

density of the community. The more diverse and heterogeneous an ecosystem, the more modified the biological remains will be. From a reductionist perspective, this could be simplified to the quality of the fossil record is inversely related to the amount of oxygen available in the environment. It has long been understood that permanent smothering/removal of oxygen/burial is an effective way of preserving biological remains. This is for two reasons: a) microbes oxidizing any available organic carbon are limited to using electron acceptors other than oxygen, at a loss of energetic return, and b) multicellular animals that would exploit the food source or substrate require oxygen for their own metabolisms, therefore if the remains are removed from oxygen they are physiologically not accessible. This intuition has developed in terms of soft tissue remains, and in complete absence of oxygen. However, the natural world is a complex of environmental gradients, with oxygen and other essential parameters varying among environments. As a function of physiological limits, environments vary in the density and diversity of biota that they contain. Biological remains are part of the resources of an ecosystem with tissues as sources of organic carbon, skeletons as potential substrates and eventually as chemical ions (particularly in marine settings). So, the more healthy the community, the more they are busy recycling and obliterating any record of previous generations/communities. Similarly, for carbonate burial, regions of the highest carbonate production are likely also regions of the highest carbonate recycling. Let this be taken as an excuse to dismiss the fossil record as biased, we would no more think of doing so than with historical or archeological records, despite the fact that those preferentially record histories of the victors, the wealthy, and the literate. Just as we look beyond well preserved accounts of life at a monastery for clues of life in urban medieval Europe, so should we look beyond well preserved fossils to glean what paleo-biological and environmental clues we can from less than beautifully preserved fossils and the sediments that contain them.

B41A-24 0830h POSTER

Exploring Quantitative Wetlands Mapping Using Airborne Lidar and Electromagnetic Induction on Mustang Island, Texas

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We combine elevation data acquired using airborne Lidar, conductivity measured using ground-based electromagnetic (EM) induction, and vegetation surveys to examine whether topography and ground conductivity can be used to map coastal wetland vegetation assemblages. In 2003, we acquired elevation data along two transects across Mustang Island, a modern coastal barrier on the central Texas coast. We combined the cm-scale elevations with conductivity measurements and vegetation surveys acquired at 20-m spacings from the gulf beach to the bay shore. Wetland vegetation responds to both elevation and salinity; because ground conductivity is strongly influenced by soil salinity, we used EM induction measurements as a salinity proxy. Elevation and conductivity information, acquired either on the ground or from aircraft, represent a quantitative complement to traditional wetland mapping methods that rely upon aerial photographs. Along both transects, conductivities were negatively correlated with elevations. Highest average conductivities (1565 to 1745 mS/m) were measured on wind-tidal flats (elevation -0.05 to 0.5 m NAVD). Salt marshes at elevations -0.1 to 0.3 m (low) and 0.2 to 0.8 m (high) had lower average conductivities of 1270 to 1365 mS/m (low marsh) and 805 to 868 mS/m (high marsh). We measured relatively low average conductivities of 92 to 223 mS/m in low and high fresh marshes at elevations of 0.5 to 3.1 m. Dunes and vegetated barrier flats with elevations as high as 7.5 m NAVD had the lowest conductivities of 12 to 96 mS/m. Combined or alone, elevation and conductivity data allow better discrimination among coastal wetland environments than can be achieved from aerial photographic interpretation.

B41A-25 0830h POSTER

Colloidal Iron is Bioavailable to Phytoplankton Communities in the North Pacific and Bering Sea

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Biological productivity in the HNLC regions of the oceans is limited by the availability of Fe. In such regions, colloidal Fe could play an important role in relieving Fe-stress, although the bioavailability of Fe in natural marine colloids has not been investigated for in-situ phytoplankton communities. In order to test the bioavailability of marine deep-sea colloidal Fe, we performed incubation experiments in the HNLC North Pacific (47.0N, 170.0E) and Bering Sea (55.3N, 176.5E). Surface water at these sites was mixed with deep water (1000-1500m) from the same location and phytoplankton growth was monitored by Chl a concentrations. Some deep waters were filtered to remove only particulate (>0.4 mm) material, while others were filtered to remove both particulate and colloidal (>0.02 mm) material. Both types of filtered deep water consistently stimulated phytoplankton growth compared to control incubations of surface water only. High concentrations of major nutrients (eg. N, P, Si) in the deep ocean and soluble (<0.02 um) Fe are of course responsible for growth enhancement. When both soluble and colloidal iron were present, Chl a increases were greater (380-450%) than in the experiments where deep water with only soluble nutrients was added (310-325%). We hypothesize that the growth-enhancing factor in deep-sea marine colloids is bioavailable Fe. Dissolved Fe concentrations in surface waters at the experiment sites was relatively low (0.3-0.35 nmol/kg). When deep water was mixed with surface waters, soluble Fe was calculated to increase the total dissolved Fe concentration by 0.3-0.65 nmol/kg, and colloidal Fe was calculated to add another 0.09-0.12 nmol/kg Fe. By the end of the incubation period, total dissolved Fe concentrations in all experiments had decreased by 30-60% as a result of biological uptake. This is the first report of enhanced phytoplankton growth resulting directly from the biological uptake of colloidal Fe.

B41A-26 0830h POSTER

Microbial evidence for sulfur cycling in the deep subsurface of the Witwatersrand Basin, South Africa

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The continental deep subsurface harbors a heterogeneous community of microorganisms that have yet to be well understood. The gold mines of the Witwatersrand Basin in South Africa provide relatively easy access to this environment and have been integral to recent attempts to characterize subsurface microbiology. Molecular evidence for the biogeochemical cycling of sulfur has been detected in fissure water from Merriespruit and Driefontein mines. PCR amplification, cloning, and sequencing of adenosine-5'-phosphosulfate reductase (APS) and 16S rRNA genes were used to assess the composition of sulfur metabolizing microbial populations. Sequences closely related to APS reductase genes of the sulfur-oxidizing bacterium *Allochromatium vinosum* were detected in the Merriespruit Mine sample. APS reductase gene libraries from the Driefontein Mine sample were dominated by sequences with high identity to known sulfate-reducing bacteria. Phylogenetic analyses of 16S rRNA sequences indicated the presence of Thiobacillus-related species (known S-oxidizing organisms) in the Merriespruit sample, while Driefontein 16S rRNA clone libraries were dominated by sequences with high identity to known sulfate-reducing organisms in the delta-Proteobacteria and Firmicutes lineages. This study provides some of the first environmental APS sequences from sulfur-oxidizing bacteria and sheds new light on the organisms participating in sulfur-cycling in the deep subsurface.

B41B CC: 524 A Thursday 0830h

Isotopes in Biogeochemistry: The Atmosphere and Aquatic Environments

Presiding: S Trumbore, University of California, Irvine; S Macko, University of Virginia

B41B-01 0840h

A record of global photosynthesis to 150ka derived from the triple isotopes of O₂ in polar ice cores

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Records of the global rate of photosynthesis have the potential to reveal the nature of large scale interactions between biology, biogeochemistry and climate. Following Blunier et al [Global Biogeochemical Cycles 16(3) 2002] we have developed a 150ka record of the global rate of photosynthesis using the ¹⁶O, ¹⁷O, and ¹⁸O content of O₂ in air bubbles in Greenland and Antarctic ice sheets. Our approach takes advantage of mass independent effects in the isotopic composition of O₂. These effects arise from stratospheric exchange reactions between O₃, CO₂ and O₂ that cause the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of O₂ to decrease equally, rather than by the common, "mass dependent" factor of 0.5. The magnitude of the mass-independent anomaly ($^{17}\Delta \sim \delta^{17}\text{O} - 0.5 * \delta^{18}\text{O}$) depends on the relative rates of stratospheric reactions and biological cycling by photosynthesis and respiration. We have made a preliminary calculation of past rates of photosynthesis by correcting for past atmospheric CO₂ concentrations (higher CO₂ promotes stratospheric exchange and enhances the anomaly) and for changes of biological isotope effects associated with shifts in the C3/C4 composition of plants. The paleoproductivity record reveals that global photosynthesis was within $\pm 5\%$ of the modern rate during glacial periods and that it was higher than Holocene levels by as much as 10% during the Eemian (last interglacial). We found no statistically significant variability in paleoproductivity at orbital frequencies of precession or tilt during our study period. These conclusions are provisional and may be modified as more is learned about triple isotope fractionation during evapotranspiration and the secondary processes of O₂ consumption.

B41B-02 0855h

Isotopic diagnosis of processes governing interannual variability of CO₂ fluxes in the tropics

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Large scale variations in precipitation and temperature in phase with ENSO dominate the interannual variability in gross primary production in the tropics. During El Niño periods, large areas of tropical ecosystems are subject to water limitation and reduction in gross primary production. Because the ¹⁸O content of atmospheric CO₂ reflects a balance between gross

uptake and back diffusion of CO₂ that has undergone isotopic exchange in the leaves, details of the processes which govern the interannual variability in carbon exchange can be exposed with isotopic analysis. Using a sophisticated model of biospheric exchange of water and CO₂ isotopes, we contrast interannual variability of modeled CO₁₈O fluxes for the period 1947-2002 with measurements from the CMDL flask network. Our analysis focuses on attributing the changes in CO₁₈O fluxes to changes in the plant physiology during times of drought stress, and changes in the isotopic state of water during those times. Water within leaves, with which the CO₂ equilibrates, changes at the same time as the physiological response, the fluxes contain a commingled signal of the two. Specifically, during times of drought, precipitation and soil water are enriched relative to the climatology due to a greater dominance of evaporation, and without consideration can mask the contributions from changes in leaf level exchange. Within the model these two components may be quantified explicitly, though testing the sensitivity to the isotopic content of precipitation. Further complications arise when the net ecosystem exchange is considered due to changes in the partitioning of CO₂ fluxes between plant processes and soil respiration. This partitioning is quantified in the model simulations. In discussion we consider the contribution to the interannual variability associated with enhanced fire activity, also in phase with ENSO, and thus the importance of fire in the global CO₁₈O variability.

B41B-03 0910h

Stable Carbon Isotope Composition and Stomatal Density of the Conifer Genus *Frenelopsis*: Effect of pCO₂, Species and Soil Salinity

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Experimental studies indicate that some modern conifers adjust their stomatal numbers in response to variations of atmospheric pCO₂, suggesting that fossil conifer leaves may provide a proxy of pCO₂. The stable carbon isotope composition of plants provides an additional constraint on the conditions during plant growth as it is known to vary, for a single species, with the δ¹³C of the source CO₂, and environmental factors such as soil salinity and water content. Our objectives were to document the variation of the stable carbon isotope composition of the fossil *Coniferale* *Frenelopsis* through the Cretaceous and to decipher the effect of pCO₂, environmental and genetic factors on the fossil record. The leaf cuticles of *Frenelopsis* present a large variation in δ¹³C values from 27‰ for *F. ugnensis* growing on freshwater lake shores to 21‰ for species growing on brackish to marine environments. The species growing on freshwater lake shore presents an increase in ¹³C through the Barremian that is consistent with an increase in aridity. It presents a low stomatal density (SD) and index (SI: stomates over stomates plus epidermal cells). Comparison of the SD and SI within a single population shows that the variability in SD essentially reflects that of the cellular size and growth rate. The δ¹³C values of species growing in brackish to marine environment are all similar but higher than freshwater ones in the late Albian. They decrease in the Cenomanian, with a much larger intra-population variability. This shift can be related to a switch from marine to brackish conditions as well as to more global change. SD and SI are higher for the late Albian-Cenomanian cuticles and appear not sensitive to the environmental change (presumably a switch from marine to more brackish conditions) recorded in the δ¹³C. The large variability in both SD and SI within the studied populations in the marine-brackish environment appears to be related to change in the stomates over epidermal cells ratio during the leaf growth.

B41B-04 0925h

Implementation of a New Isotopic Tool (18O/16O in dissolved O2) for the Management of Oxygen in the Grand River, an Impacted Watershed in S. Ontario

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Oxygen (O₂) is essential for supporting life in aquatic ecosystems, and mediates the geochemistry of the aquatic environment. Recent analytical development now permits rapid analysis of the 18O/16O ratio of dissolved oxygen (DO) in water. The 18O/16O ratio provides insight into the main processes controlling DO concentrations in rivers: gas exchange, photosynthesis and respiration. Previously, this information was only available using indirect methods that involved laborious point scale measurements that are not amenable to routine sampling. The focus of this study is the Grand River, a Canadian Heritage River that drains into Lake Erie. The receives organic and nutrient inputs from sewage treatment plants, non-point agricultural sources, and serves as a source of drinking water and supports a significant recreational fishery. Dissolved oxygen concentrations in the Grand River can cycle from 2 mg/l to 14 mg/l in the summer during a 24 hour period. The concurrent shift in 18O/16O is greater than 10 permil on a diel basis. Rigorous sampling regimes are needed in dynamic systems that experience large fluxes in O₂. Diurnal curves were analyzed for DO and 18O/16O in DO during different seasons. Gas exchange is an important constraint on the diurnal flux of DO. Currently, gas exchange coefficients for the Grand River are typically obtained using empirical estimates based on results from other rivers. Analysis of 18O/16O offers a new method to allow for the direct determination of the gas exchange coefficient for DO in rivers with diurnal cycles.

B41B-05 0940h

Evaluation of Stream Metabolism by Integration of Chemical, Isotopic, and Modeling Approaches

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Robust estimates of stream metabolism are essential for understanding the mechanisms controlling turnover and downstream export of carbon, nitrogen, and other bioelements on watershed scales. Although reach-scale metabolism estimates have become fairly common in streams, the widely used "open-channel diel O₂-change approach" has uncertainties involving some assumptions that have not been evaluated fully. For example, metabolism estimates in small shallow streams may be particularly sensitive to variability in gas transfer rates (which are not typically measured simultaneously with the O₂ concentration change), and may be subject to diel changes in respiration (which is typically assumed to be constant). In an effort to improve reach-scale metabolism estimates, we combined O₂-change measurements with simultaneous SF₆ gas transfer measurements and isotopic analyses of dissolved O₂ and inorganic carbon (DIC). In-stream tracer experiments and measurements were conducted in a first-order stream in an agricultural watershed during June and September, 2003. Closed-system water and sediment incubation experiments were also conducted to determine the stream-specific δ¹⁸O₂ isotope fractionation factor for respiration. Diel variation in O₂ and DIC concentration were reach-specific likely reflecting the size of the algal community, stream orientation (e.g. irradiance), and water depth. Stream reaches that supported high primary production were also characterized by large diel swings in δ¹⁸O₂ (12 ‰) and δ¹³C-DIC (3.5 ‰). DIC concentration and isotopes mirrored changes in O₂ and δ¹⁸O₂ but lagged by up to 2 hours. Gas transfer rates varied approximately 20% during the study in response to changes in windspeed. Rates of photosynthesis (P) and respiration (R) were estimated by various methods involving different combinations of data. Steady state models included the diel O₂-change method with tracer gas transfer data to determine P and R, and a combination of O₂ and δ¹⁸O₂ data to determine steady-state P:R ratios. The steady-state models were compared with numerical simulations using O₂, δ¹⁸O₂, DIC, CO₂, and δ¹³C-DIC data that accounted for non-steady-state conditions such as gas transfer, temperature, and reaction rates.

B41B-06 0955h

Isotopic Fractionation of Selenium Oxyanions in Wetlands

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As oxic surface waters pass through aquatic macrophytes and over anoxic sediments in wetlands and lakes, the dissolved Se load often decreases; and, Se isotope ratio measurements can provide information about the mechanisms involved. Previous work on microbially induced isotopic fractionation of Se oxyanions under nearly natural conditions using wetland sediments shows consistent Se isotopic shifts during reduction of Se(VI) and Se(IV) to insoluble Se(0). However, previous isotopic studies of total dissolved selenium in wetlands found little to no isotopic shift as dissolved selenium concentrations decreased. This suggests that plant/algal uptake, followed by deposition and degradation, is the primary route of Se transfer into sediments. However, it is possible that the effective isotopic fractionation between Se in the surface water and Se deposited into sediments is somehow much less than the fractionation induced by the reduction reaction, or that cycling of organically bound Se is involved. In this study, we report Se isotope data for Se(VI), Se(IV) and total dissolved Se, Se(T), in surface waters from three wetland/lake sites: Sweitzer Lake, CO; 33-Mile Reservoir, WY; and, a small pond adjacent to Benton Lake, MT. We isolated Se(IV) via hydride generation, and Se(VI) via ion exchange. Se(T), including any organic components, was also analyzed. Isotope analysis was performed on an Isoprobe MC-ICPMS, using a method modified from that of Rouxel et al. (2002). We used the ⁸²Se + ⁷⁴Se double spike approach, and spiked samples before species separation. Our results for all three locations indicate similar trends in concentration changes and isotopic shifts between the inflow and outflow waters. Se(T) concentrations decrease by 45-70%, and Se(VI) concentrations decrease by 60-90%, whereas Se(IV) concentrations increase by 60-150%. Concomitant ⁸⁰Se/⁷⁶Se shifts are +0.5-0.8‰ for Se(T); -0.1-0.5‰ for Se(VI); and +0.4-6.5‰ for Se(IV). These data provide greater species-specific information than those from previous studies, but they similarly suggest that Se(VI) uptake is dominated by plant or algae assimilation: a process that involves little or no isotopic fractionation. On the other hand, Se(IV) is likely reduced by microbes or abiotic reductants in the sediments. The slight shift toward isotopically lighter Se(VI) is enigmatic, but could be due to oxidation of isotopically light dimethylselenide to Se(VI) in the water column.

B42A CC: 524 A Thursday 1030h
Isotopes in Biogeochemistry: Plant Organic Matter and Soils

Presiding: S Trumbore, University of California, Irvine; **E Hobbie**, University of New Hampshire

B42A-01 1030h

Pre-Pollution Levels of Lead in Pristine Boreal Forest Soils

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Atmospheric lead pollution has an over 3500 year long history in Europe. Most of the emitted pollution lead originates from ores or coal mines having lead with low 206Pb/207Pb ratios typically between 1.05-1.19. In contrast, lead found in naturally occurring minerals in forest soils, i.e. geogenic Pb, in Sweden have 206Pb/207Pb ratios mainly above 1.30. The significant difference in isotope ratios of airborne lead pollution and natural soil lead provide excellent conditions for tracing lead cycling in boreal forest ecosystems. Previous stable lead isotope studies in Sweden have demonstrated extensive spatial and temporal pollution; even in quite remote areas there are no natural reference conditions to found. This lack of a natural reference values for lead, and for other pollutant metals, in the mor layer, i.e. the organic horizon overlying forest mineral soil of podsol type, make it difficult to assess the extent of modern soil pollution and the natural cycling of geogenic lead in forest ecosystems. We have simulated pre-pollution conditions and estimated a natural