

in H-C-O-Si bonds are formed, consistent with recent experiments (Benner et al., 2003). But even for this structure, the difference between calculated shift (-152 ppm) and observed shift (-141 ppm) is slightly beyond computational error. The hyper-coordinated organosilicates were observed in the NMR experiments at extreme pHs, and high starting concentrations of the organic and of silicic acid. Energy calculations, however, suggest that penta- and hexa-coordinated organosilicates are unlikely to be stable at the pHs and total dissolved silicon concentrations of ambient ocean water, and at the ambient pH 5 found within the silica deposition vesicle of the diatom. Further, results show that it is silicic acid is the most likely form taken up from ocean water, and that it is energetically favorable to form quadra-coordinated organosilicates for storing silicon intracellularly, thus increasing silicon solubility until required for silica precipitation.

URL: <http://www.geology.wisc.edu/people/display.html?id=36>

B21A-05 0900h

Amorphous Calcium Carbonate in Biom mineralization: Stable and Precursor Phases

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The biological formation of the crystalline polymorphs of calcium carbonate, aragonite and calcite, is widespread. The less stable polymorphs, vaterite and monohydrocalcite are also formed by some organisms. Surprisingly, the highly unstable phase, amorphous calcium carbonate (ACC), is formed by a variety of organisms from different phyla. Most of these are stable at least within the lifetime of the organism. The stable forms all have a stoichiometry of CaCO₃.H₂O. Despite the fact that they do not diffract X-rays. Studies of their short range order by EXAFS, reveal species specific variations in the number and distances of atoms that surround the calcium ion. Proteins extracted from stable biogenic ACC are able to stabilize the phase in vitro. ACC has also been identified as a transient precursor phase during the formation of the calcitic larval spicule of the sea urchin and the formation of the larval shell of a bivalve. The transient form has little or no water associated with the CaCO₃. Preliminary EXAFS data suggest that the short range order of the sea urchin spicule transient ACC resembles calcite. Proteins extracted from these spicules are able to stabilize ACC provided Mg is present in the solution. As the molluscs and the echinoderms are on two different branches of the animal phylogenetic tree, it is conceivable that the strategy of using ACC as a precursor phase at least for larval mineralization may be widespread. It has yet to be shown that it is used by adults of either phylum. The manner in which organisms precipitate, stabilize and destabilize if necessary, this highly metastable phase of calcium carbonate presents many fascinating and enigmatic questions, whose solutions could well contribute to a better understanding of basic processes in biom mineralization. For more details and references, see Addadi, L., Raz, S. and Weiner, S. (2003). Taking advantage of disorder: Amorphous calcium carbonate and its roles in biom mineralization. *Adv. Mat.* 15, 959-970.

B21A-06 0915h

Oxygen and Carbon Stable Isotope and Sr:Ca Records in Outer and Middle Microstructural Layers of Bivalve Shells (*Mercenaria campechiensis*)

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 $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and Sr:Ca records contained in the aragonitic shells of the northern and southern quahogs (*Mercenaria mercenaria* and *M. campechiensis*, respectively) have been used in paleoclimate and paleoecological studies, although these environmental proxies have not yet been calibrated. Early geochemical studies of quahog shells focused on the outer prismatic layer. Because of innovations in microsampling techniques, recent studies focus on the middle cross-lamellar layer, providing high temporal resolution. Do both microstructural layers record similar profiles of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and Sr:Ca? If not, which layer more faithfully records ambient conditions? Here, we provide a preliminary calibration of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ using shells of *M. campechiensis* and test the hypothesis that both microstructural layers record similar geochemical information. Quahogs were collected alive near Bokeelia, SW Florida. The USGS maintained fortnightly

to monthly temperature and salinity records at this site. These data, together with mixing equations of $\delta^{18}\text{O}_{\text{WATER}}$ and $\delta^{13}\text{C}_{\text{DIC}}$ -salinity, were used to construct predictive model shells. The last 2 years of shell growth were sampled at 0.1-0.5 mm intervals yielding ~100 μg of material that was split for isotopic and elemental analyses. Comparison of model and observed shells reveals a predictable offset in $\delta^{18}\text{O}$, where the model is offset by +1.3‰ relative to the observed shell. When corrected for the offset, $\delta^{18}\text{O}$ shell closely matches the model. Values range from -2.5 to +2.0‰. Profiles of $\delta^{18}\text{O}$ from outer and middle layers are nearly identical. $\delta^{13}\text{C}$ of the middle layer is more variable and can be as much as 2.4‰ more positive than the outer layer. Observed $\delta^{13}\text{C}$ in the middle layer follows the general trend of the model, but winter-spring shell growth is offset by -1.7‰ relative to the model. Sr:Ca ratios from the middle layer can be as much as 0.4 mmol/mol higher than the outer layer. We conclude that either microstructural layer can be used to study variation in $\delta^{18}\text{O}$ because both layers preserve nearly identical profiles. Observed offsets in $\delta^{13}\text{C}$ and Sr:Ca ratios between microstructural layers can potentially complicate calibration and environmental/climate reconstructions. The next phase of our research is to understand the mechanisms that control these offsets and determine which microstructural layer is better suited for geochemical study.

B21A-07 0930h

Biological Control of Uranium Incorporation Into Coralline Aragonite

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Uranium in biogenic carbonates is an important tool in paleoclimate research. In closed systems, its alpha decay to thorium and protactinium provides one of our few independent chronometers. The U/Ca ratio has also been linked to both temperature and carbonate ion variations in the surrounding water. However, an understanding of Uranium's incorporation mechanism into coralline aragonite is still missing. We have used induced fission of U-235 in deep-sea corals, both modern and fossil, to measure the U distribution as it relates to the biogenic precipitation process. Modern deep-sea corals provide a growth environment with constant U isotopic ratio, constant U/Ca, constant temperature and constant carbonate ion concentration. Induced fission, as recorded in a mica mounted flush against the polished coral surface, provides unprecedented spatial resolution and whole sample maps of relative U concentration. We find that modern corals discriminate sharply (over a factor of 4) against U incorporation during initial precipitation. Secondary growth of aragonite around the coral has much higher concentrations with a distribution coefficient close to one. The shape of the U deficient region closely resembles the coral's banding pattern. Deep-sea corals clearly control their U concentration as they first lay down new aragonite. Fossil corals also show this pattern but with a much smaller difference between primary and secondary material. We will present transects of U isotopes in these two sample types to determine if the fossil corals are exchanging U with the surroundings or merely moving U within the coral lattice. These insights into the mechanisms behind U-transport will be invaluable in assessing whether carbonate systems have remained closed, and therefore whether U-series ages are reliable.

B21A-08 0945h

Toward Understanding Sr/Ca and Mg/Ca Signatures in Biogenic Calcite: Nanoscale Observation of Two Distinct Types of Interaction Between Impurity Ions and Growing Calcite

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Sr/Ca and Mg/Ca are widely used as paleotemperature indicators in biogenic carbonates. Although Sr and Mg have similar chemical behavior in some

systems, we show here that they have very different mechanisms of interaction with growing calcite crystals. Minor element signatures in biominerals are complex products of inorganic and biological constraints; understanding how each impurity is influenced by the conditions of growth is key to robust interpretation of paleoenvironments. Using fluid cell atomic force microscopy, we measured step velocities for layer growth of abiotic calcite in supersaturated solutions containing NaCl, CaCl₂, NaHCO₃, and varying amounts of Mg or Sr. For Mg, step velocities monotonically decrease with increasing [Mg] in solution. Sr displays strikingly different behavior by increasing growth rates at low concentrations. To our knowledge, this is the first documented case of an impurity enhancing growth rates compared to the pure system. At higher concentrations, Sr pins kink-sites, blocking growth completely. With increasing concentrations of either impurity, acute (negative) step edges become rounded first, followed by rounding of obtuse (positive) step edges at higher concentrations. We conducted long-term growth experiments with identical conditions in order to measure impurity contents with the electron microprobe. Our results show that both Mg and Sr have a distinct preference for incorporation on obtuse (positive) flanks of growth hillocks. This contrasts with the work of Paquette and Reeder (1995; GCA 59:735), who found Mg partitioning strongly into acute (negative) flanks, while Sr partitioned into positive domains of calcite grown from solutions with high ionic strength and containing multiple impurities at once. This discrepancy suggests that the partitioning of Mg may not be independent of the presence or absence of other impurities. This study demonstrates the critical importance of understanding molecular-scale interactions between trace impurities and vicinal calcite faces. Our ability to unambiguously interpret trace element signatures depends on thorough quantification of the major controls on their incorporation in biominerals.

B21B MCC: Level 2 Tuesday 0830h

Molecular Biogeochemical Processes of Terrestrial Environments IV Posters (joint with H, V, MR)

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

B21B-0701 0830h POSTER

Protection of Organic Matter from Enzyme Degradation by Mineral Mesopores

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Mineral mesopores (2-50 nm diameter) may sequester organic matter (natural and pollutant) and protect it from microbial and fungal enzymatic degradation in soils and sediments. Synthetic mesoporous alumina and silica minerals with uniform pore sizes and shapes were used to test the role of mesopores in protecting organic matter from enzymatic degradation. A model humic compound, L-3-4-dihydroxyphenylalanine (L-DOPA), was sorbed to the internal surfaces of mesoporous alumina (8.2 nm diameter pores) and mesoporous silica (3.4 nm diameter pores) as well as to the external surfaces of nonporous alumina and silica analogues. A fungal derived enzyme, laccase, was added to these sorbate-sorbent pairs in aqueous solution and activity was monitored by oxygen consumption. Though enzyme activity was suppressed in both cases by mineral-enzyme interaction (enzyme inhibition likely due to adsorption of the enzyme), both the rate and total extent of enzyme-mediated degradation of mesopore-sorbed L-DOPA was 3-40 times lower than that of the externally-sorbed analogue. These results provide, for the first time, direct evidence for the viability of the proposed mesopore protection mechanism for the sequestration and preservation of sedimentary organic matter and organic contaminants. Mesopore adsorption/desorption phenomena may also help explain the slow degradation of organic contaminants in soil and sediment and may prove useful as delivery vehicles for organic compounds to agricultural, medical or environmental systems.

B21B-0702 0830h POSTER

Alginic Acid Accelerates Calcite Dissolution

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Accelerated carbonate weathering through biological activity affects both geochemical cycling and the local pH and alkalinity of terrestrial and marine waters. Microbes affect carbonate dissolution through metabolic activity, production of acidic or chelating exudates, and cation binding by cell walls. Dissolution occurs within microbial biofilms - communities of microorganisms attached to stone in an expolymer matrix. We investigated the effect of alginic acid, a common biological polymer produced by bacteria and algae, on calcite dissolution using a paired atomic force microscopy/flow-through reactor apparatus. The alginic acid caused up to an order of magnitude increase in dissolution rate at $3 < \text{pH} < 12$. Additionally, the polymer preferentially binds to the obtuse pit steps and increases step velocity. We propose that the polymer is actively chelating surficial cations reducing the activation energy and increasing dissolution rate. The role of biologically produced polymers in mineral weathering is important in the protection of cultural heritage materials and understanding of marine and terrestrial systems.

B21B-0703 0830h POSTER

Arsenic Cycling Within Bangladesh Sediments: Evidence for an Oxidative Front Causing Solid Phase Repartitioning

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Arsenic is a contaminant in the groundwater of Bangladesh and has resulted in the exposure of millions of people to drinking water above the World Health Organization standard. Solid concentrations of arsenic within the aquifer sediments typically do not exceed world averages, and, therefore, the question arises as to why arsenic is partitioned in the solution rather than the solid phase. To address this question we have obtained well-preserved deep-sediment cores from the Munshiganj District of Bangladesh. Spectroscopic analyses have been conducted to determine the speciation of arsenic, iron, and sulfur within the sediments. Additionally, laboratory studies of the sediments, in conjunction with those on model compounds, have been performed to isolate plausible desorption mechanisms of arsenic and to define the underlying chemical processes controlling arsenic cycling. Our work points to a complex cycling of arsenic in which an oxidative front has caused destruction of arsenic-bearing sulfides (which appear preserved during transport and sediment deposition!) and the concomitant repartitioning of arsenic onto oxidized solids, primarily those of Fe. Subsequent to repartitioning on ferric (hydr)oxide mineral surfaces, microbial reductive dissolution of such phases, stimulated by injection of labile carbon, has led to the concomitant release of arsenic into solution. The entire cycle implies an additional (and previously dismissed) step in the release of arsenic into Bangladesh groundwater. As a consequence, minimizing the drawdown (and thus the oxidative front) or utilizing deeper wells may provide water that is less contaminated with arsenic.

B21B-0704 0830h POSTER

Role of Water on the Fate of Organics in Reduced-Smectite Suspensions

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Clay mineral surfaces serve as a reaction site where interacting organic molecules undergo acid-base and redox transformations. Upon activation of the clay surface, water plays a key role in determining the mechanisms of transformation of adsorbing organics. The focus of this presentation will be on the reaction mechanisms of pesticides, and chlorinated and nitro aliphatics, at clay surfaces which have been modified through chemical or biological oxidation-reduction reactions. The outcome of this study indicates that the oxidation state of structural Fe in the clay strongly influences organic compounds hydration. A mechanism consistent with linear free energy relationships presented herein corresponds to organic compound hydration as the limiting step for adsorption and transformation by redox-manipulated smectites.

B21B-0705 0830h POSTER

Molecular Structure of Water Adsorbed on a Mica Surface

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The molecular structure of water adsorbed on micaceous minerals (2:1 layer-type aluminosilicates) has long been of widespread interest because of its crucial role in geochemical and biological processes. Early conceptualization of this structure imputed to it an icelike character because of its longer relaxation times when compared to bulk liquid water and its potential for epitaxy with the hexagonal array of oxygen atoms on the basal surfaces of mica and 2:1 clay minerals. These speculations have received support periodically from experimental and modeling studies, but recent spectroscopic data suggest that the hydration water on micaceous minerals is more disordered and more labile than ice Ih. Monte Carlo simulations of hydration water on the mica (001) surface under ambient conditions revealed water molecules bound closely to the ditrigonal cavities in the surface, with a lateral distribution of approximately one per cavity, and water molecules (interposed between K^+ counter ions) in a layer situated about 2.5 Å from a surface O along a direction normal to the (001) plane. The calculated water O density profile was in quantitative agreement with recent x-ray reflectivity measurements indicating strong lateral ordering of the hydration water but liquidlike disorder otherwise.

URL: http://www-esd.lbl.gov/GEO/aqueous_geochem/index.html

B21B-0706 0830h POSTER

Landscape Influences on Organic Matter Export From a Midwestern Watershed

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In an effort to characterize relationships between landscape processes and organic carbon export, molecular and stable isotope approaches have been applied to particulate, colloidal, and dissolved organic matter samples from Big Pine Creek watershed; an agriculturally-dominated watershed located in west-central Indiana, USA. Preliminary results from multiple sites within the watershed show that organic matter from this 850 km² watershed is qualitatively similar to samples collected from larger rivers in the western hemisphere, suggesting that small to mid-sized watersheds can play a prominent role in terrestrial organic carbon export. Moreover, carbon-normalized yield data

and bulk stable isotope data from the study area show that relationships between export and stream discharge can be dependant on the size fraction of the organic matter. Dissolved organic matter tends to behave linearly with discharge while particulate organic matter responds in a logarithmic manner. Finally, bulk stable carbon isotopes of samples taken from Big Pine Creek show dramatic shifts from base flow to storm flow conditions showing a shift in organic matter sources during flood events. Taken together, these results show that upland conditions can play an important role in the quantity, quality, and source of organic matter exported from terrestrial systems.

B21B-0707 0830h POSTER

The Influence of Siderophores Produced by Alkaliphilic Microorganisms on Iron and Metal Contaminant Speciation and Solubility

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Halomonas campisalis strain 4A has been identified as capable of producing siderophores under halo-alkaliphilic growth conditions. Because of the scarcity of iron under the alkaline conditions in which Halomonas campisalis thrives, we hypothesize that the siderophores secreted by Halomonas campisalis and other alkaliphilic bacteria will have a stronger affinity for binding and solubilizing ferrous iron than siderophores produced by mesophilic bacteria. Siderophore production by Halomonas campisalis was confirmed through the use of the chrome azural S (CAS) agar plate method which showed a red-orange halo around the bacterial colonies indicative of siderophore production. The siderophores were found to be produced under conditions of both high salinity and pH with a salt concentrations ranging from 0.4 - 1.8 M NaCl and pH ranging from 8 - 11. The siderophores produced have been determined to be of the hydroxamate class via the Csáky method. A negative response to the Arnow assay indicated that the siderophore produced does not contain any catechol moieties in its chemical structure. It was found that maximum siderophore production was equivalent to approximately 400 mM desferrioxamine and occurred during mid stationary phase. Similar results were found at pH 8, 10 and 11. A purification scheme was developed that involved an initial extraction of the siderophore from the growth medium into benzyl alcohol followed by precipitation with diethyl ether. Additional purification was achieved via ion exchange chromatography and size exclusion chromatography. Final purification was achieved via HPLC. The structure of the purified siderophore was analyzed via LC/MS/MS equipped with an ESI source. To date, few studies have included the siderophores produced by microorganisms capable of tolerating highly saline and alkaline environments. In addition to unique structure and high affinity for iron, it is further hypothesized that siderophores from alkaliphilic bacteria will also have a corresponding higher affinity to heavy metal and radionuclide contaminants, thus increasing the mobility of these metals in subsurface environments and influencing contaminant fate and transport. Future work will examine the stability constants for complexes of various metals including uranium with the Halomonas campisalis siderophore.

B21B-0708 0830h POSTER

Effects Of Fungal-Mineral Interactions On Chemical Weathering And Denudation Processes - Observations From Experimental Ecosystems

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A mesoscale (sandbox) lysimeter experiment was performed at Hubbard Brook Experimental Forest, New Hampshire, to study plant-growth influences on chemical weathering and chemical denudation. Weathering was estimated by mass balance for 5 and 15-year intervals, and denudation was monitored as the product of drainage flow and concentration for 20 years in large (7.5x7.5x1.5m) fully lined sandboxes a.) planted with red pine (*Pinus resinosa* Ait.), and b.) kept free of vascular vegetation. Mass-balance equations included base cations (Ca, Mg, and K) in precipitation inputs and drainage outputs, and changes of base cation contents in biomass and soil. Scanning Electron Microscopy (SEM) and Environmental-SEM studies of the coarse sandbox soils were used for detection of mycorrhizal fungal association with roots, fungal development and attachment features on mineral grain surfaces. In the non-vascular system chemical weathering and denudation fluxes did not change significantly during the monitored period, but denudation fluxes were 1.3-1.4 times higher than weathering fluxes. In the vascular ecosystem the chemical weathering flux was 3 and 1.8 times greater than the denudation flux over 5 and 15 years, respectively, but both rates decreased over time. In our experiment the pines retarded denudation and accelerated weathering relative to the nonvascular system, thereby increasing available nutrient pools. The SEM and ESEM studies indicated more weathering features (etch pits, cracks, wholes, channels, and secondary minerals) in the mineral surfaces of the vascular system associated with the mycorrhizal fungal hyphae. Profiles of base-cation concentrations in soil water suggest that hypal-mineral surface attachment might also insulate cation uptake from bulk soil water and hydrologic loss. The sandbox study offers insight into short-term effects of ecosystems on global biogeochemical processes.

B21B-0709 0830h POSTER**How the Structure of Aluminum Goethite Affects Iron Release**David C. Edwards¹ (609.258.4124; dcedward@princeton.edu)Javiera Cervini-Silva² (510.642.9690; javiera@eps.berkeley.edu)Garrison Sposito³ (510.642.2940; gsposito@nature.berkeley.edu)Satish C.B. Myneni^{4,5} (609.258.5848; smyneni@princeton.edu)¹Princeton University, Department of Chemistry Frick Laboratory, Princeton, NJ 08544, United States²University of California-Berkeley, Department of Earth and Planetary Sciences 151 Hilgard Hall, #3110, Berkeley, CA 94720, United States³University of California-Berkeley, Department of Environmental Science, Policy and Management 151 Hilgard Hall, #3110, Berkeley, CA 94720, United States⁴Princeton University, Department of Geosciences Guyot Hall, Princeton, NJ 08544, United States⁵Lawrence Berkeley National Lab, Lawrence Berkeley Lab Division of Earth Sciences 1 Cyclotron Road Mailstop 90R1116, Berkeley, CA 94720, United States

Aluminum substitution for Fe in iron(hydr)oxides often occurs in nature and is known to affect mineral weathering, Fe cycling and Fe bioavailability because it alters crystal growth rate, domain morphology, surface area, and other structural properties that influences the rates and mechanisms of mineral biodissolution and iron mobility. Of particular interest is how the structural changes of goethite associated with aluminum substitution ($\text{Fe}_{1-x}\text{Al}_x\text{OOH}$) influence solubilization of Fe by siderophores, organic ligands secreted by bacteria to selectively complex Fe(III) in iron-limiting situations. This study examines the effect of crystallinity in a series of synthetic aluminum goethites ($x = 2, 4, 6, \text{ and } 10$) on the adsorption of desferrioxamine-B (DFO-B) and oxalate and on the release kinetics of iron by these two ligands at pH 5. At low [DFO-B] and irrespective of Al-content, a poor relation between adsorption of DFO-B and the release kinetics of iron is observed, giving a strong indication that the surface density of the ligand and soluble iron concentration alone do not suffice to explain mineral dissolution kinetics. Attenuated total reflectance-Fourier transformed infrared spectroscopy analysis of the aluminum goethite samples show shifting of the central band in the 400-500 cm^{-1} region to higher frequencies with increasing Al substitution, a signature of oxygen displacement. The shifting of the bands at 400 cm^{-1} occurs at a greater extent than those observed

at $> 800 \text{ cm}^{-1}$, which confirms replacement of iron by aluminum, because of increased O^{2-} - O^{2-} repulsion. A consequence is the protonation of more stoichiometric oxygens in the structure and the formation of more stable hydroxyl units. Hydroxyl deformation and water bending vibrations indicate there are energetic constraints on the detachment of structural hydroxyl units during mineral dissolution. X-ray absorption (XANES and Al-EXAFS) spectra provided evidence for changes in the orientation and the structure of the unit cell with increasing aluminum content. These findings support the idea that structural aberrations associated with aluminum insertion in goethite bring about redistribution of OH groups in various crystal faces, and affect the dislocation of iron structural units following weathering.

B21B-0710 0830h POSTER**Effects of Organic Chelation on the Behavior of Aluminum Relative to Gallium During Pedogenesis**Meghan M Herz¹ (607-255-6329; mmh28@cornell.edu)Louis A Derry¹ (lad9@cornell.edu)¹Cornell University, Department of Earth and Atmospheric Sciences, Ithaca, NY 14853, United States

This study of gallium and aluminum behavior in the soil weathering environment provides a first step toward using Ga/Al as a tracer of aluminum dynamics during pedogenesis. Previously, the interpretation of aluminum behavior in soils was confounded by the monoisotopic nature of aluminum and its subsequent lack of a comparative tracer. Like aluminum, gallium is a strongly hydrolyzing group III element. It is included in the same mineral systems as aluminum and the two are believed to have similar chemistries in most natural environments. Aluminum is a highly toxic metal whose removal from mineral matrices is enhanced by acid deposition and chelation by organic ligands. As much as 80% of dissolved aluminum in upper soil horizons can be complexed by organic ligands, most of which are secreted by plant and soil microorganisms to detoxify their surroundings. However, gallium makes comparatively unstable complexes with organic chelators, and is not expected to be carried into solution or leached from the soil profile by them to the same extent as aluminum. The Hawaiian Islands provide a unique opportunity to study the evolution of aluminum and gallium concentrations during soil development along gradients where age or climate varies, but all other soil forming factors are held constant. Ga/Al in older and more intensely weathered soils can be as high as 2.58 (mg/g), whereas the basaltic parent material is almost 10 times lower (0.30 mg/g). The factor driving soil Ga/Al ratios away from those found in parent material may be the strong control that organic chelation exerts over aluminum mobility. The enhancement of aluminum dissolution by organic chelation can be inferred from the decrease in Ga/Al ratios of exchangeable cations along a gradient of increasing rainfall; where wetter, more organic rich sites have Ga/Al ratios 10 to 100 times lower than drier sites where organic chelation is a less important factor in driving aluminum dynamics. Along this same gradient, the bulk soil shows an increase in Ga/Al despite an overall loss of both metals, indicating a relative enrichment of gallium in the secondary minerals. The results of preliminary laboratory syntheses of allophane minerals show that there is no significant fractionation of aluminum and gallium during secondary mineral formation in the absence of organic chelators.

B21B-0711 0830h POSTER**An Investigation of Black Carbon Degradation Potential in a Forest Soil Environment**Hockaday C William¹ (614-688-4353; whockada@chemistry.ohio-state.edu)Eunjee Lee¹ (614-688-4353; elee@chemistry.ohio-state.edu)Amanda Grannas¹ (614-292-7637; agrannas@chemistry.ohio-state.edu)Patrick G. Hatcher¹ (614-688-8799; hatcher@chemistry.ohio-state.edu)¹The Ohio State University Department of Chemistry, 100 W. 18th Ave., Columbus, OH 43210, United States

Except for emission processes, there is currently little understanding of the mechanisms driving the degradation and biogeochemical cycling of black carbon (BC). Considering current estimates of the global BC pool ($>2,500 \times 10^{15} \text{ gC}$), and its annual emission rates ($55\text{-}205 \times 10^{12} \text{ gC/year}$), BC represents roughly 16% of Earth's actively cycling organic carbon. Without significant chemical and biological degradation pathways, all of the actively cycling carbon on earth would have

accumulated as charcoal in $<100,000$ years. This investigation show that charcoals recovered from experimental forest fires are altered significantly by microbial colonization, and mineral complexation during exposure to soil processes. Charcoal surface morphology and elemental composition were characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, and BET surface area measurements. The influence of 90 years aging upon carbon functionality was probed by solid-state ^{13}C NMR spectroscopy. The prevalence of fungal mycorrhizae in these forest soil charcoals also motivated an investigation of black carbon degradation via extracellular enzymes and acids known to be exuded by mycelia. Degradation is quantified by carbon loss, and soluble products are examined by mass spectrometry.

B21B-0712 0830h POSTER**Microbially-mediated Iron Dissolution and the Potential for Radionuclide Redistribution**Joseph G Lack¹ (505-665-2040; lack@lanl.gov); DelisMaldonado¹ (delmaort@yahoo.com); TessaRivera¹ (tes_riv@yahoo.com); Jennifer Forsythe¹(jforsyth@nd.edu); Hakim Boukhalfa²(hakim@lanl.gov); Christy Ruggiero²(ruggiero@lanl.gov); Mary Neu² (neu@lanl.gov);Samuel Traina³ (sam.traina@ucop.edu); LarryHersman¹ (hersman@lanl.gov)¹Los Alamos National Laboratory, Bioscience Division (B2) MS M888, Los Alamos, NM 87545, United States²Los Alamos National Laboratory, Actinide, Catalysis, and Separations Chemistry (C-SIC) MS J514, Los Alamos, NM 87545, United States³University of California-Merced, Sierra Nevada Research Institute P.O. Box 2039, Merced, CA 95344, United States

Investigation into microbial iron dissolution and the effects on radionuclides associated with Fe-containing minerals is of significant importance in determining the distribution and fate of actinides (e.g. uranium, plutonium, neptunium) in contaminated environments. Nearly all microorganisms have a metabolic requirement for iron at 10^{-7} M for growth and survival. Iron, while abundant, only has a solubility product in the range of 10-39 to 10-44 M Fe that limits its available concentration in the environment to 10^{-17} M. Thus, microorganisms are faced with a discrepancy of 10 orders of magnitude to overcome in acquiring Fe needed for growth. Experiments were performed with two ubiquitous aerobic Pseudomonads (*Pseudomonas mendocina* and *P. putida*) to determine their ability to grow on iron-deficient media utilizing insoluble Fe-oxides as well as soluble Fe as their iron sources. Bacterial growth was observed indicating that the bacteria are actively sequestering Fe from the minerals via dissolution mechanism(s). Moreover, different pathways of dissolution used in obtaining iron from different Fe-oxides (ferrihydrite, goethite, and hematite) were quantified by determining siderophore production - an average of $4\text{-}6 \times 10^{-13}$ mmol x cell⁻¹ when the cells were grown on either of the three minerals studied, while as expected much more siderophore was generated on a per cell basis in the no Fe control, $15\text{-}16 \times 10^{-13}$ mmol x cell⁻¹, and much less in the readily accessible soluble Fe control (FeEDTA), 1.5×10^{-13} mmol x cell⁻¹; and reductant production - an average of about $1\text{-}4 \times 10^{-18}$ mol x cell⁻¹ both cell associated and in the supernatant for hematite, goethite, and FeEDTA, while the cells grown on ferrihydrite produced a much greater amount of reductant per cell, $14\text{-}26 \times 10^{-18}$ mol x cell⁻¹ and the no Fe control $6\text{-}9 \times 10^{-18}$ mol x cell⁻¹. These studies of different dissolution mechanisms are not only significant from a geomicrobial view on iron distribution and cycling in the environment, but also important in the possible remobilization/solubilization of radionuclides once considered immobile as bound to/within insoluble Fe-oxides. However, little investigation has been made in aerobic environments contaminated with radionuclides. Radionuclide distribution within these environments is effected by indigenous biogeochemical processes, including the metabolic activities of aerobic microorganisms. Fe is chemically similar to several actinides, two being uranium (U) and plutonium (Pu). It is reasonable then to hypothesize that the metabolic processes of ubiquitous aerobic bacteria, such as *P. mendocina* and *P. putida*, driven by the acquisition of Fe, could also significantly effect the distribution of U and Pu in a contaminated environment. Initial studies performed on U(VI)-loaded hematite have indicated that *P. mendocina* does effect the solubility and distribution of U(VI) during growth of the bacterium in Fe-deficient media with the hematite as its source of iron. Uranium loaded onto the mineral has been measured back in solution to greater extents with bacterial growth cultures present than when no cells are added. Further experiments are now being modified and performed in order to determine the different parameters involved in resolubilization of radionuclides from Fe-oxides

B21B-0713 0830h POSTER

Agent-Based Modeling of Physical Factors That May Control the Growth of *Coccidioides immitis* (Valley Fever Fungus) in SoilsMark E Gettings¹ (mgetting@usgs.gov)Frederick S Fisher¹ (ffisher@swfo.arizona.edu)¹U.S. Geological Survey, 520 N. Park Ave, Rm 355, Tucson, AZ 85719, United States

A model of the spread and survival of the fungus *Coccidioides immitis* in soil via wind-borne spore transport has been completed using public domain agent-based modeling software. The hypothetical model posits that for a successful new site to become established, four factors must be simultaneously satisfied. 1) There must be transport of spores from a source site to sites with favorable soil geology, texture, topographic aspect, and lack of biomass competition. 2) There must be sufficient moisture for fungal growth. 3) Temperature of the surface and soil must be favorable for growth. Finally, 4) the temperature and moisture must remain in favorable ranges for a long enough time interval for the fungus to grow down to depths at which spores will survive subsequent heat, aridity, and ultraviolet radiation of the hot, dry season typical of the Southwest U.S. climate. Using agent-based modeling software, a model was built so that the effects of combinations of these controlling factors could be evaluated using realistic temperature, rain and wind models. The rain probability and amount, temperature annual and diurnal variation, and wind direction and intensity were based on the weather records at Tucson, Arizona for the 107-year period from 1894 to 2001. Favorable ground was defined using a fractal tree algorithm that emulates a drainage network in accordance with observations that favorable sites are often adjacent to drainage channels. Numerous model runs produced the following five conclusions. 1) If any property is not isotropic, for example wind direction or narrow paths of rainstorms, parts of the favorable areas will never become colonized no matter how long the model runs. 2) The spread of sites is extremely sensitive to moisture duration. The amount of wind and temperature after a rain control the length of time before a site becomes too dry. 3) The distribution of wind and rainstorm direction relative to that of the favorable sites is a strong control on the spread of colonization. East-west winds across an area that has mostly north-south favorable sites restricts spread strongly. 4) Soil temperature was the least sensitive control in the model, although it does control the ultimate dormancy of a site. Fifth, the model results cover the spectrum of complete colonization of all favorable sites from a few source sites to none, one, or two new sites in three years of model simulation. This implies the probability of new sites depends on the four factors in a Bayesian way. These results indicate that the complexity introduced in the model from site favorableness, temperature, moisture, and duration of favorable temperature and moisture conditions is adequate to explain observed distributions of real sites.

B21B-0714 0830h POSTER

Variations in Particulate Organic Matter Across the Drake Passage

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Modeling studies have shown that the Southern Ocean plays an important role in the global carbon cycle and is a relatively large sink for anthropogenic CO₂. The formation, sinking, and eventual burial of particulate organic matter (POM) is a crucial component of this cycle, which removes gaseous carbon from the short-term atmospheric system and deposits it in a long-term sedimentary system. This study analyses surface POM from five cruise tracks taken between 1997 and 2002 across the Drake Passage between 54.11 S and 67.22 S. We determine the relationship between the stable carbon and nitrogen isotopes of the POM from underway samples and the pCO₂, temperature, and salinity of the surface water for these cruises. The δ¹³C of these samples, a proxy for productivity, ranges from -18.13 per mil to -33.40 per mil, with the least negative values closest to South America. The isotope values become more negative further south, showing the highest levels of seasonal variability (11 per mil) around 65 S at the approximate location of the Antarctic Divergence. The δ¹³N record, a proxy for nutrient utilization, shows an equally large range from -7.22 per mil to 8.64 per mil. Like the carbon isotopes, these nitrogen POM isotopes exhibit the highest values near South America. Between 54 S and 56 S, the values drop to -4 per mil and then show an increasing trend further

southward, with a relative maximum at 65 S. The nitrogen POM isotopes show considerable seasonal variability throughout all five of the tracks studied here. We use this data to define the latitudinal and seasonal variation of these parameters, as well as address the significance of the seasonally varying locations of water fronts across the Drake Passage.

B21B-0715 0830h POSTER

Effects of Microbial Colonization, Liquid Flow and Textural Heterogeneities on Gas-Phase Transport in Unsaturated Systems

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Gaseous flow dynamics in unsaturated media were examined with respect to microbial colonization, liquid flow rates, and textural heterogeneities. A light transmission chamber consisting of two glass sheets mounted in an aluminum frame in front of a light bank was packed with translucent quartz sand and brought to unsaturated conditions. To visualize gas transport, carbon dioxide was introduced to the chamber at varying rates in combination with different liquid flow rates and textural inclusions. A methyl red pH indicator solution was used in conjunction with a liquid-cooled camera to monitor carbon dioxide concentrations and infer transport dynamics throughout the system. To explore whether gas-phase nutrients would stimulate microbial growth, acetate and ammonia vapors were pumped through a chamber inoculated with *Pseudomonas fluorescens* HK44. Naphthalene vapor pulses were used to induce bioluminescence, allowing imaging of responsive colonies.

B21B-0716 0830h POSTER

Influence of Pedogenic Iron-oxyhydroxides on the Ge/Si Weathering Tracer

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Germanium/silicon ratios are a promising tracer of the silica cycle in both marine and terrestrial environments. Prior work shows that Ge/Si ratios are fractionated by at least two distinct mechanisms in the weathering environment: sequestration of Ge by soil clay minerals and biological fractionation during plant phytolith formation. Ge may also be sequestered by pedogenic iron oxyhydroxides, resulting in a decoupling of the Ge and Si geochemical cycles. Ge/Si ratios in Hawaiian soils are high (3.5-25 μmol/mol) relative to the ratio in the basaltic parent rock (2.5 μmol/mol). We are examining Ge behavior in a well-characterized climate gradient on the Hawaiian island of Maui to elucidate the relationship between Fe geochemistry and Ge/Si ratios. The Maui precipitation gradient is made up of 7 sites on the flank of Haleakala Volcano ranging in mean annual precipitation from 875 mm rain/year to 5066 mm rain/year (Schurr et al., 2001). All sites are developed on ~400 ka parent material and are highly weathered (>80% Si loss relative to immobile Nb). Sites experiencing less than 3338 mm rain/year display characteristics typical of oxic, highly weathered basaltic soils. In these soils, Fe weathered from parent material is not mobile and accumulates as secondary Fe(III) minerals (ferrihydrite). The wetter sites (>3338 mm/yr) show evidence of extensive Fe reduction, resulting in mobilization and loss. Ge/Si ratios in relatively dry sites (<3338 mm rain/year) are as high as 21 μmol/mol, nearly 10 times higher than parent rock ratios. Fe-depleted horizons in the wettest sites have Ge/Si ratios as low as 3.5 μmol/mol. Reductive loss of Fe-oxyhydroxides results in a dramatic drop in Ge/Si ratios, suggesting that Ge is in part accumulating in the Fe oxyhydroxide component of soil. However, nearly Fe-free soils maintain Ge/Si ratios elevated with respect to parent material, consistent with partitioning of Ge into secondary soil aluminosilicates. Regardless, the influence of pedogenic Fe-oxyhydroxides must be taken into account when using the Ge/Si system as a weathering tracer.

B21B-0717 0830h POSTER

Tracing Terrestrial Silica Cycling Using Ge/Si Ratios, Luquillo Mountains, Puerto Rico

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Ge/Si ratios are fractionated by several processes in the weathering environment, potentially providing insight on silicate weathering processes and providing a tracer of Si sources in streamwater. We are analyzing Ge/Si ratios in soils, soilwaters, streams, and plants from the USGS Luquillo Water, Energy and Biogeochemical Budgets research watershed in Puerto Rico in an effort to apply this tracer system to granitoid weathering in a tropical environment. This system has many features in common with our previous work in the Hawaiian Islands, but the mineralogy here is more complex and more globally representative. Bedrock is a quartz diorite pluton with a Ge/Si ratio of 2.4 μmol/mol. Soil and saprolite ratios range from 2.6 to 3.6 μmol/mol. Soil Ge/Si ratios are lower than ratios measured in basaltic soils due to the accumulation of primary quartz with a low (0.5 μmol/mol) Ge/Si ratio. Soil kaolinite has a Ge/Si ratio of 5.9 μmol/mol demonstrating preferential partitioning of Ge into secondary soil clays. Nine common plant species were sampled from the Luquillo site to investigate the role of plants in the terrestrial silica cycle. Many plant species contain abundant opal phytoliths (as much as 4.4 wt% SiO₂ in aboveground biomass). Consistent with our work in Hawaii, plant phytolith opal at Luquillo has very low Ge/Si ratios (0.05 to 0.6 μmol/mol). Recycling of phytolith opal likely explains surface (top 20 cm) maxima in soil-saprolite porewater [Si] profiles measured in lysimeter samples. Globally, most streams have Ge/Si ratios that vary with discharge and can be explained by mixing of a low-Ge/Si, high [Si] component, and a high Ge/Si, low [Si] component. Our prior work in Hawaii suggests that the low Ge/Si ratios commonly seen in streams reflect a contribution of plant-cycled Si that is particularly important at base flow. We will test this model with samples collected this fall by automatic streamwater samplers during storm events at two gauged stations in the Río Icacos basin.

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B21C MCC: Level 2 Tuesday 0830h

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

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

B21C-0718 0830h POSTER

Soil Microbial and Enzymatic Responses to Complex and Labile Nutrient Inputs

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Microbial extracellular enzymes are essential for converting complex organic compounds into smaller molecules that are available for plant and microbial uptake. However, enzyme production represents a substantial resource cost for microbes, and microbes may be under selection to produce enzymes only when benefits exceed costs. We predicted that soil enzyme activities would be highest when complex substrates were abundant, but available nutrients were scarce (large potential benefit from enzyme production). We also predicted that rates of nutrient and carbon mineralization would correspond to observed shifts in enzyme activities. To test these predictions, we added insoluble