the response of forest trees and forest soils to acidic deposition. The goal of our dendrochemical research was to test the hypothesis that dendrochemistry provides a marker system for the occurrence and the timing of chemical changes in the tree rooting environment. Stringent comparisons of individual and aggregated radial trends of Ca, Mg, Mn, and K indicated that far from being a passive record of the external environment, dendrochemical patterns of these elements were based upon the factors of: 1) the active exclusion and preferential uptake and translocation of elements, 2) tree maturation from the formation of juvenile to mature wood, 3) wood maturation from sapwood to heartwood, 4) the interaction of tree wounding, infection, and tree response, and finally 5) changes in the external environment. Dendrochemical patterns need to be interpreted with consideration of these internal influences before attributing patterns to the external environment. Sample trends and qualitative models based on these factors will be presented. Preliminary analysis of Picea, Abies, Juniperus, Acer, Nothofagus, and Betula indicated that they may be even more rigorously limited in their utility as recorders of environmental factors that affect base cations.

### B12F-05 1700h INVITED

## Measuring Mercury and Other Elemental Components in Tree Rings Using Particle Induced X-Ray Emission

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There has been considerable interest in measuring heavy metal pollution, such as mercury, using tree ring analysis. Since 1970, this method has provided a historical snapshot of pollutant concentrations near hazardous waste sites. Traditional methods of analysis have long been used with heavy metal pollutants such as mercury. These methods, such as atomic fluorescence and laser ablation, are sometimes time consuming and expensive to implement. In recent years, ion beam techniques, such as Particle Induced X-Ray Emission (PIXE), has been used to measure pollutant concentrations in tree rings. PIXE is very useful in characterizing samples containing large numbers of elements. Most of the existing research in this area has been completed for low to medium atomic number pollutants, such as titanium, cobalt, nickel, and copper. Due to the reduction of sensitivity, it is often difficult or impossible to use traditional low energy (few MeV) PIXE analysis for pollutants with large atomic numbers. For example, the PIXE detection limit for mercury was recently measured to be about 1 ppm for a spiked Southern Magnolia wood sample. This presentation will compare PIXE and standard chemical concentration results for a variety of wood samples.

### B12F-06 1715h

## Applications of Tropical Isotope Dendroclimatology in Thailand

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Reconstructing the terrestrial expression of tropical climate variability over the last several centuries remains a challenge despite advances in the development of a variety of proxy records (e.g. corals, speleothems, ice cores). The use of traditional dendrochronological techniques has been hindered in the tropics because of invisible or indistinct banding in the wood. The seasonality in rainfall and relative humidity in the tropics, while not large enough to cause the creation of visibly distinct rings, may still generate seasonal signals in the oxygen and carbon isotopic composition of tree cellulose. Recent analytical advances in sample preparation, chemical extraction and continuous flow gas-source mass spectrometry have made possible the recovery of long term seasonal isotopic records in tropical trees. Previously, we have demonstrated that these techniques are capable of resolving seasonal climate signals on a variety of tropical tree species from Indonesia, including some for which no visible growth rings are present. We further explore this approach using trees from monsoonal northern Thailand in an attempt to characterize the most suitable species for this application. Analysis of $\delta^{18}O$ of cellulose from 10 trees coming from 4 different regions of northern Thailand highlights the difficulties in developing these new records as many species show very irregular seasonality. In contrast, some species show very regular and pronounced seasonality in $\delta^{18}O$. In addition, seasonal variations in $\delta^{13}C$ can assist with chronology when seasonal variability in $\delta^{18}O$ is less distinct. The coherence between oxygen isotopic records extracted from different tree species growing in the same geographical region confirms the existence of a common environmental control. Comparison with instrumental records of precipitation is complicated by a high degree of spatial variability between sparsely distributed stations. This suggests the potential for creating an alternative index of regional meteorological conditions using a network of many isotope dendrochronological records.

### B12F-07 1730h

## Dendrochemistry of Urban Trees in an Environmental Exposure Analysis of Childhood Leukemia Cluster Areas

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Currently in the US, there are at least two ongoing clusters of childhood leukemia, where the incidence rate over the last several years has far and away exceeded the national norm. In Fallon, Nevada, a town of 10,000 people, 16 children have been diagnosed with leukemia since 1995, three of whom have died. In Sierra Vista, Arizona, a town of 38,000 people, 11 children have been diagnosed since 1998, one of whom has died. A possible third cluster of childhood leukemia and other cancers is being monitored in Elk Grove, California, a suburb of Sacramento. For the purpose of providing a suite of many elements from which to search for temporal changes in environmental chemical availability that might have possibly contributed to these clusters, increment-core samples were collected from trees within these three communities and measured for elemental concentrations using inductively coupled plasma mass spectroscopy. Two time periods of rings were analyzed, one representing the cluster period (1997 to present) and one representing some period in the past, usually dating into the early 1980s. Among many elements that were measured, only tungsten showed a reasonably consistent change through time across the several trees that were sampled initially. In many cases, tungsten increased in the rings by as much as a doubling from past to present. The obvious dendrochemistry question applies: Does this increase in tungsten through time in tree rings represent a true increase in environmental exposure to tungsten, or is it merely an internal physiological phenomenon? To date, other trees sampled away from the cluster areas have shown variable changes in their tungsten concentrations, with some increasing and others decreasing through time. A CDC study of human tissue samples from Fallon showed high tungsten levels in people of Fallon, and a USGS study of drinking water in Fallon also showed high tungsten there. Filtered samples of inhalable air in Sierra Vista have more tungsten than other nearby areas of southern Arizona. Some medical research work has shown at least a possible connection between tungsten and leukemia or cancer generally.

### B12F-08 1745h

## Wetland ecosystem hydroperiods: long-term variability reconstruction using isotopic signatures from tree rings

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In order to restore altered wetlands to their natural state and/or water levels an independent measure of past water depths will be necessary where no historical documents/data exist. Presently the United States Geological Survey (USGS), SFWMD, and the National Parks Service (NPS) maintain an extensive network of gauge stations through out South Florida, but locally, theses stations typically have data only going back for the last 20 to 30 years (and more typically only 10 years). We propose to investigate the stable isotopic signatures within ring forming tree species in several wetland settings in South Florida including Everglades National Park (ENP) and within Big Cypress National Preserve, in order to reconstruct past changes in water levels/precipitation. Our preliminary work has demonstrated that the $\delta^{13}C$ values from the annual rings of Pond Cypress (*Taxodium ascendens*) trees in the C-111 basin (Tayler Slough, south-east Everglades) has a positive correlation with rain fall amount (Fig. 2). Therefore as the amount of precipitation increases, accompanied by a relative increase in water level adjacent and around the plant, a physical drought may occur, causing a change in stomatal conductance, resulting in an increase in intercelluar $^{13}C/^{12}C$ ratios. As water levels increase the plant experiences a stress which affects the $\delta^{13}C$ values of its fixed sugars, and this signal is in turn transferred to the trunk/annual rings. Note, this relationship is the opposite of terrestrial trees, where decreases in relative precipitation are normally correlated with increasing $\delta^{13}C$ of plant material, water-stress or -limitation.

B

# B12G MCC: 3014 Monday 1600h

## Disturbance, Climate, and Management Impacts on Carbon Budgets of Forested Ecosystems III

*(joint with A, GC)*

***Presiding:*** **K A Hibbard,** Oregon State University**; M Apps,** Canadian Forest Service**; D J Barrett,** CSIRO Plant Industry

### B12G-01 1600h

## Looking at Boreal Ecosystem Dynamics With a Disturbance Perspective

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Disturbances such as fire, insect outbreaks and storm damage play pivotal roles in dynamics of terrestrial ecosystems, especially in the boreal zone. Not only do such disturbances facilitate the adaptation of these biomes to the changing environmental conditions associated with global change pressures (Overpeck et al 1990), they can also trigger changes at the landscape scale that can result in ecosystems switching from sources to sinks of atmospheric CO2 (Kurz and Apps 1999) or from sinks to sources (Kurz et al 1998). The intrinsic connection of the influence of age-class structures on ecosystem productivity and carbon cycle processes, and the focus this brings to the importance of understanding and documenting past disturbance regimes has clear implications for mitigation issues, influenced by both natural and human-induced processes. Gaining improved data for, and predictive understanding of the role of disturbances in the state and dynamics of terrestrial ecosystems, especially in the boreal zone where very large carbon stocks are affected, is clearly an important goal for terrestrial ecosystem research. Equilibrium and steady-state approaches are inadequate: disturbances are intrinsically non-linear processes associated with complex systems whose subsystem parts are driven away from equilibrium by changes within these subsystems and the interactions between them. This gives rise to a rich pattern of variation and change over both time and over space in which the complex web of interacting subsystems and non-linearities forces us to adopt new systems approaches. Emergent properties and new system states are characteristic features of such approaches. As pointed out by Per Bak (1996), self-organized criticality is the new way of viewing nature - perpetually out-of-balance, but organized in a poised state. In this

new view, disturbances play a strong role in the coupling of the subsystems and act as triggers that alter the distribution of these systems (structure and pattern) in both time and space. These structural changes in turn alter the behavior (function) of these subsystems and become imbedded in the dynamics of the larger system. Disturbances, and the long-term response of the affected subsystems, thus play an integral role in linking across scales of time and space.

### B12G-02 1615h

### The effect of Arctic warming and sea ice loss on the growing season in northern terrestrial ecosystems

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High-latitude regions are particularly sensitive to climate change, with warming over three times the global mean expected in the twenty-first century. One aspect of polar climate that can exacerbate Arctic change is the sea ice state. Here the impact of sea ice loss on Arctic warming and growing season length is evaluated using an atmospheric general circulation model. High-latitude change in a simulation representative of 2080 conditions with enhanced greenhouse forcing was contrasted with change deduced from a simulation in which only the sea ice state was degraded. In winter, sea ice loss advances the timing of minimum temperature and promotes heating of the atmosphere by the ocean. Because of this, high-latitude terrestrial systems experience earlier thaw, however, only with enhanced greenhouse forcing did the summer maximum temperature increase and did the onset of freezing become substantially delayed. The sea ice alone accounted for an increase in the growing season length of typically 5-7 days because of earlier onset; lengthening of the growing season by 9-12 days was realized with enhanced greenhouse forcing because of the delayed freeze. Gross primary production also increased because of greater water availability in summer, associated higher precipitation rates throughout the year. As such, while changes in the atmospheric circulation conditions at non-polar latitudes in response to greenhouse forcing are important also in the Arctic, the role that sea ice plays in amplifying high-latitude change is of equal concern. It was also found that warmer Arctic conditions decreased variations in near surface temperature associated with both storminess and the diurnal cycle. The probability of freezing point in the 36 days near the onset of growing halved when change due to sea ice was considered in concert with other changes with greenhouse forcing, while there was a slightly greater probability of frost when changes due to sea ice were considered alone. These results suggest that the susceptibility of high-latitude net ecosystem production will depend on changes in the probability of extreme weather as well as the mean state.

### B12G-03 1630h

### Disturbance-Driven Ecosystem Productivity Estimates From the Integration of a Biogeochemistry Model and Landsat Remote Sensing

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Accurately modeling carbon fluxes between the land biosphere and atmosphere requires knowing the age structure and disturbance regime of forests. Recent eddy flux experiments within forest chronosequences have supported the theory that net ecosystem productivity (NEP) increases during the first decades after a stand-clearing disturbance, and then drops toward equilibrium. While the magnitude of this trajectory depends on stand type, it is possible that changes in disturbance rates could help explain both decadal and year-to-year variability in atmospheric carbon dioxide concentrations. However, testing this hypothesis requires forest disturbance and recovery histories at regional to continental scales. We are exploring approaches to derive disturbance history from Landsat surface reflectance data, and integrate this information with the CASA biogeochemistry model to make geographically explicit predictions of NEP and its variability. Using a test area in Central Virginia, we have mapped the extent of forest harvest and regrowth since 1973. We have modified the CASA model to account for the effects of disturbance and recovery on NPP and carbon pools. Inventory data from the USDA Forest Service have been used to calibrate CASA to predict NEP as a function of age for planted pine and mixed pine-hardwood forest types. This presentation will describe interannual changes in NEP resulting from disturbance and recovery dynamics, and compare the magnitude of these changes to those expected from a model driven by climate variability alone. The possible extension of this approach to the continental scale in support of the North American Carbon Program will also be discussed.

### B12G-04 1645h

### Towards Land Structure Parameters from Multi-angular Remote Sensing Data

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Recent studies have highlighted the importance of vegetation structure, both in the context of landscape dynamics and with regard to ecosystem productivity. Quasi-simultaneous multi-spectral and multi-directional remote sensing measurements from space, as provided by the Multi-angle Imaging SpectroRadiometer (MISR), offer new and unique opportunities to document the angular variations of land surface reflectances. The geophysical interpretation of such reflectance anisotropy patterns over terrestrial surfaces has only recently permitted to relate these signatures in a quantified manner to the structure and heterogeneity of the underlying surface. This contribution outlines simple physical principles supporting the interpretation of the anisotropy of spectral radiances exiting terrestrial surfaces in terms of a signature of surface heterogeneity. The shape of the anisotropy function is represented with two model parameter values which may be mapped and interpreted in their own right. Beyond the information about the heterogeneity of the surface, the value of one of these parameters also permits identifying geophysical conditions where the surface heterogeneity becomes significant. Structure functions and singularity measures can be employed to describe the non-stationary and intermittent behaviour of geophysical fields. This approach is applied on synthetic height field measurements of a large variety of vegetation canopies. The joint analysis of the shape of the anisotropy function together with the height fields yields remarkable patterns of organization: It is possible for multiangular instruments, like MISR, to deliver information about the type of surface heterogeneity at the subpixel scale, that is in agreement with canopy structure characterizations obtained by other means.

URL: http://www.gvm.sai.jrc.it/stars/

### B12G-05 1700h

### Linking Ecosystem Modeling with Remote Sensing and Field Observations for Integrated Assessment of Ecosystem Carbon Budget in forested landscapes of southeastern US

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The rapid urbanization in southeastern US has greatly reduced the extent of forested land and thereby lead to a release of carbon to the atmosphere. On the other hand, recovering vegetation from abandoned agricultural land and forest plantation can take up a significant portion of that released. Climate variability and land management have added additional uncertainty of the role of southern forests in carbon sources and sinks of the nation. In this study, we have used a newly developed terrestrial ecosystem model (TEM) to integrating multi-scale data sets from remote sensing and field observations in the forested landscapes, located in west Georgia. Our analyses show changes in carbon storage in both vegetation and soils in the past decades. Also we quantify the relative contribution of land use, climate and management to net carbon exchange between the atmosphere and the forested landscapes.

### B12G-06 1715h

### Accounting for age Structure in Ponderosa Pine Ecosystem Analyses: Integrating Management, Disturbance Histories and Observations with the BIOME-BGC Model

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Disturbance and management regimes in forested ecosystems have been recently highlighted as important factors contributing to quantification of carbon stocks and fluxes. Disturbance events, such as stand-replacing fires and current management regimes that emphasize understory and tree thinning are primary suspects influencing ecosystem processes, including net ecosystem productivity (NEP) in forests of the Pacific Northwest. Several recent analyses have compared simulated to measured component stocks and fluxes of carbon in Ponderosa Pine (Pinus ponderosa var. Laws) at 12 sites ranging from 9 to 300 years in central Oregon (Law et al. 2001, Law et al. 2003) using the BIOME-BGC model. Major emphases on ecosystem model developments include improving allocation logic, integrating ecosystem processes with disturbance such as fire and including nitrogen in biogeochemical cycling. In Law et al. (2001, 2003), field observations prompted BIOME-BGC improvements including dynamic allocation of carbon to fine root mass through the life of a stand. A sequence of simulations was also designed to represent both management and disturbance histories for each site, however, current age structure of each sites wasn't addressed. Age structure, or cohort management has largely been ignored by ecosystem models, however, some studies have sought to incorporate stand age with disturbance and management (e.g. Hibbard et al. 2003). In this analyses, we regressed tree ages against height ($R2 = 0.67$) to develop a proportional distribution of age structure for each site. To preserve the integrity of the comparison between Law et al. (2003) and this study, we maintained the same timing of harvest, however, based on the distribution of age structures, we manipulated the amount of removal. Harvest by Law et al. (2003) was set at stand-replacement (99%) levels to simulate clear-cutting and reflecting the average top 10% of the age in each plot. For the young sites, we set removal at 73%, 51% and 61% for sites averaging 9,16 and 23 years, respectively. It was assumed that changes in long-term pools (e.g. soil C) were negligible within these timeframes. In Law et al. (2003), the model performed well for old and mature sites, however, model simulations of the younger sites (9-50Y) were weak compared to NEP estimates from observations. Error for the young plots in Law et al. (2003) ranged from 150 - >400% of observed NEP. By accounting for the observed age structure through harvest removal, model error from this study ranged from 20-90% in young plots. This study is one of a few that have sought to account for age structure in simulating ecosystem dynamics and processes.

### B12G-07 1730h

### Disturbance and Net Ecosystem Production Across Three Climatically-Distinct Forest Landscapes

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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 $gCm^{-2}y^{-1}$ 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 $gCm^{-2}y^{-1}$ 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 $gCm^{-2}y^{-1}$ 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

### Biomineralization 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 $H_2S$ 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 $Na_2S$, 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 $Na_2S$, 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 akaganeite ($\beta$-FeOOH) crystals at the center of these mineralized filaments. We are using synchrotron-based X-ray spectromicroscopy (PEEM-photoelectron emisson microscopy and STXM-scanning transmission X-ray microscopy), which has the ability to give chemical information on heterogenous samples at high spatial resolutions. Both PEEM and STXM show that these filaments contain polysaccharides, which are likely templating the akaganeite 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 phyollomanganate with an oxidation state similar to that in delta-MnO2. XRD data show the biooxides to have a phyllomanganate 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 latyers 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.

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### 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-membred spirocyclic rings where Si bonds to oxygens atoms such that six symmetrically equivalent H atoms



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