

B11A MCC: Hall C Monday 0830h Microbial Activity on Mineral and Rock Surfaces I Posters (joint with OS, V)

Presiding: G A Icopini,

Biogeochemical Research Initiative for
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B11A-0700 0830h POSTER

Structures of Si-Carbohydrate Aqueous Complexes: Comparison of NMR Spectra and Molecular Orbital Results

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Researchers recently have made the discovery that hypercoordinate Si-sorbitol complexes will readily form in biologically relevant fluids, and they have reported the first evidence for a transient organosilicon complex generated within the life cycle of an organism. These interpretations are based upon peak assignments of Si-29 NMR spectra that invoke Si-polyol complexes with Si in five- and six-fold coordination states. However, ab initio analyses of the proposed organosilicon structures do not reproduce the experimentally observed chemical shifts. We have successfully modeled one of the observed Si-29 chemical shifts with a 5-fold Si-disorbitol complex involving 5-membered ring configurations (i.e., Si-O-C-C-O), which yielded Si-29 chemical shifts that closely matched the observed values in the -100 to -102 ppm range. Likewise, Si-29 NMR peaks near -144 ppm were well fit by a model in which a 6-fold Si was complexed to three sorbitol molecules in a 5-membered ring configuration. The ability to simulate observed NMR signals using molecular orbital calculations provides strong support for the controversial role of hypercoordinate organosilicon species in the uptake and transport of silica by biological systems. The existence of such complexes in turn may explain other puzzles in Si biogeochemistry, such as the persistence of monomeric silica in concentrated biological fluids and the biofractionation of Si isotopes and Ge.

B11A-0701 0830h POSTER

Short-Range Interaction Energies and Forces Between Glucose and Silica

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Many researchers have attempted to explain bacterial adhesion with DLVO theory and have had some success in describing long-range interactions. However, DLVO theory cannot properly explain the energetics of adhesion on a short-range scale (less than 1 nm). To understand short-range interactions of bacterial lipopolysaccharides (LPS) with mineral surfaces, we have calculated the structure and energetics of a glucose monomer interacting with a model silica surface (silsesquioxane). Glucose was chosen because it is the monomeric unit of the polymer Dextran which has been used as a model LPS. Silsesquioxane was selected because it is a convenient molecule that captures the most important silanol functional groups of the silica surface.

Ab initio calculations were carried out with Gaussian 98 using both the HF/3-21G(d,p) and B3LYP/6-311++G(d,p) methods. The former basis set was used to generate approximations for the structure of the glucose-silsesquioxane dimer and the latter was used to calculate potential energies. A full energy minimization without any constraints was conducted to determine the most stable configuration of the dimer. Constrained energy minimizations were then conducted based on the optimized structure with the atoms of the silsesquioxane constrained. In addition, the interatomic distances between four atoms in the glucose molecule and four atoms in the silsesquioxane were also

constrained to mimic the approach of the end of a LPS to a silica surface. The derivatives of the calculated potential energy were used to predict a force versus distance curve for these two molecules. The model predicts the formation of four H-bonds between the glucose and silsesquioxane that result in a minimum energy distance of approximately 2.4 Angstroms between the two molecules. The total interaction energy is close to -40 kJ/mol, which is reasonable based on experimental H-bond energies. The maximum attractive force predicted at 2.8 Angstroms is -0.24 nN, and the maximum repulsive force calculated was +0.32 nN at 1.8 Angstroms. These values are within the range measured experimentally for silica-LPS interactions when scaled for system size based on a normalization of contact area.

B11A-0702 0830h POSTER

Mechanisms of Adsorption of the Neutral Polysaccharide Dextran on Hematite, Goethite and Amorphous Silica

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The adhesion of bacteria to materials is an issue of fundamental importance for many medical (e.g. avoiding infection of replacement bones) and environmental (economically applying bioremediation, understanding rock weathering) applications. In the absence of pili or flagella the exterior of Gram negative cells is characterized by various proteins and polysaccharides. Recent work has suggested that bacterial adhesion may be mediated by the interaction of these polysaccharides with materials. Gram negative cell surface polysaccharides take two general forms which both occur on individual cell surfaces: a polysaccharide composed, predominantly, of glucose monomers which is neutral at physiological pH and a polysaccharide which is polyelectrolytic at physiological pH. In this work we conduct batch adsorption experiments of varying sizes of the D-Glucose polymer dextran to goethite, hematite and silica particles. We find that dextran does not adsorb under our experimental conditions to silica, and is ~2x as adsorptive to goethite as hematite. We rationalize these observations with a series of vibrational spectroscopy measurements and ab initio electronic structure calculations. Taken together the results of each approach are consistent with a scenario in which dextran adsorption is controlled by the strength of hydrogen bonds formed between glucose and various surface groups. This conclusion is qualitatively consistent with the observed adhesion of bacteria in the subsurface.

B11A-0703 0830h POSTER

Adsorption of *B. Subtilis* and *P. Mendocina* Onto Fe-Oxide Coated Quartz and Pure Quartz

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Understanding the controls on bacterial adsorption onto mineral surfaces is crucial in order to model a range of processes, such as contaminant transport, mineral dissolution behavior, and bioremediation techniques. At present, little is known concerning the adsorption behavior of bacteria, even onto some of the most common mineral surfaces present in near-surface environments.

In this study, we measured the adsorption of a Gram positive bacterial species (*B. subtilis*) and a Gram negative species (*P. mendocina*) onto a quartz sand, and onto an Fe-oxide coated quartz sand, both as functions of time, pH and bacteria:mineral mass ratio. The extent of adsorption was determined by measuring the concentration of free bacteria in the mineral-bacteria systems both before, and after, reaction, using a uv-vis spectrophotometric approach. pH and bacteria:mineral ratio exert strong controls on the extent of bacterial adsorption of both species onto Fe-coated quartz. The extent of adsorption of *B. subtilis* onto the Fe-coated quartz increases with decreasing pH from close to 0% at pH 10 to a plateau of approximately 80% adsorption between pH 6 and 4. Below pH 4, adsorption of *B. subtilis* decreases to 50% at pH 2. Adsorption of *P. mendocina* is similar to that observed for *B. subtilis*, only it is significantly less extensive under otherwise identical conditions. These adsorption behaviors are in

marked contrast to that observed for both species onto the uncoated quartz. There is little to no adsorption of either species onto the uncoated quartz sand over most of the pH range studied.

We use a thermodynamic approach to model the adsorption behavior of each species onto the Fe-coated quartz sand, determining equilibrium constants for the dominant adsorption reactions. Our results demonstrate that bacterial adsorption within geologic systems can be strongly dependent on mineralogy, fluid composition, and on the bacterial species present. However, our modeling approach enables the prediction of the extent of adsorption of each bacterial species under a wide range of geologic conditions.

B11A-0704 0830h POSTER

Mineral Mesoporosity and its Effect on the Adsorption of Organic Matter

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It is well known that mineral surface area may control mineral dissolution rates and microbial interaction with mineral surfaces. However, surface morphology may also play an extremely important role in microbial- and organic matter-mineral interactions. Much of the surface of natural sediment and soil minerals may be found within mesopores (2-50 nm diameter). These pores may sequester and protect organic matter (natural and xenobiotic) from bacterial and fungal enzymatic degradation. To test this idea, we carried out batch aqueous experiments to examine adsorption of amino acid monomers and polymers onto synthetic mesoporous and nonporous alumina and silica with controlled intraparticle porosity and with similar surface chemistry.

Nearly all amino acid monomers and polymers tested exhibited significantly greater adsorption to mesoporous (8.2 nm mean pore diameter) versus nonporous alumina when normalized to surface area. In addition, desorption of these compounds from the mesoporous alumina occurred more slowly (greater hysteresis) compared to nonporous alumina. In contrast, only the more hydrophobic amino acids adsorbed to the silica phases. Of these, only the monomers exhibited greater surface area-normalized adsorption to the mesoporous phase; this observation is consistent with the smaller pore size of the mesoporous silica material (3.4 nm mean pore diameter). All of the adsorption isotherms could be fit to a hybrid Langmuir-Freundlich model.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra show absorption bands for both sorbed glutamate and diglutamate at 1615 cm⁻¹ and 1570 cm⁻¹ for the nonporous and mesoporous alumina, respectively. This may indicate a stronger carboxylate bond (possibly bidentate versus monodentate) within mesopores. Additional spectrographic and molecular modeling results will be presented. Since we also observed that larger macromolecules (such as enzymes and proteins) are hindered from entering mesopores, these findings provide a potential mechanism for organic matter preservation and point to the importance of mineral surface morphology in governing microbial-mineral interaction.

B11A-0705 0830h POSTER

Etch Pit Formation and Metal Release During Siderophore-Promoted Dissolution of Iron-Silicate Surfaces

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Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and vertical scanning interferometry (VSI) were used to investigate Fe-silicate surfaces after incubation in buffered growth medium for 46 days with the siderophore desferrioxamine mesylate (DFAM) or with a soil bacterium *Bacillus sp.* These

bacteria use Fe as a micronutrient, adhere to surfaces, and release a siderophore that liberates Fe from hornblende when stressed for Fe. In this work, a glass was synthesized to provide a homogeneous, smooth surface chemically similar to hornblende. The stoichiometry of dissolution of Fe and Al relative to Si was investigated by performing simple calculations using solution data and by comparing atomic ratios (Fe/Si, Al/Si) of incubated surfaces to those of untreated surfaces.

AFM and VSI analyses reveal widespread, small etch pits on the DFAM-exposed surfaces and localized groups of larger etch pits on the bacteria-exposed surfaces. Analyses of the filtered solutions revealed negligible Al and Fe release in abiotic control experiments and significant release of Al and Fe in experiments containing DFAM. Low Fe and Al concentrations in filtered solutions from the biotic experiments are consistent with uptake by bacteria or other components of the biomass. XPS results indicate stoichiometric dissolution of Fe with respect to Si from surfaces exposed to DFAM or bacteria. Modeling of the solution chemistry using Geochemists Workbench 3.0 indicated likely precipitation of FeOOH in the control experiment only. Higher Fe/Si measured by XPS on the control suggests that FeOOH precipitates may have attached to the surface. Preferential release of Al relative to Si is indicated by the XPS results for all but the DFAM-exposed surface, which shows congruent loss of Al and Si.

Stoichiometric dissolution and widespread pitting on DFAM-exposed surfaces demonstrates the ability of siderophores to promote dissolution and alter surface morphology. Groupings of microbial etch pits may reflect a relationship between pitting and colonization and may be formed by siderophores in the extracellular polymers produced by the bacteria.

B11A-0706 0830h POSTER

Iron Fractionation During Microbial Reduction of Iron

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The isotopic fractionation of iron during the biological reduction of iron by microbes has received much attention due to the possible use of iron isotopes as an indicator of biological activity in ancient and extraterrestrial environments. However the mechanisms of dissimilatory iron reduction have not been fully characterized. We are investigating the mechanisms by which *Shewanella putrefaciens* strain CN32 reduces ferric iron in the form of goethite, as well as, the resulting iron isotopic fractionation. In the experiments a PIPES buffered minimal media was used in an effort to eliminate or control the formation of secondary ferrous solids. *S. putrefaciens* is thought to also produce an electron shuttle, which carries electrons from the cell to the iron solid. In one set of experiments, *S. putrefaciens* was cultured in minimal media containing goethite both with and without anthraquinone-2,6-disulfonate (AQDS, an artificial electron shuttle). Preliminary data indicates that the fractionation of iron in solution in the AQDS amended cultures is -1.57 per mil lighter than the starting goethite. This fractionation corresponds well with previously reported fractionations in similar systems. However, other researchers have shown that, in these systems, much of the reduced Fe(II) sorbs to the goethite. An acid extraction is often used to remove this sorbed Fe(II) and determine the total amount of reduced iron. This extraction was used to extract sorbed Fe(II) for isotopic analysis. Although the extraction itself may cause a fractionation effect, less than 1% of the total iron in the extraction can be attributed to this effect. Therefore, the observed fractionation should be primarily a function of the microbially reduced iron and not an artifact of the extraction. The isotope fractionation in the extraction, which includes both soluble and sorbed Fe(II), is -2.42 per mil relative to the starting goethite. We are currently combining parts of the cell involved in iron reduction (cell wall components) with an electron shuttle and goethite to accomplish *in vitro* Fe reduction. We will compare the *in vitro* iron isotope fractionations that occur without live cells to those with live cultures in an effort to elucidate iron reducing mechanisms and pathways.

B11A-0707 0830h INVITED POSTER

Microorganisms and Volcanic Glass

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Volcanic glass is primarily found on Earth as quenched basalt magma or as high-silica ash deposits. Basalt magma is quenched to glass as it erupts into water or sediment, making pillow lavas, sheet flows, or highly fractured rocks (hyaloclastites). Silicic, explosive volcanism produces thick deposits of ash composed primarily of glass shards. Volcanic glass is unstable in the presence of water and is weathered (chemically and mineralogically altered) to clays, oxides, and other minerals. Weathering can be abiotic, but microorganisms appear to be associated with the weathering of volcanic glass in many environments. A number of techniques were used to determine the presence, location, and identity of microorganisms in volcanic glass. Volcanic glass from pillow basalts from fresh and salt water, from hyaloclastites, and from rhyolite ash deposits on arid land all appear to have microorganisms associated with the weathering. It has not been determined what role the microbes play in the alteration of the glass. If microbes are active agents of alteration, then the range of environments and glass compositions in which they occur suggests wide physiological diversity.

B11A-0708 0830h POSTER

Disappearing Glass: What Happened to the Volcanic Glass from the Tops of Shallow Seamounts in the Northeast Pacific?

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Lines of hotspot-generated seamounts stretch from the Juan de Fuca Ridge to the Aleutian Trench on the Pacific Plate. Basalts from these seamounts are of various ages and in situ depths, and thus are valuable for identifying environmental factors that influence the alteration of basalts by microorganisms. Pillow basalts were collected from the Axial-Cobb-Eickelberg-Patton line of seamounts with the submersible ALVIN during three cruises with R/V Atlantis. The ages of the basalts range from 9 years (1993 CoAxial eruption) to more than 30 Ma (Patton Seamount). Other seamounts in the chain that were sampled were Axial Seamount (< 0.1 Ma), Brown Bear Seamount (about 1 Ma), Cobb (2 Ma), Warwick (about 6 Ma), and Murray (about 30 Ma). Precise (usually ± 10 m) depths and locations of samples were achieved with the ultrashort baseline navigation system aboard Atlantis. For all seamounts the sample depths range from 320 to nearly 3000 m below sea level. The range of depths from which pillows were collected on individual seamounts were 320 to 1909 m on Cobb Seamount, 603 to 1323 m on Brown Bear Seamount, 618 to 2091 m on Warwick Seamount, 327 to 2964 m on Patton Seamount, and 686 to 2768 m on Murray Seamount. The presence and thickness of glass was determined on pieces cut from the pillow basalt rims. Glass is absent from basalts collected above 900 m and is present in basalts below 1500 m. The shallowest basalts appear to have lost glass by abrasion in the surf zone, and some deeper samples have lost part of their glass rims during mass wasting of steep outcrops. Alteration of glass by chemical or biological action is evident in hand specimens by the replacement

of glass by clay. In some shallow samples this replacement is complete. The proportion of alteration in these basalts that is biologically controlled has not yet been determined, but in some environments biologically mediated alteration of glass is the dominant process. It appears that basalts are dissolving more completely at shallow depths. Higher water temperature, higher organic matter concentration or other factors may influence the rate of glass alteration. We are examining thin sections from each of the seamounts in an attempt to determine how much alteration is due to microorganisms.

B11A-0709 0830h POSTER

Bacterial Disproportionation of Elemental Sulfur in Marine Sediments Amplified by a Seafloor Fuel Cell

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Bacteria known to disproportionate elemental sulfur to sulfate and sulfide and to grow only in the presence of a sulfide scavenger have been enriched electrochemically in marine sediments. During a 7-month experiment designed to demonstrate sustained electrical energy harvesting by a seafloor fuel cell (Tender et al. 2002), a graphite anode embedded in sediment within Yaquina Bay, OR, developed a biofilm showing a 60% enrichment in δ -Proteobacteria belonging to the genera *Desulfobulbus/Desulfocapsa*. Cytophagales showed a secondary enrichment in 36.7% of 16S rDNA sequences. These two groups of microorganisms made up 23.5% and 8.8%, respectively, of clones derived from graphite scrapings of a control cell with zero current. Sediment porewater profiles show millimolar increases in sulfate and iron concentrations, but also sulfide depletion approaching the active anode. Electron microprobe analyses reveal accumulations of sulfur and iron between the graphite surface of the anode and the overcoating biofilm with a Fe/S ratio below one. Extractions of iron mineral phases also indicate a small decrease in crystalline iron oxide near the anode. These chemical changes are consistent with four interactive processes. (1) Sulfide is oxidized to elemental sulfur directly at the anode. (2) The elemental sulfur promotes the microbial production of sulfate and FeS + FeS₂. (3) Iron sulfide apparently dissolves to re-supply sulfide that is consumed by the anode. (4) Released Fe⁺² accumulates and with organic ligands may catalyze the reduction and dissolution of crystalline iron oxide (Luther et al. 1992). Thus, we conclude the anodic half-cell reaction of the marine fuel cell provides a novel experimental approach for in situ enrichment of bacteria that disproportionate elemental sulfur while highlighting a biogeochemical cycle usually obscured by competing processes. Tender L. M., Reimers C. E., Stecher H. A. III, Holmes D. E., Bond D. R., Lowy D. A., Pilobello K., Fertig S. J., Lovley D. R., Harnessing microbially generated power on the seafloor, Nature Biotechnology (2002) 20: 821-825. Luther G. W. III, Kostka J. E., Church T. M., Sülzberger B., Stumm W., Seasonal iron cycling in the salt-marsh sedimentary environment: the importance of ligand complexes with Fe(II) and Fe(III) in the dissolution of Fe(III) minerals and pyrite, respectively, Marine Chemistry (1992) 40: 81-103

B11A-0710 0830h POSTER

Microbially-Mediated Mineralization at Hydrothermal Vents: Searching for Nanoscale Biosignatures

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Microbial communities constitute a major portion of the total biomass and biodiversity found at hydrothermal vents. With a wide range of metabolic strategies, microbes within the chimney wall can exert significant control over hydrothermal minerals by (1) providing surfaces for crystal nucleation and overgrowth (2) changing the pore fluid chemistry and redox conditions across the chimney wall, or (3) complexing and absorbing certain chemical species. We are exploring how these microbially-mediated processes in chimneys may lead to nanoscale structural and morphologic features unique to biogenic mineral assemblages.

We examined samples from six vents representing a diverse array of chemical and thermal conditions along the East Pacific Rise crest at 9-10°N. Environmental Scanning Electron Microscopy (ESEM), Scanning Electron Microscopy (SEM), X-ray energy dispersive analysis (EDS), powder X-ray diffraction, and optical microscopy were used to characterize chimney minerals. Estimates of *in situ* conditions within chimney walls based on mineral assemblages, and microbe-mineral associations observed directly with ESEM were used to infer possible microbial influence on specific chimney minerals. These putative biominerals were compared chemically, morphologically, and optically to minerals located in abiogenic zones (>200°C) within the same chimney. We found that some morphological correlations existed between colloidal iron sulfide minerals and areas of increased microbial activity in three of the six vents sampled. In addition, EDS analyses showed systematic variations in Fe/Cu and Fe/S ratios across abiogenic and biogenic assemblages of pyrite, pyrrhotite, and chalcocite in four of the six chimney samples. Electron diffraction studies and crystal structure analysis using Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED) are pending.

B11A-0711 0830h POSTER

Life, Decay and Biosignatures of Lithobiotic Extremophiles

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Current knowledge of fossils of microorganisms as traces of microbial activity once present within terrestrial rocks is extremely scarce. The principal aim of this study is to improve the knowledge of endolithic tufa pinnacles microbial communities from Mono Lake, California. Furthermore, we study their death processes *in situ* to be able to find sign of past life in the mineral deposits. The study of microorganisms colonizing the inside of lithic materials has been confronted with enormous difficulties. However, the advent of new scanning microscopy techniques with backscattered electron imaging (SEM-BSE) combined with an auxiliary X-ray energy dispersive spectroscopy (EDS) has implemented the methods for the study of lithobiotic microbial communities. This technique permits the chemical characterization of mineral features, and the observation of the ultrastructural characteristic of the cells without the need to remove them from their environment. The living endolithic biofilm of cyanobacteria serves as a nucleation site for aragonite crystals. After the decay of the filaments the growth of the crystals continues without the preservation of the organic material. Finally the aragonite crystals became embedded in a calcite matrix during the growth of the tufa pinnacle. In this ecosystem the formation of aragonite crystals surrounded by calcite is a biosignature not predicted to occur by abiotic process. The application of *in situ* microscopy methods permitted describe the relationship between biomineralization processes happening in the living biofilm and detecting traces of the past presence of the biofilm in geological materials.

B11A-0712 0830h POSTER

Stereochemical recognition revisited: A step-specific model for shape control

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By utilizing small molecules, peptides, and proteins to modulate crystal nucleation and growth, living organisms produce single crystals and crystal composites that provide materials solutions to their functional requirements. In doing so, they exhibit control over the location, phase and crystallographic orientation of the nuclei, as well as the morphology and kinetics of the growing crystals. A common paradigm for interpreting this phenomenon is that the stereochemistry of the growth modifiers is matched to that of a particular crystallographic plane that would not naturally be expressed during nucleation and growth in pure environments. This paradigm is generally referred to as "stereochemical recognition". Using *in situ* AFM, we have investigated growth in a number of crystal-impurity systems. Our results suggest that, while control over nucleation can be understood within this paradigm, to understand the controls on growth kinetics and morphology it should be rejected in favor of a model that emphasizes the importance of step-specific impurity interactions on existing faces. The systems examined include carbonates, phosphates, oxalates, and phthalates, grown in the presence of inorganic ions, amino acids, organic dyes, and proteins. We show that, in all of these systems, the growth kinetics and resulting crystal habit are defined by modifications to existing atomic steps and that these modifications vary dramatically depending on the step direction, even on a single crystal face. Furthermore, we show that the addition of chiral molecules can be used to break the natural crystal symmetry and produce right- and left-handed crystals. We show that while the exact mechanism of growth modification is different in each system we have examined, the one feature that these systems have in common is that the important molecular-scale interaction that gives rise to growth modulation is between the impurity and a specific set of steps. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

B11A-0713 0830h POSTER

Nanoscale Effects of Strontium on Calcite Growth: A Baseline for Understanding Biomineralization in the Absence of Vital Effects

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The compositional signatures of Sr and Mg in calcium carbonate biominerals have become a widely used tool for deciphering paleoenvironments of formation. Studies investigating correlations between Sr concentrations and calcification environment report that the quantity of Sr in calcitic biominerals is far less variable and have much lower absolute levels than Mg. These relationships are further complicated in biogenic calcites by complex biological processes, termed vital effects, which influence the composition of skeletal materials during mineral formation. Quantifying molecular-scale controls on mineralization in the absence of vital effects is essential to sorting out the principles that control compositional signatures of biogenic carbonates.

Here we use *in situ* atomic force microscopy (AFM) to directly observe the molecular scale effects of Sr on the layer growth of abiotic calcite and couple these insights with quantitative measurements of the kinetics and thermodynamics of growth. By this approach, we learn the kink site-specific effects of Sr on the positive and negative surface coordination environments that characterize calcite step edges. Along the positive directions, there are larger and geometrically more open kink sites compared to the smaller and more shielded sites along negative directions.

A recent study from our group using AFM showed that Mg inhibits growth by enhancing calcite solubility through preferential incorporation of the Mg into negative step edges. In a preliminary study that employs a similar approach, we are finding that Sr affects growth along negative directions by adsorption and pinning at step edges to kinetically impede step flow during layer growth. Decreases in step migration rates along positive directions appear to be a combination of both step-pinning and incorporation mechanisms.

Our finding that Sr and Mg have different surface interaction mechanisms offers a microscopic explanation for previous macroscopic observations. These results suggest that Sr and Mg will likely exhibit different dependences upon variable conditions including temperature and growth rate. This research steps toward our long-term goal of understanding microscopic mechanisms controlling minor element contents of calcitic biominerals formed in seawater.

B11A-0714 0830h POSTER

The Role of Mg²⁺ in the Dissolution of Pure Calcite: Insights from AFM and Vertical Scanning Interferometry

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It has long been recognized that magnesium exerts important and complex thermodynamic and kinetic controls on the mineralogy and composition of sedimentary carbonates. Mg/Ca ratio is viewed as a key descriptor of the chemistry of ancient oceans and the mass-age distribution of (magnesian) calcite and aragonite. Recent AFM work (Davis *et al.* 2000) has confirmed the mechanism of Mg²⁺ inhibition of calcite crystal growth through formation of a more soluble magnesian calcite (Berner 1975). The understanding of the mechanistic role of Mg²⁺ in calcite dissolution, however, is comparatively weak. Previous work using calcite powders has shown Mg²⁺ retards the dissolution rate in pure solution, but this inhibition appears to be important only at concentrations that are high compared to those required for other inhibitors of like charge (Sjöberg 1978; Gutjahr *et al.* 1996).

Recent single crystal experiments in pure solutions have shown that calcite dissolution rates derived from vertical scanning interferometry (VSI) are in good to moderate agreement with rates derived from AFM step velocities, but substantially slower than "bulk" rates recovered using mineral powders. Here we present data from similar experiments designed to examine the role of Mg²⁺ on dissolution rate. Preliminary results show that AFM initial step velocities (and thus initial dissolution rate) may actually increase with added Mg²⁺ at concentrations up to ~1 mM. In addition, Mg²⁺ may also be incorporated in a surface phase during net (pure) calcite dissolution. These results are combined with the distribution of rates recovered from VSI experiments using both added Ca²⁺ and Mg²⁺ to develop an understanding of the relationship between Mg/Ca ratio in solution, dissolution rate, and surface phase composition.

B11A-0715 0830h POSTER

Modulation of Calcium Oxalate Crystallization by Proteins and Small Molecules Investigated by *In Situ* Atomic Force Microscopy

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Understanding the physical mechanisms by which biological inhibitors control nucleation and growth of inorganic crystals is a major focus of biomineral research. Calcium oxalate monohydrate (COM), which plays a functional role in plant physiology, is also a source of pathogenesis in humans where it causes kidney stone disease. Although a great deal of research has been carried out on the modulation of COM by proteins and small molecules, the basic mechanism has not yet been understood. However, because the proteins that play a role in COM growth have been identified and sequenced, COM provides an excellent model system for research into biomineral growth. In this study, *in situ* atomic force microscopy (AFM) was used to monitor the COM surface under controlled growth conditions both from pure solution and those doped with citrate and osteopontin (OPN) in order to determine their effects on surface morphology and growth dynamics at the molecular level.

As with other solution-grown crystals such as calcite, COM grows on complex dislocation hillocks. In pure solution, while growth on the (010) face is isotropic, hillocks on the (-101) face exhibit anisotropic step kinetics. Steps of [-10-1] and <120> orientation are clearly delineated with the [-10-1] being the fast growing direction. When citrate is added to the solution, both growth rate and morphology are drastically changed on (-101) face, especially along the [-10-1] direction. This results in isotropic disc-shaped hillocks a shape that is then reflected in the macroscopic growth habit. In contrast, no large growth changes were observed on the (010) facet. At the same time, molecular modeling predicts an excellent fit of the citrate ion into the (-101) plane and a poor fit to the (010) face. Here we propose a model that reconciles the step-specific interactions implied by the AFM results with the face-specific predictions of the calculations.

Finally, we present the results of doping with aspartic acid as well as OPN, an aspartic acid rich protein and a powerful inhibitor of COM growth. The AFM results show that OPN, like citrate, inhibits growth on the (-101) face through a step pinning mechanism at concentrations in the nM range. The implications of the findings to the field of medicine will also be addressed. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

B11A-0716 0830h POSTER

Production of Submicron-Sized Elemental Selenium Spheres by Anaerobic Bacteria that Breathe Oxyanions of Selenium

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Since the phenomenon of dissimilatory selenate reduction (DSeR) was first reported in (Macy et al., 1989; Oremian et al., 1989) at least 13 phylogenetically and physiologically diverse species of prokaryotes have been isolated from both the Bacterial and Archaeal domains that are capable of growth via DSeR. These microbes link the oxidation of various electron donors (e.g. lactate, acetate, hydrogen) to the terminal electron acceptors selenate, or in some cases selenite. The reduction product is amorphous, elemental selenium [Se(0)] that accumulates in large quantities in the medium as a bright orange-red precipitate. It was not clear to us how this precipitate was first formed on the cell surface. We first noted the accumulation of sub-micron sized spheres of Se(0) on the surface of *Bacillus selenitireducens* (Switzer Blum et al., 1998) grown on selenite. Here we report that this phenomenon occurs in at least 3 other species, including another haloalkaliphile *B. arsenico-selenatis*, the moderate halophile *Selenihalanaerobacter shriftii*, and the fresh water isolate *Sulfurospirillum barnesii*. Cell suspensions of all four species examined by scanning electron microscopy were noted to form spheres of Se(0) on their surfaces that sometimes accumulated in clusters. In general, the diameter of these spheres uniformly ranged in size between 100 - 200 nm. These results imply that most, if not all species of prokaryotes that respire via DSeR form these spheres. Although Se(0) spheres have not been as yet looked for in anoxic sediments via imaging techniques, we would predict that they occur therein. Moreover, the emerging field of nanotechnology could find some application for uniformly-sized spheres of these dimensions because Se(0) is both a semiconductor and photoconductor.

Macy et al. 1989, FEMS Microbiol. Lett. 61: 195 - 198.

Oremian et al., 1989. Appl. Environ. Microbiol. 55: 2333 - 2343.

Switzer Blum et al., 1998. Arch. Microbiol. 171: 19 - 30.

B11A-0717 0830h POSTER

Periplasmic Manganese in a Subsurface Bacterium During Anaerobic Growth on Birnessite

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In subsurface environments, where oxygen is not metabolically available for energy production, bacteria use alternate terminal electron acceptors (TEAs) to respire and grow. Anaerobic TEAs include, but are not limited to, Fe³⁺ and Mn⁴⁺. These metals can be present as mineral phases (e.g., ferrihydrite and hematite in the case of iron; birnessite and pyrolusite in the case of manganese). Bacteria bind strongly to minerals and reduce the metal by a process called dissimilatory metal reduction (DMR). *Shewanella putrefaciens* strain CN32 is a Gram-negative bacterium capable of DMR. In previous reports, when this organism was grown on birnessite, we observed cytoplasmic granules of a Mn-rich mineral phase, and an unusual deposition of electron-dense material within the periplasm (that region of the cell located between the inner and outer membranes). In an attempt to characterize the periplasmic precipitates, CN32 was inoculated into an anaerobic defined medium (DM), supplemented with 20 mM Mn (birnessite) and incubated in an anaerobic chamber. Reduced and total Mn concentrations were monitored using atomic absorption spectrophotometry, and cell numbers determined by viable counts on trypticase soy agar. TEM, combined with energy dispersive X-ray spectroscopy (EDS), was used to localize and confirm the presence of any Mn-rich depositions. Soluble Mn concentration increased steadily after inoculation, indicating active metabolism and metal reduction by the cells. Viable counts indicated that the cells reached their maximum number on day 9. Stained thin sections from 4-day-old samples examined with TEM showed cells in close association with the mineral. Secondary mineral products derived from birnessite reduction were evident (e.g., manganese phosphate). TEM-EDS also revealed the presence of ~30 nm-thick deposits of electron-dense material in the periplasm of some cells. However, examination of similar sections which had not been previously stained with osmium tetroxide (an oxidizing EM stain), failed to reveal similar periplasmic depositions. We therefore speculate that soluble manganese accumulated within the periplasm of the cells. This pool of soluble manganese was then precipitated upon addition of the oxidizing osmium stain, and appeared as the electron-dense precipitates in stained sections. We believe this is the first report of a pool of soluble manganese accumulating within the periplasm of cells during DMR. At this point, we do not know whether the accumulation is related to the anaerobic metabolism of the cells (i.e., biologically induced), or is simply a passive by-product of their growth on manganese minerals. Further studies are needed to fully investigate this point.

B11A-0718 0830h POSTER

Sensitivity of Nuclear Magnetic Resonance Relaxation Measurements to Changing Soil Redox Conditions

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Few processes are as important for environmental geochemistry as the interplay between the oxidation and reduction of soil and groundwater components. We have investigated a new method for non-invasive monitoring of changing redox conditions proton nuclear magnetic resonance (NMR) relaxation measurements. The measured parameter, the NMR relaxation time, is known to be sensitive to the presence of paramagnetic species and, as a result, is predicted to be affected by changes in the amount dissolved oxygen in the pore water and by changes in the redox state of any iron present in a soil. Laboratory NMR relaxation measurements were made on fluid-saturated soil samples under reducing and oxidizing conditions. We used well-characterized kaolinite and sand samples with known concentrations of Fe(II) and Fe(III) compounds. Soil samples with dissolved Fe(II) ions, FeS coatings and pyrite grains were prepared in oxygen-free water under a nitrogen atmosphere in a glove bag. In the absence of Fe(II), changes in dissolved oxygen concentration in the water in the soils caused changes in relaxation time that are too small to be reliably detected by field NMR

measurements. In contrast, NMR relaxation measurements were shown to be very sensitive to small changes in the concentration of Fe(III) species in soil, caused by changing redox conditions. Oxidation of as little as 0.030 mg/g of Fe(II) species to Fe(III) oxyhydroxides resulted in a 30 to 50% decrease in relaxation time. We conclude that surface or borehole NMR is a potential method for measuring changing redox conditions using the Fe(III)-Fe(II) redox couple as an indicator.

B11A-0719 0830h POSTER

The Temperature Dependence of Calcite Growth Rates: An Essential Step Toward Robust Biogenic Carbonate Paleothermometry

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The critical need for paleoclimate proxies independent of ocean salinity and polar ice volume has directed much attention to biogenic carbonate minerals as hosts of chemical records of formation temperatures. The minor and trace element signatures in these carbonates are complex products of inorganic and biological, or 'vital,' controls. In order to interpret these records accurately and unambiguously, it is essential to deconvolve the thermodynamic, kinetic, and biological influences on minor and trace element incorporation in calcite, particularly over the range of temperatures relevant to natural waters. Toward this end, we present well-characterized, *in situ*, molecular scale measurements of calcite growth rates as a function of temperature. This work yields precise information about the thermodynamic and kinetic effects of temperature on calcite precipitation, which is critical for eventual assessment of the biological processes that also contribute to the relationships between biomineral compositions and conditions of formation.

We used fluid cell atomic force microscopy (AFM) to observe the flow of monomolecular steps on calcite growth hillocks. This technique enables direct, microscopic measurement of growth rates of individual, 3.1 Å steps on calcite seed crystals. Near-equilibrium growth solutions with supersaturation values (ln [aCa²⁺ x aCO₃²⁻ / K_{sp}]) ranging from 0.9-1.7 were cooled or heated with a Peltier device and pumped continuously through the fluid cell chamber at 20°C or 30°C for each experiment. Temperature was monitored at the exit port of the fluid cell and remained within 1.5°C of the target temperature. Experimental results and preliminary geochemical modeling show that, although the degree of supersaturation changes little as a function of temperature, both obtuse (positive) and acute (negative) angle steps migrate nearly twice as quickly at 30°C as at 20°C, suggesting that the kinetic effects of changing temperature dominate over thermodynamic effects within the range of conditions studied thus far. Further work will span the range of temperatures relevant to natural waters and will define precisely the relationships between temperature, supersaturation, and crystal growth rates.

This study represents an important step toward development of robust and accurate paleothermometric techniques based on biogenic calcite. Once we have established inorganic baseline information about calcite growth as a function of temperature, we will continue with measurement of the extent and distribution of impurity incorporation with temperature variation. This in turn will set the stage for comparison with biogenic samples to precisely constrain information about paleoclimates and global cycling of carbon.

B11A-0720 0830h POSTER

Amino Acids as a Source of Organic Nitrogen in Antarctic Endolithic Microbial Communities

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In the Antarctic Dry Valleys, cryptodolicholithic microbial communities occur within porous sandstone rocks. Current understanding of the mechanisms of physiological adaptation of these communities to the

harsh Antarctic environment is limited, because traditional methods of studying microbial physiology are very difficult to apply to organisms with extremely low levels of metabolic activity. In order to fully understand carbon and nitrogen cycling and nutrient uptake in cryptoendolithic communities, and the metabolic costs that the organisms incur in order to survive, it is necessary to employ molecular geochemical techniques such as amino acid analysis in addition to physiological methods. Low-molecular-weight biomolecules such as amino acids can be used as tracers of carbon and nitrogen uptake and loss by microbial communities living in solid-state matrices such as rock or sediment.

We have measured the concentrations and D/L ratios for several amino acids as a function of depth in a large sandstone boulder. Concentrations of both free and bound amino acids decrease by more than two orders of magnitude from the surface to the visible base of the community (approximately 1.2 cm depth), while the D/L ratios of the amino acids increase from near zero to 0.2 or greater over the same depth interval. We interpret these data as an indication that one or more community members are selectively scavenging L-amino acids as the amino acids are transported through the rock by intermittently percolating meltwater. This is consistent with the known preference of lichens for amino acids as nitrogen sources rather than inorganic nitrogen under conditions of nutrient limitation. It is not yet clear whether there is also a contribution to amino acid uptake from heterotrophic bacteria associated with the cryptoendolithic community. The increase in D/L ratios with depth observed in the rock is too great to be attributable solely to the natural occurrence of D-amino acids in bacteria.

Amino acid concentration and D/L profiles remain relatively constant below the 1.2 cm level. This may be due to aqueous transport from the upper levels. It is also possible, however, that heterotrophs at very low cell densities may exist several cm below the bottom of the bulk endolithic community.

B11A-0721 0830h POSTER

Amino acid and hexosamine in the equatorial western Pacific: vertical fluxes and individual preservation through water column to surface sediments

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Amino acids (AA) and hexosamines (HA) are major constituents for all living organisms, constituting important fractions of labile organic carbon and nitrogen. They usually decompose rapidly than bulk OM and must be expected to be closely linked to biogeochemical processes. In spite of such importance, our understanding of degradation processes of labile components is still limited. Therefore vertical fluxes and preservation of AA and HA from water column to surface sediments are investigated at the western equatorial Pacific. The settling particles were composed of fairly fresh AA, which could be derived from siliceous diatom with less amount of calcareous plankton. In contrast, AA were degraded in sediments and porewaters. Each AA showed highly variable preservation ratio from settling to sedimentary particles. Compared with glycine, the calculated preservation ratio was the lowest (0%) for cysteine, followed by phenylalanine (6%), tyrosine (17%), methionine (47%), leucine (60%), isoleucine (65%), proline (67%), valine (91%), serine (99%), arginine (107%), threonine (112%), alanine (115%), glutamic acid (114%), aspartic acid (150%), lysine (166%) and histidine (186%). Beta-alanine and gamma-aminobutyric acid were the least labile AA. Probably they are so difficult to degrade for bacteria to get biochemical energy that the degradation proceeds fairly slowly. In contrast, after burial, even most labile, aromatic and sulfur-containing AA, degrade at a rate similar to the other protein AA. In spite of complicated reactions, most of the AA showed first-order reaction kinetics during the degradation in the sediments. The decomposition rate constant k (kyr⁻¹) in this study was 2-3 orders lower than those in coastal marine environments. Better preservation of HA over AA in the sediments was probably due to the general incorporation of HA into structural biopolymer matrices, such as bacterial cell-walls and chitinous material. Abundant glycine in the AA in the sediments is due to contribution from diatom cell-walls, bacterial peptidoglycan, and the degradation by bacterial activity. Dissolved combined AA (DCAA) showed enrichment in glutamic acid, glycine and threonine, and depletion in aspartic acid and alanine. Bacterial biomass and/or

activity influences DCAA in porewaters more than AA in the sediments. Phenylalanine was abundant in the dissolved free AA (DFAA). Both aromatic and acidic AA are generally concentrated in diatom cell protoplasm, which is more rapidly degraded than cell-walls. Good correlation between aspartic acid and carbonate contents in the sediments and poor correlation in the settling particles indicates that aspartic acid is significantly controlled by the reaction or adsorption with carbonates during early diagenesis. Abundant occurrence of clay minerals in sediments would be responsible for the enhanced accumulation of basic AA and arginine. During diagenesis, bulk Corganic/N ratios are mainly controlled by more contribution of ammonium, which is incorporated into the lattice of clay minerals, not by the compositional change in AA. Microbial degradation continued to reduce AA and OM in the sediments, which has implications for appreciable under-estimates of paleoproductivity.

B11B MCC: Hall C Monday 0830h

Aqueous Microbial Geochemistry: Extreme and Contaminated Environments I Posters (joint with H, OS)

Presiding: M E Kauffman, Idaho National Engineering and Environmental Geomicrobiology Group; L A Warren, McMaster University

B11B-0722 0830h POSTER

The Reductive Immobilization of Pertechnetate by Bioreduced Sediments

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Sediments from the Hanford Site, WA, and Oak Ridge, TN, were incubated for up to 60 d with *Shewanella putrefaciens*, washed and pasteurized, then contacted with 20 micromolar pertechnetate. The clastic Hanford sediment was fluvioacustrine in origin, and the Oak Ridge sediment was fine weathered shale. In Hanford sediment only 1% of the total Fe (8 wt. %) was reduced after 50 d incubation; in Oak Ridge sediment 18% of the total Fe (5 wt. %) was bioreduced, 72% of the Hanford Mn (1 wt. %), and all of the Oak Ridge Mn (0.2 wt. %) were bioreduced. Mn(III/IV) oxides buffered the sediment redox potential and inhibited Tc(VII) reduction. Examination by EMP and XMP showed the absence of discrete Mn(II) solids after bioreduction. Individual microXANES analyses of Hanford sediment indicated the presence of Mn(II) and Mn(III/IV), even after Mn bioreduction reached a terminal state after 23 d. In Hanford sediment Tc(IV) was associated with Fe-Mn oxides and weathered biotites including interlamellar Fe-Mn oxides. On the biotites, Tc(IV) was concentrated at grain boundaries, where Fe and Mn were most available to microbial reduction. In Oak Ridge sediment, Tc(IV) was associated with one of two morphotypes of weathered shale.

B11B-0723 0830h POSTER

Metal Reduction and Mineral formation by a Psychrotolerant Fe(III)-Reducing Bacterium Isolated from an Iron-Rich Waters near a Hydrothermal Vent

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Although dissimilatory metal reduction and mineral formation under mesophilic and thermophilic conditions are extensively examined, they are poorly understood under low temperature. The objective of this study was to examine metal reduction and mineral

formation using a psychrotolerant iron-reducing bacterium (*Shewanella alga*, PV-4) isolated from iron-rich waters associated with the Naha vents off the Hawaiian coast. The psychrotolerant iron-reducing bacterium was able to use lactate, formate, and hydrogen as an electron donor while reducing Fe(III)-citrate, Fe(III)-EDTA, Co(III)-EDTA, Cr(VI), Mn(IV), and iron oxyhydroxide (FeOOH) at temperatures between 0 and 37°C. The psychrotolerant bacterium exhibited diverse mineral precipitation capabilities including the formation of magnetite (Fe₃O₄), siderite (FeCO₃), and rhodochrosite (MnCO₃). Transmission electron microscopic data showed that PV-4 formed mainly superparamagnetic magnetite at temperatures ranging from 0 to 14°C and formed mainly single-domain magnetite at temperatures ranging from 18 to 37°C. This study indicates that iron-reducing bacteria may contribute to the biogeochemical cycling of metals and carbon at low temperatures and may contribute to the natural remnant magnetism of marine sediments.

B11B-0724 0830h POSTER

Metal Reduction and Mineral Formation by an Alkaliphilic Fe(III)-Reducing Bacterium Isolated from an Alkaline Leachate Pond

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Microbial metal reduction plays an important role in biogeochemical cycling of carbon and has the potential for immobilizing metals and radionuclides in diverse environments. The objective of this study was to examine metal reduction and mineral formation using an alkaliphilic bacterium, *Alkaliphilus* (QYMF), isolated from a leachate-pond containing high levels of salt (Na concentration = 440 - 12,100 ppm) and boron (2,000 - 3,000 ppm) at pH 9.0-10.0. The bacterium was able to use lactate, acetate and hydrogen as alternative electron donors and Fe(III)-citrate, Fe(III)-EDTA, selenate, Cr(VI), Co(III)-EDTA, and iron oxyhydroxide (FeOOH) as electron acceptors. The reduction of Fe(III)-citrate and Fe(III)-EDTA in the presence of H₂PO₄ and boron resulted in the precipitation of vivianite [Fe₃(PO₄)₂8H₂O]. Formation of sparingly soluble precipitates, mediated by the alkaliphilic Fe(III)-reducing bacterium, may sequester iron, phosphate, and other metals into more stable and less toxic forms. These results suggest that bioremediation of metal-contaminated alkaline environments may be feasible, and that the process of metal-reduction may occur in alkaline habitats.

B11B-0725 0830h POSTER

Effect of Sediment Mineralogy on Microbiologically Induced (DMRB) Changes in Divalent Metal Speciation

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Dissimilatory metal reducing bacteria (DMRB) can either directly mediate or indirectly induce geochemical processes that alter the speciation and lability of metallic contaminants within natural environments. Most investigations into the effect of DMRB on metal speciation utilize synthetic iron oxyhydroxide minerals as the Fe(III) source, thereby allowing well-controlled experiments. However, this technique does not emulate the actual mineralogical composition of natural systems and does not account for the small-scale heterogeneity that may control metal geochemistry within these systems. Our experiments with a divalent metal that is subject to both surface complexation and ion exchange reactions (Zn²⁺) indicate that clay minerals place an important control on DMRB-induced changes in metal speciation. Our data demonstrates that microbial Fe(III) reduction alters the proportion of Zn-aq