

**B21D MCC: Level 2 Tuesday 0830h**

**Geologic Aspects of Carbon and Other Biogeochemical Cycles II Posters** (joint with A, H, OS, PP, GC)

**Presiding:** E Barrera, National Science Foundation; D Sahagian, University of New Hampshire

**B21D-0735 0830h POSTER**

**Anaerobic Methane Oxidation and the Formation of Dolomite**

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The environment and conditions necessary for the formation of dolomite has been a long standing problem in many scientific fields. In particular, the formation of organogenic dolomites and how they relate to the degradation of organic matter have been the focus of numerous studies. We examine the link between organic matter degradation, anaerobic methane oxidation (AMO), and sulfate depletion, and explore how these processes potentially influence dolomitization. We determined rates and depths of AMO and dolomite formation for a variety of organic-rich sites along the west African Margin at sites occupied during Ocean Drilling Program Leg 175. Our data set is porewater and gas data gathered during the cruise (alkalinity, sulfate, methane, Ca, and Mg), as well as postcruise analyses of  $\delta^{13}\text{C}$  of DIC. We find that the rates of dolomite formation are relatively constant regardless of the depth at which it is forming, indicating that the diffusive fluxes of Mg and Ca are not limiting. Based upon the calculated log IAP values, log  $K_{sp}$  values for dolomite was found to narrowly range between -16.1 and -16.4. Dolomite formation is controlled in part by competition between AMO and methanogenesis, which controls the speciation of dissolved  $\text{CO}_2$ . AMO increases the concentration of  $\text{CO}_2^{2-}$  through sulfate reduction, favoring dolomite formation, while methanogenesis increases the  $p\text{CO}_2$  of the pore waters, inhibiting dolomite formation. By regulating the  $p\text{CO}_2$  and alkalinity, methanogenesis and AMO can regulate the formation of dolomite in organic-rich marine sediments. In addition to providing a mechanistic link between AMO and dolomite formation, our findings provide a method by which the stability constant of dolomite can be calculated in modern sediments, and allows prediction of regions and depth domains in which dolomite may be forming.

**B21D-0736 0830h POSTER**

**Effects of pressure and solution composition on mineral weathering rates as applied to geologic storage of carbon dioxide**

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$\text{CO}_2$ -mediated weathering of silicate minerals and subsequent carbonate mineral precipitation may allow permanent trapping of carbon dioxide stored in deep saline aquifers. The time-scales and extents of the relevant reactions, however, are incompletely understood for receptor reservoir conditions. To address current shortcomings, experiments were conducted to investigate the effects of pressure, pH, and dissolved inorganic carbon (C) concentration on rates and mechanisms of silicate mineral dissolution. A 500  $\text{cm}^3$  high-pressure stirred flow-through reactor was used to contact 53-106 mm size-fraction forsteritic olivine

(( $\text{Mg}_{0.89}\text{Fe}_{0.11}$ ) $_2\text{SiO}_4$ ) with C-rich and C-free aqueous solutions. The system allowed monitoring and control of temperature (40°C), total pressure ( $10^5$  and  $10^7$  Pa), pH (3.1 and 7.1), flow rate (0.03 and 0.13  $\text{cm}^3 \text{ s}^{-1}$ ), and dissolved inorganic carbon concentration. Effluent samples were analyzed using inductively coupled plasma spectrometry to determine total aqueous magnesium, iron, and silicon concentrations for inference of quasi-steady state mineral dissolution rates. Mineral solids were characterized both pre- and post-dissolution using  $\text{N}_2$ -adsorption and scanning electron microscopy with energy dispersive X-ray analysis. Mean forsteritic olivine dissolution rates derived from aqueous silicon concentrations show strong dependence on pH ( $3.0 \times 10^{-12}$  mol  $\text{cm}^{-2} \text{ s}^{-1}$  at pH 3.1 and  $1.0 \times 10^{-13}$  mol  $\text{cm}^{-2} \text{ s}^{-1}$  at pH 7.1) and are consistent with previously published values at ambient conditions. No effect of pressure on dissolution rate was observed in the absence of dissolved inorganic carbon, suggesting ambient pressure measurements may be used to characterize deep subsurface mineral dissolution rates. However, preliminary analyses indicate a possible olivine dissolution rate enhancement due to the presence of inorganic carbon. Minor morphological alteration with no apparent chemical modification was observed in post-dissolution olivine grains; however, discrete Fe-carbonate precipitates appear to have formed during pH 7.1, C-rich experiments.

**B21D-0737 0830h POSTER**

**Non-steady State Soil Organic Carbon Storage in Undisturbed Watersheds Due to Diffusive Sediment Transport**

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Most soil C models assume that plant C inputs are matched by C loss through heterotrophic respiration. While these models are applicable for level terrain, on soil mantled uplands in hilly to mountainous regions, persistent soil mass transport represents a potentially large, but unstudied, flux of soil C. In this research we quantify the soil C erosional fluxes and non-steady state soil C storage within two undisturbed grass-covered hillslopes in Coastal California: Tennessee Valley (TV) (coastal Marin County) and Black Diamond (BD) (interior Contra Costa County). At both sites, previous geomorphic studies have quantified both the sediment transport processes (TV= gopher driven sediment transport; BD= abiotic soil shrink/swell) and their rates. Hillslope patterns of soil C storage were examined in relation to slope position with a hillslope sediment transport model. The average C erosion rates from convex slopes are between 1.4 and 2.7  $\text{g C m}^{-2} \text{ yr}^{-1}$  at TV and approximately 8  $\text{g C m}^{-2} \text{ yr}^{-1}$  at BD. The C erosional flux is locally as high as 14% of above ground net primary productivity (NPP) at TV and 8% at BD. The convex slopes are net C sinks because NPP likely exceeds respiration by a value equaling the size of C erosion. Eroded soils ultimately accumulate in depositional settings which have residence times on the order of 13kyrs at TV and 5.3kyrs at BD. At TV hollow, 15-24  $\text{kg C m}^{-2}$  of soil C has accumulated at a long-term rate of 1.6-1.9  $\text{g C m}^{-2} \text{ yr}^{-1}$ . The present rates of C accumulation were calculated to be 0.3  $\text{g C m}^{-2} \text{ yr}^{-1}$  at TV and 0.6  $\text{g C m}^{-2} \text{ yr}^{-1}$  at BD. During the hollow infilling, the depositional C inputs have been greater than C accumulation rates, meaning that much of the incoming eroded C is ultimately oxidized to  $\text{CO}_2$ . At both sites, a fraction of the eroded C is exported from the watershed (C of 0.1-0.5  $\text{g C m}^{-2} \text{ yr}^{-1}$  at TV and 2  $\text{g C m}^{-2} \text{ yr}^{-1}$  at BD). When all hillslope components are integrated, these watersheds are continuous atmospheric C sinks at rates of up to 0.3 and 2.4  $\text{g C m}^{-2} \text{ yr}^{-1}$ . We suggest that the upland soil C cycle may significantly affect the global C balance if scaled to continental levels.

**B21D-0738 0830h POSTER**

**Ancient Organic Matter Sources to the Hudson-Mohawk River System: Implications of Riverine Transport of Ancient Organic Matter for the Global Biogeochemical Carbon Cycle**

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The connection between erosion of rocks on the continents and deposition of marine sediments is riverine transport. Rivers are an important component of both the contemporary and long-term geologic carbon cycles. They erode ancient organic matter [OM] buried in sedimentary rock, carbon stored in soils, and carbonate bearing rock. Current understanding is that ancient OM is chemically and biologically reactive during weathering and riverine transport. However, while much OM exposed during weathering and transport is oxidized to  $\text{CO}_2$ , a significant portion is not remineralized, but instead is delivered downstream and reburied in marine sediments. This riverine conduit potentially allows ancient organic carbon to remain chemically distinct from pools of the contemporary carbon cycle. If a significant portion of ancient organic carbon remains sequestered in reduced form via this mechanism, there are important implications for the global carbon cycle over geologic time. These include carbon isotope effects, reservoir sizes and turnover rates, and ultimately, the composition of earth's atmosphere over geologic time. The Ordovician and Devonian shales of the Hudson-Mohawk watershed in upstate New York, USA, provide an ideal location to study the behavior of OM in a river system. In this study, we quantify sources of the dissolved and particulate organic carbon load of headwater streams draining these organic rich black shales using isotopic and molecular tracers of organic matter source. These tracers include stable isotopes of carbon and nitrogen, radiocarbon isotope ratios, and chromatographic signatures produced by pyrolysis-GC. We employ a GIS-based matrix of field sites in watersheds of contrasting lithology (OM-rich shales vs. OM-free crystalline basement) and surface cover, under the assumption that the two main controls on riverine carbon under similar climatic conditions are land use and underlying rock type. Samples include stream waters as well as endmember soils, rocks and plants. Together, these data provide the necessary information to construct a mixing model and determine the relative contribution of ancient sedimentary OM to the river system.

**B21D-0739 0830h POSTER**

**Soil N and C Geography of the Salmon River Watershed and the Oregon Coast**

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Diverse soil and geology influence the rich terrestrial and aquatic biota of the Oregon Coast. We characterized the spatial patterns of soil organic C (SOC) and N by assembling county and forest soil surveys combined with the new fieldwork, and analyses from sampled soils. The headlands have maximum SOC and N where wind deposited volcanic soil is coupled with a cool, moist climate. The SOC and N decreases inland in similar soils that have a less marine climate influence. The underlying geology (basalt or sedimentary rock) had no affect in SOC and N. The remainder of the watershed has less SOC and N depending on rock content and soil depth which were affected by lithology as well as microclimate, and tree stand history. Extrapolating SOC and N trends to the region provides information for an area with no significant N deposition from air pollution.

## B21D-0740 0830h POSTER

### Bedrock Nitrogen and Hydrothermal Ammonium in Yellowstone National Park, WY, USA

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High ammonium concentrations in some of the hot springs of Yellowstone National Park (up to 880 mg L<sup>-1</sup> as N at Washburn Hot Springs) have been attributed to leaching of sedimentary rock by hydrothermal solutions. However, relatively little is known about the direct relationship between rock geochemistry in volcanic centers and nitrogen in thermal waters. For this study, a suite of core samples from US Geological Survey drill holes in Yellowstone National Park were characterized for nitrogen and carbon in different lithologies. These data were related to the aqueous geochemistry and  $\delta^{15}\text{N-NH}_4^+$  of thermal waters in different hot spring basins in the park to better understand the water-rock interactions. Core samples selected for study included tuff, water-retorted volcanic sediments, glacial sediment, lacustrine sedimentary rock, and marine sedimentary rock. Substantial amounts of nitrogen were present in all bedrock types, with the highest nitrogen concentrations measured in marine sedimentary rocks (50 to 420 mg N kg<sup>-1</sup>) from Y10, which is located at Mammoth Hot Springs. Although the underlying bedrock has elevated nitrogen concentrations, hydrothermal ammonium concentrations at Mammoth Hot Springs are relatively low (1 mg L<sup>-1</sup> as N). These solutions are buffered by carbonate (pH >8) and may have lost some N by volatilization as ammonia gas. Thermal waters in Norris Geyser Basin are acid to circumneutral with ammonium concentrations ranging from <0.03 to 80 mg L<sup>-1</sup> as N. Nitrogen in tuffs (<10 to 30 mg N kg<sup>-1</sup>) from drill holes Y9 and Y12 at Norris Geyser Basin may be present as a result of ammonium partitioning from solution to zeolites or other secondary minerals. Thermal waters sampled at Mammoth, Norris, and other geyser basins in the park varied widely in ammonium concentrations and isotopic compositions ( $\delta^{15}\text{N}$ ), from <0.3 to 450 mg L<sup>-1</sup> as N and -5 to +25‰, respectively. The isotope data are interpreted to reflect multiple processes, including leaching of nitrogen from sedimentary sources, partitioning of ammonium from solution to secondary minerals, with fractionations resulting from boiling and steam distillation of ammonia gas.

## B21D-0741 0830h POSTER

### The Biogeochemistry of Silica in Grassland Ecosystems of the North American Great Plains

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Over geologic timescales, biologically mediated weathering processes influence atmospheric CO<sub>2</sub> content and global climate because the net effect of silicate weathering is the transfer of atmospheric CO<sub>2</sub> to HCO<sub>3</sub><sup>-</sup>. These weathering processes further influence atmospheric CO<sub>2</sub> due to a net transfer of dissolved silica to the oceans which promotes diatom production and sedimentation there by adding carbon to the oceanic reservoir. There is a substantial body of evidence that suggests that plants may transform silica into more stable or labile forms thus acting as potential sinks or sources of silica. We are currently conducting research that investigates the changes in the biogeochemistry of silica along bioclimatic gradients and soil chronosequences in temperate grassland ecosystems. The goal of our research was to use a systematic approach to identify the possible effects of plant type and production on the losses, gains and compartmentalization of silica during soil development. To further quantify biological cycling of silica we present the initial results of field studies in which we utilized state factor analyses, constituent

mass balance analyses, and mineralogical and geochemical characterization of soil and biogenic silica to quantify the role of plants in regulating the biogeochemistry of silica in terrestrial ecosystems. Our results suggest that grassland ecosystems have considerable variation in biogenic silica production and storage as a function of landscape age and bioclimatic conditions. In general Holocene aged soils of temperate grassland ecosystems have a net accumulation of silica while soils of Pleistocene age have experienced a net loss of silica. However, all grassland systems accumulate biogenic silica. Shortgrass steppe ecosystems have greatest accumulations of biogenic silica in soil and the lowest storage in biomass, whereas, tall grass systems have greatest biomass silica and lowest Biogenic Si accumulation in soil and appear to show a "net transfer" of silica to clay fraction of soils. Estimates of soil weathering rates need to include the influence of biogenic Si in "dampening" primary silicate weathering. Our studies demonstrate that biogenic Si derived from terrestrial systems may be important to consider when evaluating paleo-record of CO<sub>2</sub> and climate change.

## B21D-0742 0830h POSTER

### An example of volcano-hydrothermal sequence in Middle Archean: 3.2-Ga Dixon Island Formation, coastal Pilbara terrane, Australia.

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The 3.2-Ga Dixon Island Formation in the coastal Pilbara terrane, Australia, preserves Middle Archean hydrothermal stratigraphy and contains microbial material. Many black-chert vein swarms imply intensive low-temperature hydrothermal activity during deposition of black chert. Absence of detrital sediments of continental origin in this formation implies that this sedimentary facies represents a hydrothermal environment at about 500 2000 m in paleodepth in an immature island arc setting. Microbial material has been preserved well in the Black Chert Member, which is composed of massive black chert, laminated black chert, dark greenish siliceous shale and tuffaceous laminated chert. The massive black chert has carbonaceous peloids (0.3 mm 2 mm in diameter) similar to those in the black chert veins. The massive black chert contains wriggle-, rod- and dendrite-shaped bacterial material. Total organic carbon (TOC) in the black chert and black chert veins varies within 0.05 0.16% (average 0.1%) and the carbon isotope ( $\delta^{13}\text{C}$ ) values of these rocks are -32 -27 per mil (average 30 per mil). This evidence suggests that the carbonaceous grains and bacteria-shaped material in the black cherts are biogenic and formed close to a hydrothermal vent system. Field observations and geochemical evidence suggest that the Dixon Island Formation is one of the best examples of a biogenic microbial colony near hydrothermal vents in the Archean ocean. The microbial colony might have been quickly fossilized by silicification related to hydrothermal activity.

## B21D-0743 0830h POSTER

### Changes on a glacial-interglacial timescale in the oceanic inventory of phosphorus and its relation to climate change

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Phosphorus (P) is an important nutrient, which, along with other macro- and micronutrients, limits productivity in oceans. On a glacial-interglacial timescale, potential variations in the oceanic inventory of P, which are invoked by changes in the continental weathering regime, may have an impact on global primary production, on CO<sub>2</sub> drawdown from the atmosphere, and

on climate. It is crucial, therefore, to constrain P inventory changes throughout glacial and interglacial periods. We present new data that illustrate how P is distributed in marine sediments and how its inventory changed during the last 150,000 years. We have applied the SEDEX technique (Ruttenberg, 1992) on sediments from eight different Ocean Drilling Program (ODP) Sites (Northeastern Atlantic; Peru margin; Oman margin; Japan Sea; Ontong Java plateau; North Atlantic; South China Sea). Authigenic and Fe-bound minerals, and organic material represent the principal sinks of reactive P in oceanic sediments. Regardless of the environmental setting and type of sediment, P phases have been detected at all sites. Moreover, average reactive P concentrations are in the same range of values, between 0.3 and 0.6 mg/g. Only concentrations at the Oman and the Peru margin sites fall outside this interval, showing concentrations characteristic of phosphogenesis. Average concentrations calculated over glacial and interglacial periods do not show any significant difference. Changes in P distribution and concentrations in the sediments, and mass accumulation rates seem closely linked to local climatic and oceanographic conditions, but still reflect global processes (i.e., oceanic circulation and climate). On a global average, P accumulation rates in the sediments increased during the last glacial, suggesting a positive relationship between cold climate, increased physical weathering and P sink in the ocean sediments. Reactive P inventory variations seem paced by the precessional cycle (23 kyr), pointing at the ultimate control of low latitude processes on the oceanic P cycle. Ruttenberg, K. C., 1992 - Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnology and Oceanography*, 37(7), 140-1482.

## B21D-0744 0830h POSTER

### Soil Phosphorus Supply Under Different Soil Redox Conditions: Implications of Mineral Dissolution and Soil Organic Matter Turnover

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In humid tropical environments, phosphorus (P) limitation to net primary productivity (NPP) has been associated with the formation of secondary phosphate minerals with aluminum (Al) and iron (Fe) oxides. Under low oxygen (O<sub>2</sub>) availability, iron-reducing bacteria use Fe oxides and oxyhydroxides as the terminal electron acceptors for anaerobic respiration and phosphate ions that are associated with the mineral surfaces are released when the surface is reduced. Surface soils of humid tropical forests are often characterized by low and fluctuating O<sub>2</sub> availability. In this study we examined the effect of soil O<sub>2</sub> depletion on Fe-P relationships in humid tropical forest soils from Puerto Rico. Surface mineral soils (0-10 cm depth) were incubated under oxic (ambient air), suboxic (94% N<sub>2</sub> - 6% O<sub>2</sub>) and anoxic (100% N<sub>2</sub>) conditions for 39 days and analyzed periodically for P fractions and CO<sub>2</sub> efflux. The moderately labile inorganic P fraction (NaOH-Pi) was the most sensitive to changes in soil redox conditions showing a rapid increase over the first 2 days of incubation. Under suboxic and oxic conditions, NaOH-Pi increased after 25 days of incubation, and was correlated with soil CO<sub>2</sub> efflux suggesting that mineralization of organic matter led to increased labile P in these samples. Under anoxic conditions HCl-Pi was correlated with the most labile P pool (water available Pi) suggesting that soil reduction causes a rapid pulse of P from the geochemical pool. This short term release of P is likely to be important in maintaining the high NPP characteristic of humid tropical forests.

## B21D-0745 0830h POSTER

### Sediment and nutrient accumulation in Bear Lake post reconnection with Bear River

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Historical rates of bulk sediment accumulation were calculated based on the ages within the sediment cores. Bulk sediment accumulation rates increased throughout the last 100 years. According to the

CRS model, bulk sediment accumulation rates were <25 mg/cm<sup>2</sup>/yr prior to 1935. Between 1935-1980, bulk sediment accumulation rates increased to approximately 40 mg/cm<sup>2</sup>/yr. This increase in bulk sediment accumulation probably resulted from the re-connection of Bear River to Bear Lake. Bulk sediment accumulation rates accelerated again after 1980. Accumulation rates of total phosphorus (TP), total nitrogen (TN), total inorganic carbon (TIC), and total organic carbon (TOC) were calculated using bulk sediment accumulation rates and sedimentary concentrations of these nutrients. The accumulation rates of TP, TN, TIC and TOC increased after the re-connection of Bear River with Bear Lake as a consequence of increased bulk sediment accumulation rates. Eutrophication either has not occurred or has not been recorded in the sediment record of Bear Lake.

## B21D-0746 0830h POSTER

### Differentiating atmospheric and mineral sources of sulfur during snowmelt using $\delta^{34}\text{S}$ , $^{35}\text{S}$ activity, and $\delta^{18}\text{O}$ of sulfate and water as tracers

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The biogeochemical cycling of sulfur was studied during the 2000 snowmelt at Sleepers River Research Watershed in northeastern Vermont, USA using a combination of isotopic, chemical, and hydrometric measurements. The snowpack and 10 streams of varying size and land use were sampled for sulfate concentrations and isotopic analyses of  $^{35}\text{S}$ ,  $\delta^{34}\text{S}$ , and  $\delta^{18}\text{O}$  of sulfate. Values of  $\delta^{18}\text{O}$  of water were measured at one of the streams. Apportionment of atmospheric and mineral S sources based on  $\delta^{34}\text{S}$  was possible at 7 of the 10 streams. Weathering of S-containing minerals was a major contributor to sulfate flux in streamwater, but atmospheric contributions exceeded 50% in several of the streams at peak snowmelt and averaged 41% overall. In contrast,  $\delta^{18}\text{O}_{\text{sulfate}}$  values of streamwater remained significantly lower than those of atmospheric sulfate throughout the melt period, indicating that atmospheric sulfate undergoes microbial redox reactions in the soil that replace the oxygen of atmospheric sulfate with isotopically lighter oxygen from soil water. Streamwater  $^{35}\text{S}$  activities were low relative to those of the snowpack; the youngest  $^{35}\text{S}$ -ages of the atmospheric S component in each of the 7 streams ranged from 184 to 320 days. Atmospheric S contributions to streamwater, as determined by  $\delta^{34}\text{S}$  values, co-varied both with  $^{35}\text{S}$  activity and new water contributions as determined by  $\delta^{18}\text{O}_{\text{water}}$ . However, the  $\delta^{18}\text{O}_{\text{sulfate}}$  and  $^{35}\text{S}$  ages clearly show that this new water carries very little of the atmospheric sulfate entering with the current snowmelt to the stream. Most incoming atmospheric sulfate first cycles through the organic soil S pool and ultimately reaches the stream as pedogenic sulfate.

## B21D-0747 0830h POSTER

### Quaternary Branched Alkanes: A Geologic Proxy for Biological Sulfur Oxidation in Pleistocene Coastal Sediments of California

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Branched alkanes with quaternary substituted carbon atoms (QBAs) have been identified in two Pleistocene sedimentary sequences exposed along the California coastline. While these compounds have yet to be isolated from cultured microorganisms, a growing body of evidence points towards their origin as membrane components of colorless sulfur oxidizing bacteria (Kenig et al., 2002). This evidence includes an association with sulfide minerals, an association with environments or paleoenvironments with sharp sulfide: oxygen gradients, a positive correlation with the bacterial lipid diplotene, and (in this study) a positive correlation between the abundance of QBAs and the abundance of elemental sulfur in organic extracts. The wide distribution of QBAs in modern environments (deep sea hydrothermal systems, Arctic shelf sediments, and sediment traps from an oligotrophic marine site) may implicate chemoautotrophic and/or chemoorganotrophic members of the epsilon Proteobacteria as the source of QBAs. Sediments of the neritic to nonmarine Merced Formation near San Francisco and the bathyal to neritic Rio Dell Formation north of Cape Mendocino have been found to contain QBAs - predominantly 5,5-diethylalkanes and 2,2-dimethylalkanes. 5,5-diethylalkanes were identified by comparison of their spectra and elution time with published reports. 2,2-dimethylalkanes were identified through the chemical synthesis of authentic standards. In both sedimentary sequences, QBAs vary in abundance by more than two orders of magnitude over glacial-interglacial cycles. This variation appears to be crudely correlated with the abundance of elemental sulfur. In the Rio Dell Formation QBAs show an inverse correlation with the neritic benthic foraminifer biofacies as well as trace and macrofossil assemblages indicative of higher benthic oxygen concentrations. The occurrence of QBAs in shelf deposits of the lower Merced Formation supports previous interpretations that suggest a restricted basin setting with limited circulation. This is consistent with shoreface deposits indicative of low wave energy (on a currently high energy coast), a low diversity foraminifer assemblage, and the preservation of fine laminae and physical sedimentary structures in deeper water shelf facies. Variation in the relative abundance of different QBAs and related monomethyl alkanes may reveal finer taxonomic or environmental detail. Reference: Kenig, F., D. -J.H. Simons, D. Crich, J.P. Cowen, G.T. Ventura, T.C. Brown and T. Rehbein., (2002), Goldschmidt Conference Abstracts, p. A393.

## B21D-0748 0830h POSTER

### Ca Isotope Fractionation in the Hawaiian Ecosystem

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Investigations of the nutrient budgets in Hawaiian soils show the sources of major cations to be weathering of volcanic rock, marine aerosols, and Asian dust inputs. Especially at deeply weathered sites older than 150 ka, soils show strong depletion of the macronutrient calcium. Most of the calcium supply in these soils is of atmospheric origin (marine aerosols and continental dust). In contrast, younger soils are mainly supplied by calcium from weathering of volcanic bedrock. Based on the results of previous studies using strontium isotopic signatures and Sr/Ca ratios (e.g. Kennedy et al. 1998, Chadwick et al. 1999, Whipkey et al. 2000, Stewart et al. 2001) we have conducted research focusing on the isotope composition of calcium as a new tool for the investigation of sources of calcium and biogeochemical processes affecting Ca isotope fractionation in the plant-soil system. The study combines  $\delta^{44}\text{Ca}$  with  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr/Ca data of soils (bulk compositions and extractable Ca and Sr from soil exchange sites) and different plant species including native Ohia trees (*Metrosideros polymorpha*) from a soil chronosequence along the Hawaiian Island chain. The study sites differ in age of the underlying substrate from 0.3 ka to 4,100 ka, but show similar recent climate (mean annual temperature of 16 °C) and amount of precipitation (about 2,500 mm/y).  $^{44}\text{Ca}/^{40}\text{Ca}$  ratios were measured on a MAT262 at Stanford University, using a  $^{42}\text{Ca}$ - $^{48}\text{Ca}$  double spike, and are reported as  $\delta^{44}\text{Ca}$  values relative to seawater ( $\delta^{44}\text{Ca} = 0 \text{ ‰}$ ). Results of the extractable, plant available calcium from six soil sites show  $\delta^{44}\text{Ca}$  values in the range of +1.2 ‰ to -1.3 ‰ with generally more negative values related to younger soil sites where calcium is mainly derived from

weathering of volcanic rocks. Bulk soil samples, however, show  $\delta^{44}\text{Ca}$  values between -0.1 ‰ and -2.5 ‰, indicating differences in composition as a result of contributions from volcanic minerals, continental dust, and marine aerosols in different proportions. Leaves and wood material of different plant species have  $\delta^{44}\text{Ca}$  values in the range of -0.1 ‰ and -2.1 ‰, suggesting biological fractionation of Ca isotopes during calcium uptake in plants. From our results we conclude that the pattern of Ca isotope fractionation in the Hawaiian ecosystem depend on several factors (1) the source of calcium, (2) physiological processes, and (3) soil biogeochemical processes. Reference: Chadwick et al. (1999) Nature 397: 491-497. Kennedy et al. (1998) Geology 26: 1015-1018. Stewart et al. (2001) Geochim. Cosmochim. Acta 65: 1087-1099. Whipkey et al. (2000) Chem. Geol. 168: 37-48.

## B21D-0749 0830h POSTER

### Iodine in Rivers: Indicator of Geologic Effect on Iodine Deficiency Disorders?

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A contrast in goiter prevalence between populations living north and south of the Main Karakoram Thrust (MKT) in northeastern Pakistan suggests that plate tectonics may be involved. We report ICP-MS measurements of the total dissolved iodine levels in the headwater tributaries of the Indus River draining either side of the MKT. For global geochemical context, we also analyzed samples from the Lena, Yana, Kolyma, Indigirka, and Anadyr in eastern Siberia, the Orinoco in tropical South America, and rivers in western China and Tibet. We find statistically significant difference in iodine concentration between the right bank tributaries of the Indus draining the Karakoram metamorphic complex north of the MKT and the left bank tributaries draining the Kohistan-Ladakh island arc south of the MKT. At least in these rivers, lithology and the tectonic exposure appear to be more important than atmospheric transport and deposition.

## B21D-0750 0830h POSTER

### Exacerbation of Atmospheric Mercury Emissions From Substrates by Atmospheric Oxidants

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Previous studies have identified a variety of meteorological parameters such as incident radiation and temperature, which appear to control the temporal variations and magnitude of Hg emissions from natural substrates. New datasets show variations in Hg emissions over time which differ significantly from meteorological changes suggesting that other mechanisms control Hg emissions. This study investigated the potential control of atmospheric oxidants on Hg emission from substrates. In this laboratory-based study, emissions of elemental Hg ( $\text{Hg}^0$ ) and reactive gaseous Hg (RGM) were measured from 5 substrates in Hg and oxidant free air (zero air),  $\text{O}_3$  enriched (50 ppb) zero air, and ambient air. The experiments were conducted in a temperature-controlled environment with no light. Results showed a 2-4 order of magnitude increase in both  $\text{Hg}^0$  emissions and RGM concentrations in ambient air and  $\text{O}_3$  enriched zero air relative to emissions in zero air for all 5 substrate samples. Significant relationships ( $p < 0.05$ ) between ambient  $\text{O}_3$  concentrations and Hg emissions were also observed. This suggests that atmospheric oxidants, and possibly some other components in ambient air, facilitate Hg emission from soil. The proposed mechanism for this reaction is the physical displacement of Hg from the substrate surface by  $\text{O}_3$ . Experiments using only  $\text{Hg}^0(g)$  and  $\text{O}_3$  demonstrated that the increased RGM concentrations associated with experiments employing soils were not an effect of homogeneous gas-phase oxidation of Hg. The increased RGM concentrations are therefore due to 1) physical displacement of the RGM by  $\text{O}_3$  or; 2) heterogeneous oxidation of  $\text{Hg}^0$  on the soil surface. An important implication of this work is that increasing concentrations

of O<sub>3</sub> and other atmospheric oxidants since the industrial revolution may have triggered an increase of atmospheric Hg emissions and re-emissions from natural substrates during the same time period.

## B21E MCC: Level 2 Tuesday 0830h

### Validation and Application of Land Surface Products From the MODIS Sensor I Posters (*joint with H, GC*)

**Presiding:** F A Heinsch, University of Montana; J L Privette, NASA Goddard Space Flight Center

## B21E-0751 0830h POSTER

### Land Surface Product Validation Using the DOE ARM Southern Great Plains Site

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The University of Wisconsin Space Science and Engineering Center (UW-SSEC) is making use of the U.S. Department of Energy Atmospheric Radiation Measurement (DOE ARM) program Southern Great Plains (SGP) site for validation of NASA EOS land surface products. The DOE ARM site covers a 250 km square region that includes most of Oklahoma and southern Kansas. The site is dominated by a mixture of vegetation and bare soil with a vegetation fraction that changes with the growing season. The land use is divided between cattle ranching (permanent pasture) and wheat farming (seasonal). The DOE ARM site provides routine state-of-the-art vertical profile measurements of the atmospheric state. Special radiosonde launches have been conducted by DOE ARM to coincide with overpasses of the NASA Aqua platform. The UW-SSEC has provided ground truth measurements of surface characteristics using a mobile research vehicle (the AERIBAGO) during several aircraft field campaigns. The UW-SSEC Scanning High-Resolution Interferometer Sounder (S-HIS) has provided high altitude observations of the thermal infrared spectrum for comparison to satellite observations. Coincident measurements of ground-based and aircraft observations with AIRS and MODIS satellite observations have been obtained during TX-2001, TX-2002, and IHOP. Preliminary land surface products from AIRS will be compared with MODIS land products and the validation measurements obtained from aircraft and ground-based sensors.

URL: <http://airs3.ssec.wisc.edu/~airs/lste>

## B21E-0752 0830h POSTER

### Data Supporting the Validation of MODIS Land Products

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Data from multiple types of local and regional studies are needed to extrapolate from site studies to larger-scale products derived from remote sensing or global-scale modeling. This poster describes data compiled at the Oak Ridge National Laboratory (ORNL) Distributed Active Archive Center (DAAC) to support the validation of MODIS land products. The ORNL DAAC provides data from several sources to support

this effort: (1) a global network of flux tower sites (FLUXNET), (2) subsets of remote sensing products from MODIS, (3) ground-based studies designed to validate remote sensing products, and (4) regional and global data set of key environmental parameters. The FLUXNET database contains carbon, water vapor, sensible heat, momentum, and radiation flux measurements along with associated ancillary and value-added data products for a wide range of ecosystems on five continents. Subsets of selected MODIS products are provided in ASCII format for an area 7 x 7 km around each of 274 field sites. The MODIS products posted at the ORNL DAAC include surface temperature, reflectance, albedo, vegetation indices, land cover, leaf area index, photosynthetically active radiation, and photosynthesis. Data collected from land validation field studies are registered in the DAAC's Mercury metadata search and data retrieval system. Data on the global distribution of net primary production and leaf area index, based on 1000s of point measurements, are available from the ORNL DAAC for use in validation. Validation of MODIS Products has benefited from the use of core validation sites, where a suite of field, airborne, and satellite data is used to extrapolate from site studies to large-scale products. Existing in situ networks (e.g. flux towers, AERONET, LTER/ILTER) and field investigations (e.g., LBA, SAFARI 2000) as well as international partnerships and coordination, mainly through CEOS/IGOS, have been key components of the validation approach. We have learned that simplified data access with dedicated archives and easy-to-use data formats (e.g., ASCII subsets) as well as frequent communication between Product PIs, Validation PIs, and data facilitators all play a significant role in improving the understanding of the MODIS Land Products.

URL: <http://www.daac.ornl.gov>

## B21E-0753 0830h POSTER

### Remotely Sensed and In Situ Data Availability for Validation of EOS Land Data Products

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In support of the NASA Earth Observing System (EOS) Land Product Validation investigations, numerous remotely sensed data and field measurements are being collected at core validation sites around the world. These core sites' represent different biomes and include locations at which in situ measurements are routinely collected. The types of remotely sensed data that are being acquired and analyzed over these sites include Landsat 7 ETM+, ASTER, MODIS, and SPOT VEGETATION. The data being collected over these sites are being used to monitor ecosystem status, compile time-series records of biophysical and geophysical parameters, and to validate the suite of land products being derived from MODIS data. In order to facilitate easy access to the remotely sensed data being collected over these core sites, the data are stored online under FTP directories established by the Land Processes Distributed Active Archive Center (LP DAAC) at the USGS EROS Data Center. In situ measurements and data collected through field campaigns are being coordinated by the Oak Ridge National Laboratory Distributed Active Archive Center (ORNL DAAC) and being made accessible through the Mercury system, which is a web-based search engine (<http://mercury.ornl.gov/ornldaac/>). Access to many of the remotely sensed and in situ data sets collected over the EOS Land Validation core sites' can be accessed through Mercury or the MODIS Land Validation web page (<http://modarch.gscf.nasa.gov/MODIS/LAND/VAL/>). We are hoping to stimulate interest and participation by the Validation of Land European Remote Sensing Instruments (VALERI, <http://147.100.0.5/valeri/>) to extend the network and diversity of sites as well as increase collaborative research. We have developed a web portal that enables investigators to select a particular site of interest, determine what data are available for that site, and select datasets for ftp download. Certain services may be requested to be applied to the data prior to download, including: spatial and parameter subsetting, projection transformation, and file format conversion. The scientific rationale for this project is predicated on improving international and interdisciplinary collaboration in the assessment, application, and improvement of remotely sensed data products and services available to the research community. Efforts to validate remotely sensed data products at a global scale are unprecedented, yet such efforts are necessary in order to quantify the errors or uncertainties associated with these derived geophysical and biophysical parameters. These products must be evaluated over a wide range of land surface conditions and on a regular basis.

## B21E-0754 0830h POSTER

### Obtaining and Using the MODIS Snow and Ice Products for Land Surface Research

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Snow and sea ice cover are some of the more important spatial features of the Earth's surface that can be readily measured from space. Moderate Resolution Imaging Spectroradiometer (MODIS) instruments onboard NASA's Terra and Aqua spacecraft collect spectral data that are used to routinely produce snow cover and sea ice products. With higher spatial and spectral resolution, the MODIS snow and ice products (including snow albedo and sea ice surface temperature) improve upon a long history of global coverage satellite-derived products that have been produced from polar-orbiting satellites since the early 1970s. Fully automated, quality controlled, daily global maps of snow cover and sea ice extent, produced at 500m, 1000m, and 0.05° spatial resolutions by the MODIS Land Team, are available from the National Snow and Ice Data Center (NSIDC) Distributed Active Archive Center (DAAC). MODIS snow and ice products from the Terra satellite have been produced since 2000; most of these products have been validated over a wide range of locations and time periods. Production of comparable snow and ice products using Aqua data will begin during the next few months after final testing of an algorithm that uses a slightly different set of spectral bands. Recent work to improve the performance and utility of the products includes: subsetting, gridding, and resampling tools; an easy-access Data Pool of recent and popular data holdings; reduced-resolution browse data available through the ordering systems; and plans for new products including a snow albedo product as well as a sea ice product on a climate modeling grid. Through examples of current MODIS data usage, we describe the characteristics and state of validation of the MODIS snow and ice products, their accessibility from the NSIDC DAAC, and current user support and tools.

URL: <http://nsidc.org/modis>

## B21E-0755 0830h POSTER

### Biospheric Monitoring and Ecological Forecasting using EOS/MODIS data, ecosystem modeling, planning and scheduling technologies

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The latest generation of NASA Earth Observing System satellites has brought a new dimension to continuous monitoring of the living part of the Earth System, the Biosphere. EOS data can now provide weekly global measures of vegetation productivity and ocean chlorophyll, and many related biophysical factors such as land cover changes or snowmelt rates. However, information with the highest economic value would be forecasting impending conditions of the biosphere that would allow advanced decision-making to mitigate dangers, or exploit positive trends. We have developed a software system called the Terrestrial Observation and Prediction System (TOPS) to facilitate rapid analysis of ecosystem states/functions by integrating EOS data with ecosystem models, surface weather observations and weather/climate forecasts. Land products