alkaline hot springs, but that upper temperature limits decrease with decreasing pH below ~7. As an example, we found no strong evidence for photosynthesis above 45°C at pH ~2. In several locations, photosynthesis appears to be suppressed despite temperatures and pH values that permit photosynthesis elsewhere. Preliminary results indicate that salinity variations are not responsible for suppression of photosynthesis, but that sulfide concentrations may be. Studies of five hot spring outflow channels, together spanning pH values from 2.5 to 8.6, show that photosynthesis appears once sulfide concentrations drop to < 20% of the source values. In one channel where total sulfide varies by only a factor of two over more than 100 m of flow, we found no evidence of photosynthesis despite temperatures ranging from 60 to 35°C and mild pH values of 5.8 to 6.5. These observations lead us to propose that photosynthesis becomes possible after a large decrease in initial sulfide concentration. Although abiotic processes (degassing, mineral precipitation, surface reactions) may explain decreases in total sulfide concentrations, preliminary results suggest that rates of microbial sulfide oxidation determine whether hot spring habitats become suitable for microbial photosynthesis. Alternatively, once sulfide concentrations decrease below some threshold level sulfide oxidizers may be outcompeted by photosynthesizers.

B41D-0928 0830h POSTER

Effects of Siderophores on Metal Adsorption to Kaolinite

Sarah E Hepinstall[1] (574-631-4307; shepinst@nd.edu)

Patricia A Maurice[1] (574-631-9494; pmaurice@nd.edu)

Marvin J Miller[2] (mmiller1@nd.edu)

[1]University of Notre Dame, Department of Civil Engineering and Geological Sciences, 152A Fitzpatrick Hall of Engineering, Notre Dame, IN 46556, United States

[2]University of Notre Dame, Department of Chemistry and Biochemistry, Stepan Chemistry Hall, Notre Dame, IN 46556, United States

Siderophores are metal-complexing ligands with high affinities for Fe(III), produced by many microorganisms in Fe-deficient environments. Siderophores can also form strong complexes with other metals such as Pb and Cd; hence, siderophores may play an important role in controlling metal mobility in porous media. This study compared the effects of siderophores desferrioxamine-B (DFO-B), desferrioxamine-D (DFO-D1), desferrioxamine-E (DFO-E), as well as siderophore-like ligand acetohydroxamic acid (aHA) on Pb and Cd adsorption to kaolinite (KGa-1b) at pH 4.5 to 9, in 0.1 M $NaClO_4$, at 22 °C, in the dark. At pH > 6.5 all of the siderophores plus aHA, inhibited Pb adsorption, with inhibition increasing in the order aHA < DFO-D1 < DFO-B < DFO-E. At lower pH, all four ligands slightly enhanced Pb adsorption. These ligands also inhibited Cd adsorption at high pH, but had little or no effect at low pH. These results suggest that siderophore effects on metal mobility through porous media are likely to be complex and variable with pH.

B41D-0929 0830h POSTER

Isotopic Analyses of a new Cold Seep locality, Guenoc Ranch, Great Valley Group, Northern California

Kristin Hepper[1] (650-804-0747; KristinHepper@aol.com)

Lisa White[1] (650-338-1778; lwhite@sfsu.edu)

Kathleen Campbell[2] (64-9-373-7599 ext. 7418; ka.campbell@auckland.ac.nz)

[1]San Francisco State University, Department of Geosciences 1600 Holloway Avenue, San Francisco, Ca 94132, United States

[2]The University of Auckland, Department Of Geology Level 1,Chemistry Building 23 Symonds Street, Auckland 92019, New Zealand

A new Mesozoic cold seep limestone locality has been discovered in Great Valley Group (GVG) forearc strata of the Guenoc Ranch, bordering southeast Lake and northern Napa counties, northern California. Numerous scattered outcrops occur over 4 km, of which one petroliferous deposit (extending across 1.8 km) has been analyzed in detail. Petrographic and paleontologic observations indicate that this limestone unit formed via cold seep related processes during deposition of the GVG. Petrographic observations show clotted microbial and detrital micrite, pyritic corrosion surfaces, burrows, foraminifers, wood fragments, as well as fibrous, yellow, and sparry calcite; all of which are components typical of hydrocarbon seep deposits in the GVG. Lucinid and solemyid bivalves are also present, as are both large and small worm tubes, gastropods, and a Campanian (?) ammonite. The petrographic and paleontologic analyses strongly suggest that the Guenoc material resulted from venting methane. Carbon and oxygen isotope analyses are also being performed on the various micrites and cements seen in the Guenoc thin sections to add credence to the cold seep origin. Preliminary isotopic values for carbon and oxygen fall into the known range for cold seeps found within the GVG and worldwide. Generally, $\delta^{13}C$ values have been found to vary from seep to seep, ranging anywhere from -110 per mil to -20 per mil. Assuming no post-depositional alteration has occurred, values heavier than -20 per mil can still indicate a partial influence of venting methane on the carbon being incorporated into the carbonate. If post-depositional alteration has occurred however, the results of the isotopic data are inconclusive until further analyses are performed to ascertain the degree of alteration.

B41D-0930 0830h POSTER

What explains the sulfur isotope fractionation observed in the aquifer system of Puebla Valley, Mexico?

Guadalupe Velazquez-Oliman[1] (gvo@geol.niu.edu)

Eugene C Perry[1] (T60ecp1@wpo.cso.niu.edu)

Rosa M Leal-Bautista[1] (rlb@geol.niu.edu)

Melissa E Lenczewski[1] (melissa@geol.niu.edu)

[1]Northern Illinois University, Geology and Environmental Geosciences, DeKalb, IL 60115, United States

Puebla Valley, Mexico is located in the central part of the Trans Mexican Volcanic Belt and is surrounded by 3 large volcanoes: Popocatepetl (active since 1994), Iztaccihuatl (extinct), and Malinche (dormant). The aquifer system of the Valley contains at least two productive units: an unconfined aquifer formed mainly of alluvial and volcanic deposits and a second, confined aquifer, which has chemically distinct water that is sulfur-rich, high in CO_2, and high in alkalinity. There is a current debate about the origin of the sulfur-rich water, which is being used, after treatment, to lessen the deficit of water supply to the city of Puebla (with a population of approximately 1.5 million). Sulfate and sulfide species in water from the confined aquifer have an average sulfur isotope fractionation difference of 24.6 %. This fractionation is, at least in part, the result of bacterial sulfate reduction as evidenced by testing for bacteria with BART kits. Molecular analysis to identify the specific bacteria is underway. However, analysis of carbon isotopes of dissolved CO_2 (with average delta ^{13}C of 4.4%) and $^3He/^4He$ with average ratios of 2.1 for specific wells, located in the upper aquifer and characterized by having low sulfate but also rich in CO_2 and alkalinity, suggest a possible magmatic component. The carbon and helium isotope analysis of water from the confined aquifer is currently underway.

B41E MCC: 3014 Thursday 1020h

Regional-Scale Isotopic Interactions Between the Biosphere and the Atmosphere II *(joint with A, H, OS, GC)*

Presiding: **D Pataki,** University of Utah**; J Ehleringer,** University of Utah

B41E-01 1020h INVITED

Selective Logging Disturbance And Isotopic Composition Of Repired CO2 In Western Amazonia, Brazil

Jean P Ometto[1,2] (55 19 34294677; ometto@biology.utah.edu); Luiz A Martinelli[1] (martinelli@cena.usp.br); James R Ehleringer[3] (ehleringer@biology.utah.edu); Joseph Berry[3] (joeberry@globalecology.stanford.edu); Scott Miller[4] (sdmiller@uci.edu); Michael Goulden[4] (mgoulden@uci.edu)

[1]Centro de Energia Nuclear na Agricultura/USP, Av. Centenario, 303, Piracicaba, SP 13416-000, Brazil

[2]University Of Utah, Department of Biology 257 South 1400 East, Salt Lake City, UT 84112, United States

[3]Carnegie Institution of Washington, Department of Global Ecology 260 Panama St., Stanford, CA 94305, United States

[4]University of California, Dept. of Earth System Science, Irvine, CA 92697-3100, United States

Understanding the controls of gas exchange in primary and disturbed forests within the Amazon Basin is central to understanding the global carbon cycle, since tropical forests account for 40% of the carbon stored globally in terrestrial biomass. Stable isotope ratio analyses (13C, 18O) of atmospheric CO2 provide useful information regarding the balance between photosynthetic carbon gain and respiratory carbon loss in rainforest ecosystems and of the stomatal constraints on photosynthetic gas exchange. One useful isotopic parameter we have measured is the carbon isotope ratio of all respiration emerging from the ecosystem (del13Cr). Our recent observations suggest a direct relationship between logging activities and del13Cr values in these forests. Logging activities at the LBA site in Santarem, Para, began with the removal of lianas before the dry season and afterward selective logging. This logging activity opened the forest and resulted in a 4per mil shift in del13CR. During the following wet season (2002/2003), eddy covariance measurements at the logged site reported increased ecosystem gas exchange. Coincident with this increase in net ecosystem exchange, we observed a decrease in del13CR consistent with a decreased stomatal limitation on photosynthetic gas exchange in the logged forest.

B41E-02 1035h

Temporal variability in 13C of respired CO2 in a pine and a hardwood forest subject to similar climatic conditions

Behzad Mortazavi[1] (850-645-4639; mortazavi@ocean.fsu.edu); Jeffrey P Chanton[1] (850-644-7493; chanton@ocean.fsu.edu); Jim Prater[1] (850-644-6700; prater@ocean.fsu.edu); Christopher Oishi[2] (919-682-3803; andrew.oishi@duke.edu); Ram Oren[2] (919-613-8032; ramoren@duke.edu); Gaby Katul[2] (919-613-8033; gaby@duke.edu)

[1]Florida State University, Dept of Oceanography, Tallahassee, FL 32306-4320, United States

[2]Duke University, Nicholas School of the Environment and Earth Sciences LSRC, Box 90328, Durham, NC 27708, United States

The temporal variability in the 13C of ecosystem (äCr), soil (äCs) and foliage (äCf) respired CO2 were contrasted in a 18 m tall evenly aged loblolly pine forest and in a 35 m tall unevenly aged mature second growth deciduous mixed hardwood forest in North Carolina, USA, over a two year period. These two sites are located within a kilometer of each other and are subject to identical climatic and edaphic conditions. äCr varied in response to time lagged vapor pressure deficit (VPD) at both forests. However, the response of äCr to VPD was more dynamic at the pine relative to the hardwood. äCr at the pine forest varied from -31.0 to -26.4 per mill and at the hardwood forest from -26.0 to -27.0 permill during the growing season. äCr at the hardwood forest was 13C enriched during the growing season, on average, by 1.4 permill relative to äCr at the pine forest for the same time periods. Three factors influence these results. Canopy height and composition were different between the two sites, and also at the pine forest äCr values generally were more similar to äCf values, while at the hardwood forest, äCr values were more similar to äCs values. At the hardwood forest, the temporal variability in äCs was less that of äCf and buffered changes in the äCr. The results indicate that within a forest mosaic the vegetation structure needs to be considered for predicting realistic äCr values. Inclusion of a temporally and spatially variable äCr into the atmospheric inversion models will lead to a more realistic estimate of the partitioning of the global carbon uptake into oceanic and terrestrial sinks. Because äCr within each ecosystem varies in response to VPD in a predictable fashion, a variable äCr can be incorporated to better constrain atmospheric inversion models.

B41E-03 1050h

Disequilibrium of $^{13}CO_2$ fluxes between photosynthesis and respiration in North American temperate forest biomes

Chun-Ta Lai[1] (801-581-8917; lai@biology.utah.edu); James Ehleringer[1] (801-581-7623; ehleringer@biology.utah.edu); Andrew Schauer[1] (801-581-8917; schauer@biology.utah.edu); Pieter Tans[2] (Pieter.Tans@noaa.gov); Dave Hollinger[3] (davidh@hypatia.unh.edu); Kyaw Tha Paw U[4] (ktpawu@ucdavis.edu); Steven Wofsy[5] (wofsy@fas.harvard.edu)

[1]Department of Biology, University of Utah, 257S, 1400E, Salt Lake City, UT 84112, United States

[2]Climate Monitoring and Diagnostics Laboratory, National Oceanic and Atmospheric Administration,, 325 Broadway, Boulder, CO 80303, United States

[3]USDA Forest Service, Northeastern Research Station, P.O. Box 640, Durham, NH 03824, United States

[4]4. Department of Land, Air and Water Resources, University of California, University of California, Davis, CA 95616, United States

[5]Division of Engineering and Applied Science and Department of Earth and Planetary Science, Harvard University, Harvard University, Cambridge, MA 02138, United States

We report the first weekly dataset of seasonal and interannual variability in $\delta^{13}C$ of CO_2 fluxes from dominant forest ecosystems in the US. We observed large variations in the $\delta^{13}C$ of respired biosphere-atmosphere fluxes ($\delta^{13}C_R$) across 3 temperate coniferous and deciduous forest ecosystems (-24.9 $\pm$ 0.4 to -31.3 $\pm$ 0.6 per mil). Values of $\delta^{13}C_R$ were significantly correlated with growing-season soil water availability. By analyzing daytime flask measurements collected at the top of canopies, we estimated an annual mean, flux-weighted $\delta^{13}C$ of net ecosystem CO_2 exchange fluxes ($\delta^{13}C_{net}$). Combining $\delta^{13}C_R$ and $\delta^{13}C_{net}$, along with eddy-covariance measured fluxes, we estimated regional discrimination against ^{13}C during photosynthesis (Δ_A) for these 3 forest ecosystems. Our approach allows for examination of the interannual correlations between gross primary production fluxes and Δ_A that could potentially modulate atmospheric 13C budget. The results showed that C_3 forests in temperate regions in the U.S. exhibited a slight isotopic disequilibrium (< 1 per mil) on an annual basis, despite significant seasonal variations in respired $\delta^{13}CO_2$ values (> 3 per mil). Such subtle isotopic disequilibrium however, when associated with enormous one-way gross fluxes, can effectively affect atmospheric ^{13}C budget.

B41E-04 1105h

Partitioning Net Ecosystem Carbon Exchange Into net Assimilation and Respiration With Canopy-scale Isotopic Measurements: an Error Propagation Analysis With Both ^{13}C and ^{18}O Data

Philippe Peylin[2] ((33) 1 69 08 77 18; peylin@lsce.saclay.cea.fr); Jerome Ogee[1] ((33) 1 69 08 77 18; ogee@lsce.saclay.cea.fr); Matthias Cuntz[1] ((33) 1 69 08 95 06; cuntz@lsce.saclay.cea.fr); Thierry Bariac[2] (thierry.bariac@inra.fr); Philippe Ciais[1] (ciais@lsce.saclay.cea.fr); Yves Brunet[3] (yves.brunet@inra.fr)

[1]LSCE, CEA-Orme des merisiers, Gif sur Yvette 91191, France

[2]BiomCo, Inra-grignon, Thiverval Grignon 78850, France

[3]Bioclimatologie, Inra-Bordeaux, Villenave d'ornon 40000, France

Stable CO_2 isotope measurements are increasingly used to partition the net CO_2 exchange between terrestrial ecosystems and the atmosphere in terms of non-foliar respiration (F_R) and gross photosynthesis (F_A). However the accuracy of the partitioning strongly depends on the isotopic disequilibrium between these two gross fluxes and a rigorous estimation of the errors on F_A and F_R is needed. In this study we account and propagate uncertainties on all terms in the mass balance equations for total and "labeled" CO_2 in order to get precise estimates of the errors on F_A and F_R. We applied our method to a maritime pine forest in the Southwest of France. Using the δ^{13}C-CO_2 and CO_2 measurements, we show that the resulting uncertainty associated to the gross fluxes can be as large as 4 mol m^{-2} s^{-1}. In addition, even if we could get more precise estimates of the isoflux and the isotopic signature of F_A we show that this error would not be significantly reduced. This is because the isotopic disequilibrium between F_A and F_R is around 2-3$^o/_{oo}$, i.e. the order of magnitude of the uncertainty on the isotopic signature of F_R (δ_R). With δ^{18}O-CO_2 and CO_2 measurements, the uncertainty associated to the gross fluxes lies also around 4 mol m^{-2} s^{-1}. On the other hand, it could be dramatically reduced if we were able to get more precise estimates of the $CO^{18}O$ isoflux and the associated discrimination during photosynthesis. This is because the isotopic disequilibrium between F_A and F_R is large, of the order of 10-15$^o/_{oo}$, i.e. much larger than the uncertainty on δ_R. The isotopic disequilibrium between F_A and F_R or the uncertainty on δ_R vary among ecosystems and over the year. Our approach may help to choose the best strategy to study the carbon budget of a given ecosystem using stable isotopes.

B41E-05 1120h

Isotope discrimination and partitioning exercises at the scale of the atmospheric boundary layer

Joseph Berry[1] (650-325-1521 x363; joeberry@catalase.stanford.edu)

brent helliker[1] (helliker@catalase.stanford.edu)

Peter bakwin[2] (Peter.Bakwin@noaa.gov)

kenneth davis[3] (davis@essc.psu.edu)

margaret torn[4] (mstorn@lbl.gov)

[1]carnegie institution of washington, dept of global ecology, 260 panama st., stanford, ca 94305, United States

[2]National Oceanic and Atmospheric Administration-Climate Monitoring and Diagnostics Lab, 325 Broadway R/CMDL1, boulder, co 80305, United States

[3]Department of Meteorology, Pennsylvania State University, 512 Walker Building, University Park, pa 16802, United States

[4]Lawrence Berkeley National Laboratory, Earth Sciences Division, 1 Cyclotron Road Mailstop 90-1106, Berkeley, ca 94720, United States

During the daytime the atmospheric boundary layer (ABL) is typically well mixed by convection up to about 1.5 km and moves across the land about 500 km per day. Underlying ecosystems modify carbon dioxide in the ABL through photosynthesis and respiration, and ABL air is ultimately replaced by air from the overlying free troposphere. Hence, measurements of carbon dioxide and isotopes in the ABL and the free troposphere offer the potential for regionally integrated estimates of isotope discrimination. We use tall-tower and airplane measurements of carbon dioxide and carbon and oxygen isotopes to develop estimates of ABL-scale isotope discrimination. We then utilize ecosystem-level measurements of the isotope ratio of respiration and land surface model estimates of photosynthetic discrimination to deconvolve net carbon dioxide fluxes into the gross components of photosynthesis and respiration at the regional scale.

B41E-06 1135h

Constraints on the Use of ^{18}O in CO_2 as a Tracer to Partition Gross Carbon Fluxes

William J Riley[1] (510 486-5036; wjriley@lbl.gov)

Christopher J Still[2] (805.893.5501; still@icess.ucsb.edu)

[1]Lawrence Berkeley National Lab, 90-1106 LBNL, ESD 1 Cyclotron Rd, Berkeley, CA 94720, United States

[2]U.C. Santa Barbara, Geography Department 3611 Ellison Hall UC Santa Barbara, Santa Barbara, CA 93106, United States

Measurements of ^{18}O in atmospheric CO_2 can be used to partition measured net CO_2 ecosystem fluxes into photosynthesis and respiration. However, uncertainties and temporal variability in the $\delta^{18}O$ value of the soil-surface CO_2 flux (δF_s) and the retro-diffused CO_2 flux (δF_r) can lead to substantial errors in partitioning estimates. We will discuss an integrated isotope and ecosystem model (ISOLSM) that simulates exchanges of ^{18}O in H_2O and CO_2 in soil and plants, and will apply the model to identify critical factors associated with CO_2 flux partitioning. Modeling results, regression analysis of model predictions, and an analysis of characteristic times of relevant processes indicate that, in contrast to previous reports, the $\delta^{18}O$ value of soil water (δ_{sw}) in the top few cm of soil strongly impacts δF_s. Thus, accurately characterizing near-surface δ_{sw} is critical to the CO_2 flux partitioning approach. We also discuss the impact of the soil CO_2 source distribution within the column, soil temperature, and the $\delta^{18}O$ value of atmospheric CO_2 on predictions of δF_s. Disequilibrium between CO_2 and leaf water, which may be common in C_4 grasses, will impact δ F_r and therefore the partitioning of the measured net ecosystem CO_2 flux. Finally, temporal variability in δ F_r, in particular, can lead to errors in flux partitioning when measurements of the $\delta^{18}O$ value of leaf water and of ^{18}O in atmospheric CO_2 and are not made concurrently. We will present results demonstrating the impact of these factors on partitioning estimates and discuss measurement protocol necessary to accurately partition measured net ecosystem CO_2 fluxes into their component gross fluxes. We will also briefly discuss the relative merits of ^{18}O versus ^{13}C as a tracer for partitioning net fluxes.

B41E-07 1150h

Incorporating and Evaluating Stable Water Isotopes into Land-surface Parameterisation Schemes

Ann Henderson-Sellers[1] (ahssec@ansto.gov.au)

Kendal McGuffie[2] (kendal.mcguffie@uts.edu.au)

[1]ANSTO Environment, PMB 1, Menai, NSW 2234, Australia

[2]Department of Applied Physics, University of Technology, Sydney, Broadway, NSW 2007, Australia

Measuring and simulating the isotopic composition of water in the near-surface component of the hydrological budget of coupled climate system models may help to overcome the lack of observational data for validation. Isotopic investigations (Salati *et al.*, 1979) of the $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios motivated the world's first global climate model tropical deforestation simulation (Henderson-Sellers and Gornitz, 1984). The GRDC (Global Runoff Data Centre) runoff data set is problematic as a source for model validation in some areas (e.g. Amazon) because it is inconsistent with accepted precipitation data such as CMAP. However, modelled river routing systems are now being tested against river-based isotopic measurements (e.g. Gibson *et al.*, 2002). Complete interpretation of isotopic variations in terms of system variability and change is currently handicapped by the lack of agreed and validated isotopic earth system model components, although this difficulty is balanced by the fact that there has been no tuning of models to isotopic data as yet. Before databases become more prevalent and schemes are tested against, and tuned to fit, isotopic measurements, this initiative contributes an intercomparison of current state-of the-art isotope modelling. Among the land-surface schemes that incorporate isotopic representation that were compared under the auspices of IPILPS (Isotopes in the Project for Intercomparison of Land-surface Parameterization Schemes) we find three characteristic groups (Henderson-Sellers *et al.*, 2003). Results from experiments using ISOLSM (Riley *et al.*, 2002) demonstrate that the near-surface isotopic composition of the atmosphere is affected differently in different climate regimes. Our results make a persuasive case for examining other environments in which isotopic characteristics differ significantly, e.g. the tropical forests where near-isothermal conditions allow probing of the Rayleigh formulation; arid soil revealing 'pulses' of isotopically characterized water flows; and, as the solid phases of water do not exchange isotopes with the atmosphere, snow and frozen soil water, which isotopically differentiate characteristics seasonally (Gibson & Edwards 2002).

B41E-08 1205h

Climate Phase and Long-Term Site Specific Patterns of Isotopes (d18O) in Precipitation across the U. S.

Jeffrey M Welker[1] (970-491-1796; jwelker@nrel.colostate.edu); James W White[2] (303-4925495; jwhite@colorado.edu); Ryan Vachon[2] (ryan.vachon@colorado.edu); Melanie Zauscher[2] (melaine@gandulazul.com); Chris Castro[3] (chris@atmos.colostate.edu); Roger Pielke[3] (pielke@atmos.colostate.edu)

[1]Natural Resource Ecology Lab, Colorado State University, Fort Collins, CO 80523, United States

[2]Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO 80345, United States

[3]Department of Atmospheric Sciences, Colorado State University, Fort Collins, CO 80523, United States

Our understanding of the spatial and temporal patterns of the isotopic characteristics of precipitation across the U. S. has been limited because no systematic analysis have been conducted across the U. S. during divergent climate phases or over extended recent time periods. Using weekly precipitation samples from a spatially complete set of sampling stations across the U. S. we have evaluate the following questions: a) what are the seasonal patterns of the isotopic (d18O) patterns across the U. S. during Neutral and El Nino phases, b) to what degree do differences in temperature, precipitation and climatology explain El Nino affects on the seasonal patterns of isotopes in precipitation and c) what are the long-term patterns and magnitudes of d18O-values in precipitation over a recent 10-year period for sites in the western, central and eastern U. S.? We have found that depleted precipitation dominates the Northern Rocky Mountain region, while relatively enriched precipitation occurs in the western U. S. and in the southern Great Lakes region, however, these patterns are season specific, being magnified in spring and fall. These seasonal differences appear to reflect climatological changes with intensification of the sub-tropical flow and a delay in the monsoon formation during El Nino phases. Time-series data for sites in the western U. S. exhibit the strongest annual and monthly temperature correlations with slopes ranging between 0.3 to 0.6oC per mil of d18O.

B