B42B-03 1415h

Airborne Flask Measurements of O_2/N_2, Ar/N_2, CO_2 and Other Species During COBRA-NA 2003

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We present measurements of O_2/N_2, Ar/N_2, CO_2, CH_4, CO, N_2O, H_2, SF_6, and $\delta^{13}C$ and $\delta^{18}O$ of CO_2 in airborne flask samples collected during the CO_2 Budget and Regional Airborne Study, which was conducted in North America over late May and June 2003 to develop methods of observing and modeling large scale fluxes of CO_2 and other atmospheric gases. Performed on the University of North Dakota Cessna Citation II, the campaign consisted of two circuits around North America, including regional flights over Harvard Forest, ARM-CART, and coastal areas of Northern California, Maine and Texas. The data from 350 sampled flasks will be interpreted for regional-scale surface fluxes of these species and as tracers to separate terrestrial, industrial, biomass-burning and oceanic contributions to variations and fluxes of CO_2 and CO. In addition, the understanding of vertical and horizontal transport and mixing of various flux signals that is enabled by our measurements is critical to scaling-up surface and airborne CO_2 flux measurements to basin scale.

B42B-04 1430h

Interpreting concentration measurements at flux towers

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The FLUXNET network contains nearly 200 sites around the world measuring carbon, water and energy fluxes by the eddy covariance method. Concentrations are also measured at these sites, usually only as a by-product. We show that the diurnal pattern in CO_2 concentrations measured at flux tower sites can be interpreted within a simple atmospheric boundary layer model framework to predict surface CO_2 flux. Concentration measurements have a much larger footprint than flux measurements, so this method can provide estimates of regional fluxes. In combination with remote sensing data to assess spatial heterogeneity, a network of sites could provide continental-scale flux estimates. We apply this idea to forest flux tower sites in the contiguous USA within the Ameriflux network.

B42B-05 1450h

Estimation of CO2 exchange at regional scales using spatial correlations of flux fields

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At regional to continental scales (> 1000 km), measurements obtained by eddy covariance flux towers are essentially samples at individual points within a flux field. A challenge is to estimate total flux exchange over this field from a limited number of sampling observations. This difficult task can be achieved by combining eddy covariance flux observations with spatial correlation structures of the flux field. It is well known that environmental conditions at different locations of a region are correlated. Remote sensing of gross primary production and net primary production also shows distinctive and coherent spatial structures. Therefore it is not surprising that CO2 flux exchanges at different locations of a region are correlated (either positively or negatively). This correlation provides powerful constraint for regional flux integration. Here a mathematical framework for conducting this integration is outlined. A preliminary analysis of statistical structures of flux fields based on MODIS products is presented. Directions for further research are suggested.

B42B-06 1505h

Inferring Terrestrial CO_2 Fluxes From A Global-Scale Carbon Cycle Data Assimilation System (CCDAS)

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Various indirect methods suggest that much of the year-year variability in the growth-rate of atmospheric CO_2 over the last two decades is attributable to variability in the net terrestrial flux. It is much less clear which processes are responsible for this terrestrial variability. In this talk we present results from a carbon cycle data assimilation system (CCDAS) in which the controlling parameters in a terrestrial carbon cycle model are inferred by nonlinear optimization based on the model's adjoint. Uncertainties in the parameters are inferred from observational and model uncertainties via the model's Hessian and then mapped forward on predicted quantities such as net CO_2 fluxes to the atmosphere via the model's Jacobian. The adjoint, Hessian, and Jacobian are generated by automatic differentiation of the model's source code. The dataset is the set of extended CO_2 concentration records from 41 observing sites. The model is able to fit the observations moderately well although it slightly overpredicts the long-term growth rate. This occurs despite the increase in terrestrial uptake through the 1990s over the 1980s. The increase, in turn, occurs despite a reduction in net primary productivity and is hence caused by a larger decrease in soil respiration. It appears that the requirement to fit both the seasonal cycle and interannual dynamics in the CO_2 record is a strong constraint on model formulation. We will demonstrate this by describing some of the problems with the description of respiration which are highlighted by this approach.

B42B-07 1525h

Spatial Coherence of NEE Response of Different Ecosystems to the Same Climate Anomaly

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The onset of spring in 1998 was early in a large part of boreal, north central, and north eastern temperate North America. Here we compare forest ecosystem responses at several flux towers within the climate anomaly footprint. Measurements at four of these sites include both eddy covariance flux and well-calibrated carbon dioxide mixing ratio time series. The climate anomaly area is characterized by +2-4C mean temperature difference and about 50g C more uptake in spring of 1998 compared to the same period in 1997. A similar pattern of earlier uptake of carbon dioxide can be seen in the mid-day carbon dioxide mixing ratio time series. Using the global carbon dioxide mixing ratio measurement network and very simple transport assumptions, spring Northern Hemisphere carbon dioxide draw down is compared for the two years and seen to be qualitatively consistent with the local flux tower evidence. This research approaches the question of how large a land response must be, both in magnitude and area, to be detected by the global measurement network. This research also directly links the global flask network to the network of eddy-covariance flux towers. An extended network of coupled continental carbon dioxide flux and mixing ratio observations could be used to improve the accuracy of inversion-based estimates of net ecosystem exchange (NEE) of carbon dioxide.

B42C MCC: 3010 Thursday 1340h

Aqueous Microbial Geochemistry II

(joint with H, OS, V)

Presiding: **E Shock ,** Arizona State University**; L A Warren,** School of Geography and Geology, McMaster University

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B42C-01 1340h INVITED

Thermodynamic Versus Surface Area Control of Microbial Fe(III) Oxide Reduction Kinetics

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Recent experimental studies of synthetic and natural Fe(III) oxide reduction permit development of conceptual and quantitative models of enzymatic Fe(III) oxide reduction at circumneutral pH that can be compared to and contrasted with established models of abiotic mineral dissolution. The findings collectively support a model for controls on enzymatic reduction that differs fundamentally from those applied to abiotic reductive dissolution as a result of two basic phenomena: (1) the relatively minor influence of oxide mineralogical and thermodynamic properties on surface area-normalized rates of enzymatic reduction compared to abiotic reductive dissolution; and (2) the major limitation which sorption and/or surface precipitation of biogenic Fe(II) on residual oxide and Fe(III)-reducing bacterial cell surfaces poses to enzymatic electron transfer in the presence of excess electron donor. Parallel studies with two major Fe(III)-reducing bacteria genera (Shewanella and Geobacter) lead to common conclusions regarding the importance of these phenomena in regulating the rate and long-term extent of Fe(III) oxide reduction. Although the extent to which these phenomena can be traced to underlying kinetic vs. thermodynamic effects cannot be resolved with current information, models in which rates of enzymatic reduction are limited kinetically by the abundance of "available" oxide surface sites (as controlled by oxide surface area and the abundance of surface-bound Fe(II)) provide an adequate macroscopic description of controls on the initial rate and long-term extent of oxide reduction. In some instances, thermodynamic limitation posed by the accumulation of aqueous reaction endproducts (i.e. Fe(II) and alkalinity) must also be invoked to explain observed long-term patterns of reduction. In addition, the abundance of Fe(III)-reducing microorganisms plays an important role in governing rates of reduction and needs to be considered in models of Fe(III) reduction in nonsteady-state systems, e.g. subsurface environments in which Fe(III) reduction is stimulated by contamination with organics or for the purposes of metal/radionuclide bioremediation.

B42C-02 1355h

Evidence for the Occurrence of Microbial Iron Reduction in Bulk Aerobic Unsaturated Sediments

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Radionuclide transport experiments conducted in a large, meso-scale column reactor (MSCR, 10 ft high

x 3 ft dia) operated under unsaturated flow conditions with simulated rainwater influent provide evidence that microbial iron reduction can occur in bulk-aerobic vadose zone systems with a low organic carbon content (0.5 wt%). Soil gas analyses indicate that CO2 varied between 0.1% of soil gas (top) and 12% to 18% of soil gas (bottom). O2 varied inversely with CO2, and the ratio of (CO2 produced) / (O2 consumed) was 0.8 +/- 0.1. NO3- was present at high concentrations, and originated from soluble NO3- salts present in the packing material. Ammonia was present at low levels, and limited NO2- production was observed. There was no increase in aqueous iron, and methane and sulfide were not produced. Mőssbauer analyses of sediment iron mineralogy indicate that the sedimentary iron in the packing material is 63% illite Fe(III), 16% illite Fe(II), 13% hematite, and 8% poorly-crystalline/small-particulate (pc/sp) iron oxide. Sediments collected from the lower portion of the column (5.5 fbs, feet below surface) still contain illite and hematite, but have lost the pc/sp iron oxide component. The Fe(III)/Fe(II) ratio of the illite appears to be unchanged at this depth. Analyses of sediment extractable DNA and cell number indicate that bacterial abundances increase from the surface to 0.5 fbs, and then remain constant with depth. Initial results from DGGE and 16s rDNA clone libraries indicate that microbial community structure alters with increasing depth, decreasing O2 content, and loss of pc/sp iron oxides. These data indicate a predominance of *Clostridium* at the column top, with *Bacillus*, *Desulfobacterium*, and *Pseudomonas* also providing a significant contribution. At 0.5 fbs, *Clostridium* represents a larger fraction of the total community with *Desulfobacterium* present as the second most abundant component. By 5.5 fbs, *Clostridium* is a minor component and the community is dominated by microaerophiles and facultative anaerobes such as *Aquaspirillum*, *Flexibacter*, and *Verrucomicrobium*. *Desulfobacterium* and *Pseudomonas* are also present at relative proportions similar to that observed higher in the column. This trend continues to 6.5 fbs, the lowest depth sampled. Mőssbauer spectroscopy indicates that pc/sp iron is being lost from the system, and the shift in microbial community structure towards facultative anaerobes capable of this metabolism (*Pseudomonas*, *Clostridium*) indicates that this shift may be engendered by either assimilatory or dissimilatory iron reducing microorganisms. Thus, anaerobic microbial processes in general, and microbial iron reduction in particular, may be important within nutrient-poor, unsaturated, bulk-aerobic vadose zone environments. Beyond this evidence for the occurrence of microbial iron reduction in an emulated vadose zone system, these data are difficult to reconcile. As is detailed in an associated poster presentation, the *Clostridium* results may indicate the growth of an obligate anaerobe in the upper, oxic portions of the column. As the oxygen content decreases with depth, the community then shifts away from obligate anaerobes (*Clostridium*) toward facultative anaerobes. This is an area of current inquiry, and questions/suggestions are encouraged.

B42C-03 1410h

Impact of Iron Oxide Structure on Fe(II)-Catalyzed Reductive Biomineralization

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Due to the reactivity of ferrous Fe, the fate of Fe(II) following dissimilatory iron reduction will have a profound bearing on biogeochemical cycles. Ferric (hydr)oxides vary from well-ordered phases in mature environments to short-range order minerals such as ferrihydrite in those subject to varying redox conditions. Structural order may have appreciable impacts on the extent and rate of Fe(III) reduction and subsequent Fe(II) generation. Here we compare the reducing capacity, biomineralization, and microbial colonization of goethite and hematite to 2-line ferrihydrite under advective flow. Introduction of organic carbon results in the onset of reduction of all three Fe phases. Although overall surface area normalized reduction rates are equivalent, the extent of Fe(III) reduction and fate of Fe(II) differs among the three systems. The amount of Fe(III) reduced within the ferrihydrite, goethite, and hematite columns is 25, 5, and 1%, respectively. While 83% of Fe(II) produced in the ferrihydrite system is retained within the solid-phase, merely 17% is retained by goethite and hematite. The fate of Fe(II) within all three systems involves sequestration of Fe(II) within magnetite yet the degree of conversion varies as a function of Fe(II) production. Goethite and hematite illustrate a similar control on Fe(II) dynamics, where Fe(II) primarily remains in the aqueous phase and is eluted from the system. Despite differences in initial reduction and sequestration, subsequent Fe(II) generation and accumulation within the three Fe oxides reaches an equivalent steady-state (300 h), where similar aqueous Fe(II) concentrations, cell colonization, and Fe(III) reduction rates are supported. The decline in microbial reduction is, most likely, due to preferential consumption of higher energy surface sites via reductive dissolution and magnetite nucleation, regardless of oxide structural order and surface area. Due to the transient nature of reactive sites on ferrihydrite, prolonged microbial reduction and colonization of ferrihydrite may not differ substantially from that of goethite and hematite. Given the greater abundance of crystalline iron oxides in the environment, reduction of phases such as goethite and hematite may impart an equivalent or potentially greater impact on sustained Fe(II) generation and sequestration.

B42C-04 1425h INVITED

Silicification of Thermophilic Biofilms: Do Aquificales Affect the Mineralisation Process?

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In geothermal environments, biomineralisation is an inevitable consequence of microbes growing in soluterich waters. The process of silicification is of particular interest due to (1) apparent discrepancies between natural and laboratory silicification rates and (2) siliceous microfossils currently serve as the earliest physical evidence for life on Earth. Although mesophilic microbe-silica interactions have been studied in great detail, there is a paucity of information on the role that thermophiles play in the silicification process, i.e., does their metabolism in any way facilitate silicification and do their cellular remains fossilise? To help resolve some of these uncertainties, a thermophilic, biofilm-forming member of the Aquificales order, Sulfurihydrogenobium azorense, was grown in the presence of various concentrations of silica, ranging from undersaturated to those extremely supersaturated with respect to amorphous silica. Since the chemolithoautotrophic Aquificales use of a wide range and combination of electron donors and acceptors, the bacteria cultured were grown in the presence of H2 with O2, S and Fe(III) as terminal electron acceptors. This study focused on the rates of pH-induced silica polymerisation during a 48 hour interval, when the soluble silica phase was at its most reactive stage, and when the greatest amount of silica immobilisation was likely to occur. S. azorense was found to have no detectable effect on the polymerisation rate of silica under any condition tested, nor did it cause silica to precipitate in undersaturated conditions. In addition, transmission electron microscopy showed that although silica did indeed precipitate from solution, there was no obvious association between solid-phase silica and the cells walls. This suggests that under high silica levels there is such a strong chemical driving force for silica polymerisation, homogeneous nucleation, and ultimately silica precipitation that there is no obvious need for microbial catalysis.

B42C-05 1440h INVITED

Controls on Sub-seafloor Bioalteration of Mid-Ocean Ridge Basalt Glass

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Microbiological alteration of MORB glass has been documented in all the ocean basins by at least 4 research groups. It is readily recognized optically as tubular textures of micron-scale, channel-like features and branching bodies extending from palagonite alteration rims into fresh glass, or granular textures which are irregular patches of individual or coalesced spherical bodies protruding into fresh glass. SEM imaging of these features commonly reveals delicate filament-like structures, and material resembling desiccated biofilm. Bioalteration appears to be most pronounced several hundred meters beneath the seafloor at ambient temperature near 70 C and seems to follow rock permeability. The densest bioalteration reported so far has been of a submarine tuff. Bioalteration has been reported in the oldest ODP Holes and perhaps continues as long as glass persists and pore water flows. X-ray element maps show elevated levels of C, N, P, and K associated with suspected microbial alteration fronts. Rarely, sulfide grains are seen with the bio-features. Staining indicates that both Bacteria and Archea are active. Carbon isotope signatures in MORB glass show differences from those of the adjacent crystalline cores that likely relate to microbial activity during alteration. The generally low 13-C ratios of disseminated carbonates in basaltic glass are attributed to metabolic byproducts of Bacteria formed by oxidation of dissolved organic matter from pore waters. A few positive 13-C values have been observed. These come from slow-spreading ridges and suggest in those settings lithotrophic utilization of CO2 in which methanogenic Archaea produced CH4. No convincing explanations have been put forward on why or how microbes attack glass underneath the seafloor. However, this sub-seafloor ecological niche may have been exploited by microbes since the Proterozoic or even the Archean based on preliminary studies on ancient ophiolites.

B42C-06 1455h

Microbial community structures in methane hydrate baring deep marine sediments from the Peru Margin (ODP Leg. 201) and the Cascadia Margin (ODP Leg. 204)

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Current estimates of biomass in deep subseafloor sediments recovered by the Ocean Drilling Program (ODP) have lead to the conclusion that the subseafloor environment potentially represents the largest biosphere on Earth. However, neither the microbial diversity and distribution that live there nor the relationship between metabolic characteristics and geological, geochemical settings are poorly understood yet. We present here the vertical profiles of microbial community structures occurring in methane hydrate baring subseafloor sediments collected from the Peru Margin (ODP Leg 201, site 1230) and Cascadia Margin (ODP Leg 204, sites 1244, 1245, 1251). Organic rich marine sediment core lacking methane hydrates obtained from the Peru Margin (ODP Leg 201, site 1227) was also investigated as a reference site. Quantitative-PCR analysis of archaeal rDNA population and molecular phylogenetic analyses of over 3,000 archaeal and bacterial 16S rDNA clones were demonstrated vertically through the ODP sediment core columns, comparing with data from geochemical analyses. On the basis of the results from microbiology and geochemistry, we discuss the relationship between the distribution of previously unknown microbial communities and the potential source of biogenic methane associated with the formation of hydrates in two geologically discrete deep-subseafloor environments.