absorb light intensely in the blue spectrum. Observations in the ultraviolet are essential to improve our capability to distinguish these ocean constituents. A hyperspectral instrument design capable of observing in the ultraviolet, in addition to the visible and near infrared spectrum, is essential to investigate the variability, dynamics and biogeochemical cycles of the world's coastal and open ocean regions. For both terrestrial and ocean carbon cycle science objectives, a hyperspectral geostationary sensor should enable the development of new remote sensing measurements for important but as yet unobservable variables, and with the overall goal of linking both terrestrial and ocean carbon cycle processes to climate variability. The GSFC Carbon Team has been pursuing a geosynchronous hyperspectral instrument, which would revolutionize our knowledge of biological processes on land, in the ocean, and along the coast by providing multiple, diurnal coverage. Preliminary studies in Goddard's Instrument Synthesis and Analysis Laboratory indicate that we can meet many of our science requirements: full spectral coverage (360-1000 nm); narrow bandwidths (5-10 nm); adequate ground resolution (100-200 m); and continental-scale coverage 4-6 times per day; all the while achieving a signal to noise ratio of between 500 and 1000 to 1. An innovative and bold focal plane design and a large mirror (1.8 meter diameter) will be required.

## B52F MCC: 3002 Friday 1600h

## Sulfur and Isotopic Biogeochemistry

*(joint with A, H, OS)*

***Presiding:*** **S Mylon,** Environment School, Yale University**; J H Scott,** Carnegie Institution of Washington

### B52F-01 1600h

### Relative Changes in $C_3$ and $C_4$ Biomass Recorded by Carbon Isotopes of Lipid Biomarkers in the Maya Lowlands of Petén, Guatemala

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Forest disturbance in the Petén region of northern Guatemala, beginning approximately 3000 cal yrs BP, was associated with the agricultural practices of the Maya. Expansion of the Maya civilization during the Preclassic and Classic periods was accompanied by widespread deforestation of Petén watersheds and accelerated rates of soil erosion. Palynological data from the Petén region suggest the near elimination of high forest taxa during the period of Classic Maya occupation. The validity of pollen records has been questioned, however, because they represent only a small percentage of tropical vegetation that is pollinated by wind. To estimate changes in the proportion of $C_3$ to $C_4$ vegetation in the Maya forest, we measured the $\delta^{13}$C of long chain *n*-alkanes ($C_{29}$ and $C_{31}$) produced by higher terrestrial plants in a 4.1-m sediment core from Lake Sacnab, Guatemala. Deforestation during the period of Maya occupation is reflected in sediments cores by a distinct, clay-rich interval (termed the "Maya clay") that is characterized by low magnetic susceptibility and low organic carbon content. The $\delta^{13}$C of long chain *n*-alkanes average -28$^o/_{oo}$ within the Maya clay, and decreases by 10$^o/_{oo}$ above the clay unit following the demise of the Classic Maya civilization in the $9^{th}$ century A.D. Our results suggest that vegetation was dominated by $C_4$ biomass during the Classic Maya period and is consistent with previous palynological interpretations. Reforestation following the demise of the Classic Maya is apparent in the pollen and compound-specific $\delta^{13}$C records and indicates a switch back to a $C_3$ dominated ecosystem once human pressures were curtailed. Compound-specific $\delta^{13}$C analyses of biomarkers in Lake Sacnab sediment provide further evidence that the Maya had a profound impact on their lowland neotropical environment.

### B52F-02 1615h

### Carbon-Isotopic Analysis of Individual Pigments by HPLC-Moving Wire-IRMS

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We have developed a method for directly analyzing the carbon isotope ratios of individual pigments, including chlorophyll (chl) and its derivatives, by coupling a high-performance liquid chromatograph (HPLC) to an isotope-ratio mass spectrometer (IRMS) via a novel moving-wire' interface. Pigments were separated on a reversed-phase C18 column, using a binary gradient modified from Airs et al. (2001, J. Chrom. A 917, 167-177). The HPLC effluent was dried onto a continuously-spooling nickel wire, and the involatile sample residue was combusted to $CO_2$ and transferred to the IRMS for isotopic analysis. Replicate analyses of a standard solution yield precision for $delta^{13}$C of better than 0.2$^o/_{oo}$ for injections containing 5 $\mu$g of chl-a. A five-fold improvement in sensitivity should be attainable using capillary HPLC to further reduce solvent volumes. The biomarker potential of tetrapyrrole pigments, combined with the geochemical information recorded by isotopic compositions, makes this combination a potent tool for biogeochemical studies. As a demonstration, we analyzed chlorophyll degradation products in sediments from a lake and a salina. First, compounds derived from bacteriochlorophylls (bchl)-c and -d were extracted from sediment cores taken at Kirisjes Lake (Larsmann Hills, Antarctica). These pigments are products of green sulfur bacteria and indicate the presence of an anoxic photic zone. The $\delta^{13}$C values of bchl-related compounds are near -25$^o/_{oo}$. Using published fractionations for *Chlorobium* species to extrapolate, dissolved $CO_2$ in Kirisjes Lake probably had a $\delta^{13}$C value of -12 to -21$^o/_{oo}$ and was strongly influenced by the recycling of organic carbon, possibly including methane. Second, compounds derived from chl-a, bchl-c, and bchl-d were isolated from sediments taken below a living microbial mat in the hypersaline les Salines de la Trinital (South Catalonia, Spain). The sediments contain visible remnants of past microbial mats and pigment distributions that indicate the major primary producers have been cyanobacteria and green bacteria. Components derived from chl-*a* have $\delta^{13}$C values of about -9$^o/_{oo}$, and are derived mainly from cyanobacteria that lived near the surface of the mat. We estimate that dissolved $CO_2$ used by those cyanobacteria had $\delta^{13}$C near +11$^o/_{oo}$. Such a strongly enriched value would likely result from the drawdown of dissolved $CO_2$ by vigorous photosynthesis. In contrast, components derived from bchl-c and bchl-d have $\delta^{13}$C values ranging from -15 to -19$^o/_{oo}$, indicating dissolved $CO_2$ with $\delta^{13}$C of -2 to -12$^o/_{oo}$ and again suggesting a strong role for recycled organic carbon. These differing estimates of $CO_2$ isotopic composition likely reflect the different microhabitats of cyanobacteria (aerobic mat surface) versus green sulfur bacteria (lower, anoxic levels) and can be used to infer the biogeochemical structure of the mat community.

### B52F-03 1630h

### Thiols in a Connecticut Stratified Freshwater Lake

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Thiols are an important class of dissolved reduced sulfur (DRS) species in aquatic environments. They are generally formed from biological processes or during diagenesis of biogenic matter. Thiols can affect the biogeochemistry of B-type metals as they form strong complexes that influence trace metal speciation, bioavailability and toxicity. While current literature focuses on the biogeochemistry of thiols in marine systems, little is known about the biogeochemistry of thiols in oxic freshwaters. We chose to study thiols in Linsley Pond a stratified freshwater lake that has been extensively studied by Hutchinson. Our goals were to identify and quantify the range of thiols present throughout this small lake. Additionally, we hoped to discern the environmental factors that influence the production and distribution of thiols in the water column, and to evaluate importance of thiols in trace metal speciation. To identify and quantify various thiols in freshwaters, we adopted a sensitive and selective analytical method, which involves precolumn fluorometric labeling coupled to high performance liquid chromatography and sensitive fluorescence detection. Using this method, our analytical detection limit is below one nanomolar. Among others, two thiol species were observed in Linsley Pond: 3-mercaptopropionic acid (3-MPA) and glutathione (GSH). 3-MPA exists in both oxic and anoxic water layers at nanomolar levels, and increases from surface to bottom. GSH is only detected in subsurface layer and co-varies with Chl a, indicating possible biological sources of GSH in these layers. There is a third, unidentified thiol species which is currently under investigation. The unidentified thiol species appears only in anoxic lake waters, and tests indicate that it is not PC2 (phytochelatin with 2 glutamic acid-cysteine units). Throughout the water column, concentrations of all three thiols are greater in whole water samples than in the dissolved phase (0.45 um).

### B52F-04 1645h INVITED

### Determination of Strong Metal Ligands (S(II-))in Natural Waters

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Reduced sulfide (S(II-)) ligands have been measured in oxic freshwaters at 1-100s nM. "Group B" metals, such as Ag(I), Hg(II), Cu(I) and Pb(II) bind strongly to S(II-) ligands. Their role in aqueous metal speciation and suppression of metal toxicity make S(II-) ligands an important analytical challenge. S(II-) is probably stabilized in oxic environments as metal-sulfide (M-S) clusters within natural organic matter (NOM). S(II-) species are measured by Cr(II) reduction of M-S, acid reaction, purge and trap to capture H2S and measurement as the methylene diamine complex (CRS). But CRS may also detect other sulfur species. Silver is an excellent probe metal for determination of strong ligand sites(SLS)in NOM. A competitive ligand method, using Ag(I), is demonstrated. The bound Ag-ligand and the "free" silver ion concentration are measured during the titration. The total strong ligand (Lt) is determined by a Grans' approach. These values are used to determine the (Lt) and the conditional binding constant, K'. Measured Lt concentrations match CRS concentrations, and conditional stability constants for a 1:1 M-L stoichiometry range from log K'= 11+ to 13, consistent with known Ag-S(II-) values. Furthermore SLS and Lt correlate with water-effect ratios (WERs) for silver

### B52F-05 1700h

### Metal-sulfide species in oxic waters: Complexes, clusters, or colloids?

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A weight-of-evidence approach is employed to characterize metal-sulfide species that have recently been suggested to be present in oxic waters. Sulfide in synthetic Cd-, Zn-, Pb-, Cu-sulfide solutions persists in oxic waters for a prolonged period of time (2 to more than 10 weeks) whereas it is oxidized rapidly in Fe-, Mn- and Ni-sulfide solutions. Direct mass spectrometric (MS) analysis and transmission electron microscopic (TEM) analysis revealed that the metal-sulfide species resistant to oxidation in oxic waters are not soluble molecular nanoclusters as suggested previously; instead, they are a mixture of truly dissolved metal-sulfide complexes and dynamic metal-sulfide colloids. The morphology and size of the colloids change significantly with time. Nanomolar to sub-micromolar levels of acid-volatile sulfide (AVS) and chromous-volatile sulfide (CVS) were measured in oxic surface waters of

6 lakes located on the Canadian Shield and nearby areas. Thermodynamic calculations indicated that at the AVS levels measured, the dissolved metal-sulfide species play a minor role in the speciation of Class B metal ions such as Pb, Cd, Cu, Hg.

### B52F-06 1715h INVITED

### Organic Sulfur Associated with Aquatic Humic Substances

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This study examines the speciation and reactivity of organic sulfur associated with dissolved organic matter isolated from a variety of freshwater environments and the Pacific Ocean. The isolates, which included aquatic humic substances, were obtained using XAD resins and exhibited a wide range of elemental compositions, aromatic carbon contents, and molecular weights. Organic sulfur contents for the samples ranged from 0.4% to 1.9% of the atomic composition and were strongly dependent on the redox chemistry of the environments whence the samples originated, especially with regard to potential interactions with sulfide in sulfate reducing environments. The speciation of the sulfur associated with these samples was investigated using X-ray adsorption near edge spectroscopy (XANES). The samples, all obtained from oxic environments, contained reduced sulfur moieties. Reduced sulfur content (thiophene, organic sulfides and thiols) ranged from 22-70%. In general, humic acid fractions were found to have the largest percentage of reduced sulfur, followed by the fulvic acid and hydrophobic acid fractions. Hydrophilic fractions of the DOC contained a large percentage of oxidized organic sulfur (sulfonate and sulfate moieties). To assess the significance of reduced S content on interactions with soft metals, an environmentally significant process, the binding strength and binding capacity of Hg with organic matter isolated from the Florida Everglades were determined using equilibrium dialysis ligand exchange. Based on elemental analyses and XANES, the DOM sample from the Everglades used in our binding experiments had a reduced-S content of approximately 1.0%. Very strong interactions ($K_{DOM}$' $= 10^{23.2\pm0.5}$ L kg$^{-1}$) were observed at Hg/DOM ratios below approximately 1 $\mu$g Hg per mg DOM. Only a small fraction (approximately 2%) of the reduced-S groups were involved with the strongest interactions between Hg and DOM, suggesting that the binding of Hg to DOM under natural conditions (very low Hg/DOM ratios ranging from 0.01 to 10 ng of Hg/mg of DOM) is controlled by a small fraction of DOM molecules containing reactive sulfur functional groups.

### B52F-07 1730h

### Production of Thiol Species From An Exponential Growth Diatom Under Copper Exposure

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The intracellar induction of phytochelatins is a well documented response of eukaryotic microorganisms to aqueous metal exposure. The extracellular release of thiolic compounds from algal species has been observed; and in some cases, this release can contribute a significant fraction of the uncharacterized metal-complexing ligands. Glutathione (GSH) or cysteine is among the detectable thiols excreted. A quantitative assessment of the excretion of thiols from algae cells into growth media is needed to assess the significance of biogenic-thiols as a source of strong ligands in natural waters and as a "forgotten" route in sulfur biogeochemical cycle. Unbuffered growth media (e.g., without adding complexing ligand such as EDTA) have only rarely been used to study the possible release of metal-complexing ligands from algal species, and the ligand titration techniques used varied considerably. The majority of culture studies have applied metal-buffered media. A direct comparison of released ligands under buffered and unbuffered conditions is lacking, partially due to the inherent difficulties of the titration methods applied. Using HPLC with fluorescence detection of thiol-monobromobimane derivatives, we were able to follow the dynamic change of GSH released in both media types during algal growth: (1) the cell quotas for thiols and pigments varied (mostly decreases) with growth time. Therefore, pigment-normalized cellular thiol concentrations were more or less conservative. (2) GSH was released into both the EDTA-buffered and -unbuffered growth media at similar concentrations. (3) at similar available Cu concentrations, EDTA possibly enhanced, rather than hindered, the release of GSH.

### B52F-08 1745h INVITED

### Amino Acid Enantiomeric Ratios in Biogeochemistry: Complications and Opportunities

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Amino acid enantiomeric ratios have been used for many years as an indicator of the process of racemization, and thus as a method to determine the age of biological samples such as bones, shells, and teeth. Dating biological samples by this method relies on an accurate knowledge of the environmental temperatures the sample has experienced, and the racemization kinetic parameters in the sample matrix. In some environments, where an independent dating method such as radiocarbon is available, the observed amino acid D/L ratios are found to be either higher or lower than those expected due to racemization alone. The observed D/L ratios in these cases can be clues to biogeochemical processes operating in addition to, or in place of, chemical racemization. In Siberian permafrost (Brinton et al. 2002, Astrobiology 2, 77) we have found D/L ratios lower than expected, which we have interpreted as evidence for low-level D-amino acid metabolism and recycling in microorganisms previously thought to be metabolically dormant. In microbially-colonized Antarctic Dry Valley sandstones (McDonald and Sun 2002, Eos Trans. AGU 83, Fall Meet. Suppl., Abstract B11A-0720) we have found D/L ratios higher than can be accounted for by racemization alone, most likely due to the accumulation of D-amino-acid-containing peptidoglycan material from multiple bacterial generations. D/L profiles in polar ices and in ice-covered lakes (Tsapin et al. 2002, Astrobiology 2, 632) can be used to indicate the sources and histories of water or ice samples. Multiple biological and biogeochemical processes may complicate the interpretation of amino acid enantiomeric excesses in both terrestrial and extraterrestrial samples; however, amino acid racemization remains a useful tool in biogeochemistry and astrobiology. With a good knowledge of the environmental history of samples, amino acid D/L profiles can be used as a window into processes such as molecular repair and biomass turnover that are difficult to detect by other means, particularly over geological time scales.

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