of EPS play a prominent role in the adsorption process.

B11A-04 0900h

Natural Organic Matter-Promoted Metal Inhibition of Hematite Bioreduction

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A developing technology for the in situ treatment of metal and radionuclide contaminants is the stimulation of dissimilatory metal-reducing bacteria (DMRB) to reduce solid phase iron oxides which promote Fe(II) induced chemical reduction of contaminants. Natural organic matter (NOM) can stimulate the biological reduction of solid-phase iron oxides by serving as an electron shuttle and by complexing biogenic Fe(II). The addition of NOM to contaminated zones has been proposed to further stimulate iron reduction and the fortuitous reduction and immobilization of contaminants. However, little research has been conducted on quarternary systems that contain DMRB, ferric oxides, NOM, and metals or radionuclides. The effect of zinc on the biological reduction of hematite and nitrate by the DMRB *Shewanella putrefaciens* strain CN32 was studied in the absence and presence of NOM. Nitrate was used to compare results between solid-phase and soluble electron acceptors. Previous work has demonstrated that, in the absence of zinc, NOM significantly enhanced hematite bioreduction but slightly inhibited nitrate reduction. In the absence of NOM, zinc was shown to significantly inhibit both hematite and nitrate bioreduction. In the presence of NOM, zinc inhibition of nitrate bioreduction was completely eliminated, presumably due to the NOMs' ability to complex Zn(II) and decrease Zn²⁺ activity. It was assumed that the presence of NOM would also decrease zinc inhibition of hematite reduction. Contrary to this hypothesis, NOM significantly increased the inhibitory effect of zinc during hematite bioreduction. In addition, non-toxic Mn(II) became inhibitory in the presence of NOM during hematite bioreduction. These results suggest that ternary Me(II)-NOM-oxide surface complexes may specifically inhibit solid-phase bioreduction. Thus, interactions between NOM and metal/radionuclide contaminants may effect the overall efficacy of the biostimulation remediation strategy.

B11A-05 0915h

Modeling Saccharide, Amino Acid and Organophosphate Adsorption to Silica and Fe-Hydroxides

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Three main types of molecules exist within the extracellular material surrounding bacteria: polysaccharides, proteins and DNA. This study investigated short-range interactions between small-scale, simplified models of each of these types with silica and Fe-hydroxide surfaces. The results suggest that the strongest interaction is that between phosphate groups of DNA with Fe-hydroxides followed by amino acid/silica and polysaccharide/Fe-hydroxide. The interaction of polysaccharides with the silica surface is predicted to be negligible compared to the interaction of silica with water. The polysaccharide dextran (a model for LPS) has little attraction to silica and higher affinity to Fe-oxides. These observations have been explained by ab initio calculations on the H-bonding interactions between the monomer units of dextran and surface functional groups of silica and Fe-hydroxides. The methylated glucose was allowed to interact with both the hydrophilic Si-(OH) groups and the hydrophobic Si-O-Si groups of the same silica cluster in separate energy minimization calculations. The energy of interaction at both types of "surfaces" is less than that calculated for three water molecules interacting with the silica cluster. The affinity of the polysaccharide for Fe-oxides has been observed to depend on the concentration of surface functional groups on a crystal face. Surfaces with higher densities of relatively less acidic Fe-OH terminal groups tend to have higher affinities for this neutral polysaccharide. Consistent with experiment, the affinity of the methylated glucose for the terminal Fe-(OH) groups is higher than that for the bridging Fe-(OH)-Fe groups, but both result in favorable adsorption energies. We also calculated the interaction energy between lysine and silica in a same way as dextran monomer calculation. The minimum energy calculations showed that lysine forms much strong H-bonding (-116 kJ/mol) than dextran monomer (-42 kJ/mol). These preliminary calculations are in qualitative agreement with the colloid-probe AFM results. Energy calculations of a phosphate diester and a Fe-hydroxide dimer show a strong adsorption affinity. Recent work by Whittechurch et al. (2002, Science 295, 1487) has suggested that extracellular DNA is required for biofilm formation under some conditions. This work, combined with the work of Omoike and Chorover (2003, Abstr. ACS, in press), suggests a mechanism for binding DNA to Fe-hydroxides that could explain why extracellular DNA is a pre-conditioning agent for biofilm formation.

URL: <http://www.engr.psu.edu/ce/enve/craems/>

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B11A-06 0930h

Putative Mineral-Specific Proteins Synthesized by the Metal Reducing Bacterium *Shewanella oneidensis*

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For over three billion years the Earth has been home to millions of different species of prokaryotic organisms. The life and propagation of many of these microbial cells has relied on intimate contact with mineral surfaces (e.g., the use of metal oxides as terminal electron acceptors). An interface is formed at the junction of a bacterium and a mineral surface that is, by its very nature, nanoscale in size. The process of natural selection has shaped bacteria such that they are masters of the art of synthesizing fully functional structures and utilizing properties that exist only at the nanometer scale. We have begun to explore the bacterium-mineral interface to determine precisely how fundamental, nanoscale forces guide and are themselves modulated by a cell's expression of outer membrane proteins localized at a mineral surface. Recent work in our laboratory suggests that a species of dissimilatory metal reducing bacteria expresses proteins that have a high affinity for specific mineral phases. Using biological force microscopy (BFM), we have discovered that one such organism, *Shewanella oneidensis*, appears to recognize the surface of iron hydroxides - versus isostructural aluminum hydroxide counterparts - such that it produces and/or localizes putative mineral-specific proteins at the interface with goethite (FeOOH). These particular high molecular weight proteins are expressed only under anaerobic conditions, when the Fe(III) in the mineral phase is expected to serve as the microorganism's terminal electron acceptor. Protein expression patterns provided by two-dimensional gel electrophoresis confirm that specific, high molecular weight proteins are targeted to the outer membrane of *S. oneidensis* when Fe(III) is provided as a terminal electron acceptor. The results suggest that these proteins are synthesized by *S. oneidensis* under anaerobic conditions to function in iron oxide binding and/or Fe(III) reduction. If this is the case, than it is possible that the evolution of dissimilatory iron-reducing bacteria like *Shewanella*, could have been, at least in part, driven by the binding/reduction ability of certain proteins to specific mineral phases.

B11A-07 0945h

Modeling the Influence of Transport on Chemical Reactivity in Microbial Membranes: Mineral Precipitation/Dissolution Reactions.

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It has long been known that microorganisms can alter the chemical composition of their immediate surroundings and influence such processes as ion uptake or adsorption and mineral precipitation dissolution. However, only recently have molecular imaging and molecular modeling capabilities been developed that begin to shed light on the nature of these processes at the nm to um scale at the surface of bacterial membranes. In this presentation we will show the results of recent molecular simulations of microbial surface reactions and describe our efforts to develop accurate non-equilibrium thermodynamic models for the microbial surface that can describe ion uptake and surface induced mineral precipitation. The thermodynamic models include the influence of the bacterial electrical double layer on the uptake of ions from solution and the removal, or exclusion, of ions from the surface of the cell, non-equilibrium diffusion and chemical reaction within the membrane, as well as a new thermodynamic approach to representing ion activities within the microbial membrane. In the latter case, the variability in the

water content within the microbial membrane has a significant influence on the calculated mineral saturation indices. In such cases, we will propose the use of recently developed mixed solvent-electrolyte formalisms. Recent experimental data for mixed-solvent electrolyte systems will also be presented to demonstrate the potential impact of the variable water content on calculated ion activities within the membrane.

B11B MCC: 3014 Monday 0800h

Geologic Aspects of Carbon and Other Biogeochemical Cycles I (joint with A, H, OS, PP, GC)

Presiding: E Barrera, National Science Foundation; D Sahagian, University of New Hampshire

B11B-01 0800h

Neoproterozoic Seawater Sulfur Isotopes and the Evolution of Microbial Sulfur Species

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Canfield and Teske (1996) proposed that an increase in the variability of $\delta^{34}\text{S}_{\text{pyrite}}$ sometime in the Neoproterozoic—along with a corresponding increase in the isotopic difference between sulfate and pyrite ($\Delta^{34}\text{S}$)—resulted from a fundamental shift in the biogeochemical cycling of sulfur, facilitated by changes in the oxidation-state of the Earth's surface. They proposed that an increase in the depth of oxygenation of the surface ocean triggered the evolution of a non-photosynthetic sulfide-oxidizing bacteria and that these bacteria, in consortium with a host of microbes associated with the oxidative part of the sulfur cycle, were responsible for the increase in $\Delta^{34}\text{S}$ to values greater than 46‰ . However, $\Delta^{34}\text{S}$ values have been poorly constrained for the Neoproterozoic because the S isotopic composition of seawater sulfate has been largely unknown. In this study, we have reconstructed the S isotopic evolution of Neoproterozoic seawater sulfate by analyzing the isotopic composition of trace sulfate extracted from carbonates collected in South Australia, Namibia and Death Valley, CA. Our results indicate that Neoproterozoic $\Delta^{34}\text{S}$ values between ~800 to 570 Ma were less than 46‰ and that the apparent increase in $\delta^{34}\text{S}_{\text{pyrite}}$ variability during this time resulted from an ocean with low sulfate concentrations and rapidly evolving $\delta^{34}\text{S}_{\text{sulfate}}$ —likely a consequence of severe late Neoproterozoic glacial events. Therefore, it is difficult to argue using S isotopes that a non-photosynthetic sulfide-oxidizing bacteria evolved at this time. Furthermore, we speculate that the evolution of a non-photosynthetic sulfide-oxidizing bacteria was not necessary for disproportionation reactions to operate. Rather, we argue that intermediate S species and disproportionation reactions were likely occurring through much of the Proterozoic and that the overall low $\Delta^{34}\text{S}$ is simply a function of more efficient pyrite burial in an ocean with fewer oxidants and low sulfate concentrations.

B11B-02 0815h

Active Microbial Methane Production and Organic Matter Degradation in a Devonian Black Shale

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Microorganisms employ many novel strategies to derive energy and obtain nutrients, and in doing so alter the chemistry of their environments in ways that are significant for formation and transformation of geologic materials. One such strategy is natural gas generation in sedimentary basins. Previous research has shown that stable isotopic signatures of CH_4 , CO_2 and H_2O in formation waters of gas-producing black shales indicate a microbial origin for several economically viable natural gas reserves. However, these signatures leave several intriguing issues unaddressed, including the identity of the organisms and their metabolic roles and impacts on mineral, isotopic and biomarker signatures. We hypothesize that the extreme reducing conditions required for sedimentary basin methanogenesis are simply the end product of a cascade of microbial processes, initiated by anaerobic respiration of shale organic matter through NO_3 , SO_4 and/or Fe(III) reduction, secondary processing of anaerobic biomass by fermentative organisms yielding volatile fatty acids and H_2 , and ultimately CO_2 reduction and/or acetate fermentation to produce CH_4 . This research holds importance for the several aspects of the geochemical carbon cycle. It describes anaerobic hydrocarbon degradation leading to methanogenesis in a sedimentary basin; in many instances this activity has generated economically viable reserves of natural gas. It also provides a benchmark detailing how post-depositional microbial activity in rocks may confound and overprint ancient biosignatures. Interpretation of past environmental conditions depends on molecular and isotopic signatures contained in ancient sedimentary rocks, separated from signatures of metabolically similar modern microbiota living in sedimentary basins. In addition, this research sheds light on an unrecognized and thus unconstrained source of reduced gases to Earth's atmosphere, important for understanding the rates and controls on carbon cycling through geologic time.

B11B-03 0830h

Natural Variations of $\delta^{30}\text{Si}$ Values During 4 Million Years of Progressive Basalt Weathering, Hawaii

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Terrestrial silicate weathering rates and processes are important for studies of modern and paleo-climate. Recently, Si isotope geochemistry has shed light on Si cycling in marine systems, which is directly linked to the terrestrial Si cycle as nearly 80% of the Si is supplied by continental run-off water. Understanding the terrestrial Si-isotope geochemistry is crucial for a more comprehensive understanding of the global Si cycle. Weathering of primary minerals in the pedosphere releases Si that can be incorporated into secondary minerals or leached into rivers and oceans. These are active Earth surface processes that are dependent on local climate and regional tectonics. If we understand how these processes impact soil formation we can interpret present soil properties in the context of past controls on weathering systems. Few direct tracers of weathering status exist; we most commonly use Sr isotopes to track silicate weathering, but it would be far more useful to use Si isotopes. Here we present the results of the first systematic effort to understand the variations of natural abundances of Si isotopes along a soil development gradient. We find that Si isotopes in soils are a promising indicator of weathering status in terrestrial systems and the rivers that drain them. Isotopic data from rock, secondary soil minerals and soil water from 5 soil pits along a 4.1 Ma basaltic weathering chronosequence on Hawaii demonstrate large and systematic variations of $\delta^{30}\text{Si}$ values. Unweathered basalt has a $\delta^{30}\text{Si}$ value of -0.5‰ . Initial weathering leaches most of the Si from the top meter of soil, and converts the remaining Si into amorphous soil clay minerals. Bulk soil from >30 cm depth has $\delta^{30}\text{Si}$ values 0.5‰ more negative than fresh basalt. Soil water simultaneously evolves toward more positive $\delta^{30}\text{Si}$ values, leading to a Si-isotopic difference between solid and aqueous Si of 2.1‰ . As weathering progresses, primary minerals are exhausted, and secondary amorphous minerals are transformed into crystalline phases. This second stage of mineral transformation produces even more negative $\delta^{30}\text{Si}_{\text{bulksoil}}$ signatures. Repeated transformation cycles cause the Si-isotopic ratios of both soil minerals and soil water to move in parallel towards more negative values. The oldest soil has a $\delta^{30}\text{Si}$ composition 2.1‰ more negative than that of fresh basalt, but still displays a 2.3‰ solid-aqueous difference. The top 30 cm of older soils contain atmospheric dust that