

To assess the relative influence of mesoclimate stand replacing disturbance on the NEP (Net Ecosystem Production) of Oregon forests, we used biometric techniques to measure NEP at 36 independent forest plots arranged as three replicates of four age classes in each of three climatically-distinct ecoregions. Among hemlock-spruce forests growing in the coastal fog belt, NEP ranged from 200 to 600 gCm⁻²y⁻¹ with the highest rates occurring in the youngest age classes (10-20 years following disturbance) and the lowest rates occurring in the oldest age classes (>100 years following disturbance). Among Douglas fir forests growing in the W. Cascades, NEP ranged from -200 to 500 gCm⁻²y⁻¹ with the highest rates occurring in the intermediate age classes (50-150 years following disturbance) and the lowest rates occurring in the oldest age classes (>400 years following disturbance). Among ponderosa pine forests growing in the semiarid plateau of the E. Cascades, NEP ranged from -200 to 200 gCm⁻²y⁻¹ with the highest rates occurring in the intermediate age classes (50-150 years following disturbance) and the lowest rates occurring in the oldest age classes (>200 years following disturbance). For the most part, heterotrophic respiration remain similar across age classes. As such, successional trends in NEP are driven primarily by net primary production and in particular, wood production. Among stands of the same age, Oregon's edaphoclimatic gradient causes NEP to vary 90% of the regional mean. Among stands in the same ecoregion, NEP varies 140% over development following stand replacing disturbance. However, disturbance history and recovery rates on this landscape are such that some developmental stages occur less frequently than others. Consequently, the regional variation in NEP attributable to disturbance is only 60% of the mean. Simulations of age class distribution under varying disturbance frequencies suggest that the sensitivity of landscape-level NEP to disturbance regime change is highest in the W. Cascades, lowest in the E. Cascades and intermediate in the Coast Range.

B12G-08 1745h

Integrating Multiple Sources of Terrestrial Observations to Calibrate Carbon Models

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In Australia, ENSO driven climate variation plays a major role in determining inter-annual variability of net C-exchange between the land surface and the atmosphere. Annual to decadal climate variation governs C-pool dynamics and fire regimes which exert a major control on net sources and sinks on these timescales. Furthermore, a major difficulty in calibrating large scale carbon models is poor data availability. In this case, it is advantageous to exploit as many different sources of information as possible to estimate model parameters. In this presentation, we demonstrate a multiple constraints' approach to parameter estimation that combines net primary production, plant, litter and soil C observations. The method uses a genetic algorithm to solve a multi-objective optimization problem in which we minimize differences between predicted and observed long term averages of plant, litter and soil C pools while estimating parameter values. The estimated parameters were then used in the dynamical C model VAST1.2 to quantify variability in net C-exchange of the Australian continent over a 20 year period (1981 - 2000) arising from climate variability effects on both decomposition and fire. Predicted continental monthly net C exchange varied by up to 77 TgC/month from a source of 28 TgC/month to a sink of 49 TgC/month. The 95% confidence intervals of monthly net C-exchange showed that the continent could be either a source or a sink of C in any month between February and October depending on prevailing ENSO conditions. For the remaining months (November to January), the continent was a source of C to the atmosphere. Annual total net primary production varied more than two-fold between 470 and 1032 TgC/year and annual net C-exchange varied between a sink of 118 TgC/year and a source of 80 TgC/year. We also compared modeled continental net C-exchange with published troposphere CO₂ measurements over the western Pacific Ocean and show good qualitative agreement between predicted continental net C flux and atmosphere CO₂ concentration growth rate, suggesting that VAST1.2 has accurately reproduced the phase of sources and sinks for Australia.

B21A MCC: 3014 Tuesday 0800h

Biom mineralization Processes and Mechanisms II (joint with H, OS, V, MR)

Presiding: L Wasylenki, Virginia Polytechnic Institute and State University; S Weiner, Weizmann Institute of Science

B21A-01 0800h INVITED

Reductive Dissolution of Iron Oxides and Iron-Rich Clays Enhanced by Sulfate-Reducing Bacteria

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Iron oxides and iron-rich clays are abundant in low-temperature sedimentary environments where sulfate-reducing bacteria are also present. This study summarizes our research on reductive dissolution of ferrihydrite, goethite, hematite, magnetite, and a nontronite clay by *Desulfovibrio* spp. strain G-20 and strain G-11. The goal was twofold: (1) to understand the enzymatic processes of iron reduction by sulfate-reducing bacteria (SRB) using iron as the sole electron acceptor and (2) to determine whether iron reduction from the oxides and clays could be enhanced by biogenic H₂S through an enzymatic process during sulfate reduction. In the iron-oxide experiments without sulfate, iron reduction by G-20 averaged about 4.5% of total iron for ferrihydrite, goethite, and hematite. The reduction of magnetite, however, was about threefold higher (13.3%). The maximum biomass of G-20 gained during iron reduction was also highest in the magnetite culture, suggesting that reduction of magnetite may have stimulated the growth of G-20. In the presence of sulfate, iron reduction was dramatically enhanced in all cultures (>70%). In inorganic experiments using Na₂S, less than 4% total iron was reduced from goethite or hematite and about 19% was reduced from magnetite. The enhanced reduction of iron during sulfate reduction may have resulted from enzymatic activity of the SRB or through the chelation of solids with organic acids and other organic molecules. Transmission electron microscopy (TEM) showed shortened and thinned goethite and hematite crystals during sulfate and iron reduction. The magnetite crystals, on the other hand, were disintegrated extensively. For the nontronite experiments using G-11, iron reduction from the clay was about 10% of total structural Fe(III) in the absence of sulfate but reached 29% in the presence of sulfate. Abiotic iron reduction using Na₂S, on the other hand, was ca. 7.5% of total structural Fe(III). Analyses of TEM and X-ray diffraction revealed significant changes in structure and composition of the clay during its dissolution by G-11. Overall, this study demonstrates that sulfate-reducing bacteria can dramatically enhance the dissolution of iron oxides and iron-rich clays, thus accelerating the transformation of these minerals in sulfate-rich environments.

B21A-02 0815h INVITED

Molecular Mechanisms of Iron Oxyhydroxide Biomineralization

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Neutrophilic iron-oxidizing microbes such as *Gallionella* and PV-1 (Emerson and Moyer, 1997) extrude polymers that become encrusted with iron oxides. Little is known about the identity of these polymers, their biological function and the roles they play in mineralization. To this end, we are investigating iron oxidizers in natural terrestrial iron-rich microbial mat communities, culturing and characterizing them in the laboratory and performing abiotic synthesis experiments based on the natural mineralization processes. Our sampling site is in a flooded former lead-zinc

mine in Tennyson, WI, which is host to thick reddish-orange microbial mats. Scanning and transmission electron microscopy studies show that the mat is composed of iron oxide-covered stalks and sheaths (like those formed by *Gallionella* and *Leptothrix* spp.), as well as tangled masses of mineralized filaments. There is evidence of polymer influence on mineral phase and morphology in the form of extremely thin (few-unit cell wide), microns-long akaganite (β -FeOOH) crystals at the center of these mineralized filaments. We are using synchrotron-based X-ray spectromicroscopy (PEEM-photoelectron emission microscopy and STXM-scanning transmission X-ray microscopy), which has the ability to give chemical information on heterogeneous samples at high spatial resolutions. Both PEEM and STXM show that these filaments contain polysaccharides, which are likely templating the akaganite formation. Initial iron oxide synthesis experiments using model microbial polysaccharides support this hypothesis. Further synthesis and characterization by X-ray absorption and infrared spectroscopy methods is being performed in order to elucidate the molecular mechanisms of mineral nucleation and growth.

B21A-03 0830h

Structural Characterization of Biogenic Manganese Oxides Produced in Sea Water

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Manganese oxides have been coined as the "scavengers of the sea" and play important roles in both marine and freshwater systems. Natural manganese oxide nanoparticles and grain coatings are ubiquitous in the environment and profoundly impact the quality of sediments via their ability to degrade and sequester contaminants. These oxides are believed to form dominantly via oxidation of Mn(II) by marine and freshwater bacteria and have extremely high sorptive capacities for heavy metals. We have used XANES, EXAFS, and synchrotron (SR)-XRD techniques to study biogenic manganese oxides produced by spores of the marine *Bacillus* sp., strain SG-1 in seawater as a function of reaction time under fully in-situ conditions. The primary biogenic solid-phase Mn oxide product is a hexagonal layered phyllosulfate with an oxidation state similar to that in delta-MnO₂. XRD data show the biooxides to have a phyllosulfate 10 Å basal plane spacing, suggesting the interlayer is hydrated and contains calcium. As the experiment continues, the initial biooxide changes to show triclinic symmetry. Fits to these EXAFS spectra suggest the octahedral layers have low Mn octahedral site vacancies in the lattice and the layers bend to accommodate Jahn-Teller distortions creating the change in symmetry. The oxides observed in this study as models of Mn(II) bio-oxidation may be representative of the most abundant manganese oxide phase suspended in the oxic and sub-oxic zones of the oceanic water column.

B21A-04 0845h

Determining the Feasibility of Organosilicate Utilization by Diatoms for Silica Biomineralization

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The utilization of silicon by microscopic, unicellular, silica-precipitating organisms such as diatoms, sponges and radiolaria controls the cycling of silicon in oceans. A long-standing question has been the chemical form (aqueous speciation) in which dissolved silicon is utilized by the organisms. Silicic acid and organosilicates are the most commonly proposed forms in the literature. In this study, ab initio calculations at the 6-311+G(2d,p)/HF//6-31G* level were used to calculate optimized structures, formation energies, and Si-29 NMR isotropic chemical shifts of organosilicates putatively involved in diatom metabolism. Quadracoordinated, penta-coordinated and hexa-coordinated complexes of silicates with polyalcohols, polysaccharides, polycarboxylic acids, and amino acids were investigated. The Si-29 peak at -101 ppm experimentally observed by Kinrade et al. (1999, 2001), is matched by spirocyclic, penta-coordinated organosilicates in 5-membered rings, but not by the 7-membered rings previously suggested in the literature. A heptet observed at -141 ppm in the H-1-Si-29 coupled spectrum (Kinrade et al., 2001) is best explained by hexa-coordinated 5-membered spirocyclic rings where Si bonds to oxygens atoms such that six symmetrically equivalent H atoms

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.