

present a novel method capable of natural isotopic detection in the nM range. In addition to a fast analysis time (batch preparation in less than one hour for nitrogen isotopes), this method is capable of very low blanks (less than 1 nanomole) with sample precision of 0.2 permil for nitrogen and 0.5 permil for oxygen. The first step of the method is reduction of nitrate to nitrite by use of either spongy cadmium or UV light. UV light reduction has the advantage of a short reaction time (13 minutes), but is not capable of oxygen isotope analysis due to exchange with water. Reduction using spongy cadmium retains the oxygen isotopic signature, but requires up to 3 hours to react. Both reactions are non-fractionating with respect to nitrogen. The next step is the reduction of nitrite to nitrous oxide using either hydroxylamine or azide. The hydroxylamine has the advantage of being nontoxic, but the reaction time is 2 hours and oxygen is exchanged with water. The azide-nitrite reaction is complete in only 3 minutes and retains both nitrogen and oxygen isotopes of nitrate. The produced nitrous oxide is then purged and trapped in liquid nitrogen, then released into a capillary GC column connected to an isotope ratio mass spectrometer.

B31D-0340 0830h POSTER

Stable Isotope Analyses of Phosphate Oxygen From Micro-samples of Biological Apatite: A new Routine Procedure for Silverphosphate Micro-precipitation and the Removal of Organic Contamination

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Oxygen isotope analyses in bone and teeth of living and fossil animals are widely used for testing hypotheses about variability of diet and habitat. For the analysis of environmental or dietary changes in the past, tooth enamel has become the preferred study material, because its mineral content is higher than bone and dentine, and the relatively large size of the carbonato-apatite crystals of enamel make it more stable against *post mortem* diagenetic alteration than dentine or bone. Intra-tooth sampling of dental enamel is increasingly used for the investigation of seasonal climate variability, taking advantage of both the high correlation between an animal's drinking water and the $\delta^{18}\text{O}$ in its mineralized tissues and the incremental growth pattern of tooth enamel. The different oxygen-containing ions of bioapatite (phosphate, carbonate, and hydroxyl group) incorporate into the mineral lattice at different rates during enamel mineralization, and differ in their susceptibility against *post mortem* diagenetic alteration. In addition, it is difficult to account for the different reaction chemistries of phosphate, carbonate, and hydroxyl group using isotope analysis techniques that include all oxygen contained in the enamel (e.g., laser ablation). These problems can be addressed analyzing phosphate oxygen only. However, two major factors limit the potential of $\delta^{18}\text{O}$ analyses in dental enamel: A) the starting sample size for isotope analyses often precludes the use of small teeth or the intra-tooth sampling of a given tooth; B) Small amounts of biogenic organic material in tooth enamel (less than 1% by wt) can reduce the precision and lead to anomalous analytical results in $\delta^{18}\text{O}$ measurements on Ag_3PO_4 produced from tooth enamel. A new procedure was developed for the pre-treatment and $\delta^{18}\text{O}$ analysis of phosphate from small samples (500 μg) of tooth enamel containing organic matter. Ag_3PO_4 was precipitated quantitatively for analysis of $\delta^{18}\text{O}_{\text{phosphate}}$ using a Thermoquest-Finnigan TC/EA coupled to Delta^{Plus} XL. A sodium hypochlorite sample pre-treatment step was determined to remove organic matter quantitatively without altering the isotopic composition of the phosphate oxygen. The reproducibility of $\delta^{18}\text{O}$ values for pretreated samples (0.2-0.3 ‰, 1 σ) is much better than for samples without pre-treatment (1.2 ‰, 1 σ). Phosphate oxygen isotope standards processed using this technique gave measured values indistinguishable from the standard composition, demonstrating the accuracy of the new technique.

B31D-0341 0830h POSTER

A Time Series Investigation of the Oxygen Isotopic Composition of Dissolved Inorganic Phosphate in Monterey Bay Seawater

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Phosphorus is an essential and limiting macro-nutrient for productivity in marine ecosystems. Because the P-O bond in phosphate is resistant to inorganic hydrolysis and the fractionation and exchange of oxygen isotopes will only occur due to intracellular biological cycling, the oxygen isotopic composition of dissolved inorganic phosphate (DIP) in seawater may be used as a tracer for modern phosphate recycling in aquatic ecosystems. The degree of disequilibrium between the $\text{d}18\text{O}$ of DIP and that of the surrounding water will act as a proxy for the extent of phosphate recycling through the biomass in a particular system. A time series investigation of a dynamic system such as the Monterey Bay could indicate how ecosystems vary the extent of phosphate turnover as the system becomes nutrient stressed following a bloom period. The nutrient dynamics in the Monterey Bay vary temporally and are characterized by seasonal upwelling from March to September which supplies nutrients to the surface waters and sustains high productivity during these months. We conducted monthly depth profiles for a year at MBARI stations C1, M1 and M2 to assess the variation in $\text{d}18\text{O}$ of DIP over the course of the onset of the upwelling season and less productive seasons which follow. The results of this time series investigation were compared to estimates of primary productivity, chlorophyll concentrations, temperature, salinity, and nutrient concentrations to determine if phosphate turnover varies with these seasonal ecosystem changes and if during periods of higher nutrient availability phosphate is utilized less efficiently than during periods of lower nutrient availability.

B31D-0342 0830h POSTER

Sulfur Biogeochemistry and Isotope Fractionation in Shallow Groundwater of Owens Dry Lake, California

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The redox status of hypersaline, strongly alkaline groundwaters at Owens Dry Lake was investigated to help guide mitigation efforts for attenuating dust generated from the dry lakebed. Shallow (<1 m), anoxic groundwaters have been identified as a major limitation to vegetation establishment on the lakebed due to the inability of roots to grow in anoxic conditions. Previous work indicates that sulfate reduction is the dominant reaction regulating the redox status of shallow groundwaters. The purpose of this study was to evaluate sulfur biogeochemistry and formation of solid-phase sulfides in the shallow groundwater/sediments using selective sulfur speciation techniques coupled with isotopic measurements. In addition to groundwater and subsurface sediment samples (1-2 m depth) at sites representative of different groundwater pathways, selected sediment samples at 5 different depths (from oxic to anoxic layers) were collected. Sediment samples were examined for monosulfide, pyrite, sulfate, organic sulfur, and total sulfur. Organic sulfur was less than 0.01% of the total, and pyrite was the predominant sulfur-bearing phase below the groundwater capillary zone (~20cm depth) where anoxic conditions were developed. The concentration of monosulfide and pyrite were less than detection limits above

the capillary zone as these unsaturated layers were exposed to oxygen. High concentrations of dissolved sulfide (4.81 to 134.7 mg/L) and low concentrations of dissolved Fe (generally <0.5 mg/L) indicate that the availability of Fe limits pyrite formation. The high values (~50‰) of isotopic fractionations between $\delta^{34}\text{S}_{\text{pyrite}}$ and $\delta^{34}\text{S}_{\text{sulfate}}$ ($\Delta_{\text{sulfate-pyrite}}$) in anoxic zones suggest that bioavailability of organic carbon is a limiting factor for the reduction of sulfate. The values of $\Delta_{\text{sulfate-pyrite}}$ along the hydrologic flowpath indicate that the isotopic fractionations were significantly correlated with dissolved sulfate concentration, which was strongly controlled by evaporation. This indicates that spatial variations in the concentration of dissolved sulfate due to evaporation can be reflected in the pyrite content of sediments in groundwater. The important role of evaporation on the concentration of sulfate in groundwater was confirmed using hydrogen and oxygen isotope values of pore fluids.

B31D-0343 0830h POSTER

Analysis of growth and tissue replacement rates by stable sulfur isotope turnover.

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Stable isotope analysis has become a powerful tool to study animal ecology. Analysis of stable isotope ratios of elements such as carbon, nitrogen, sulfur, hydrogen, oxygen and others have been used to trace migratory routes, reconstruct dietary sources and determine the physiological condition of individual animals. The isotopes most commonly used are carbon, due to differential carbon fractionation in C3 and C4 plants, and nitrogen, due to the approximately 3‰ enrichment in ^{15}N per trophic level. Although all cells express sulfur-containing compounds, such as cysteine, methionine, and coenzyme A, the turnover rate of sulfur in tissues has not been examined in most studies, owing to the difficulty in determining the $\delta^{34}\text{S}$ signature. In this study, we have assessed the rate of sulfur isotopic turnover in mouse tissues following a diet change from terrestrial (7‰) to marine (19‰) source. Turnover models reflecting both growth rate and metabolic tissue replacement will be developed for blood, liver, fat and muscle tissues.

B31E MCC: Level 1 Wednesday 0830h

Regional-Scale Isotopic Interactions

Between the Biosphere and the Atmosphere I Posters (*joint with A, H, OS*)

Presiding: M J Kohn, University of
South Carolina; J van Haren,
Columbia University Biosphere 2Center

B31E-0344 0830h POSTER

A New Perspective on the Temperature-Dependence of Stable Isotopes in Modern Precipitation

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Distillation of water vapor from the atmosphere is primarily temperature-dependent, as illustrated by the well-known correlation between the stable isotope composition of precipitation and temperature. However, reevaluation of modern precipitation, temperature, and isotope data indicates major errors in the assignment of temperature dependencies. This has a profound impact on use of stable isotopes of precipitation for ecosystem studies, models of atmospheric circulation, and continental paleoclimate investigations. Past analysis has

used the mean surface temperature over the time interval of sample collection (e.g., mean weekly, monthly, or annual temperature) to calculate temperature coefficients, but different approaches at mid-latitudes give different temperature coefficients ($\Delta\delta^{18}\text{O}/\Delta T$). (a) Spatial correlations among geographically distinct sites yield $\sim 0.55^\circ/\text{oo}/^\circ\text{C}$; (b) Seasonal variations at single sites yield $\sim 0.2\text{--}0.4^\circ/\text{oo}/^\circ\text{C}$; and (c) 12 month running averages yield $\sim 0.5\text{--}1^\circ/\text{oo}/^\circ\text{C}$. These disparities result because there are systematic differences in temperature during precipitation events vs. time-averaged surface temperature means. Correction for this bias using hourly weather and monthly isotope data from US sites reconciles disparate temperature-dependence estimators for modern precipitation, and yields a consistent $\sim 0.55^\circ/\text{oo}/^\circ\text{C}$ for all three approaches. Revised temperature coefficients based on surface observations are also commensurate with coefficients obtained using cloud base temperatures. Revised values are within the range of theoretical distillation models $\sim 0.5\text{--}0.7^\circ/\text{oo}/^\circ\text{C}$, and provide a consistent basis for investigating atmospheric processes and isotopic response to climate change.

B31E-0345 0830h POSTER

Isotope Signals on Multiple Timescales Simulated Using a Simple Earth System Model Incorporating Variable Ecosystem Features

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Stable isotopes of water and stable and radioactive isotopes of carbon, are employed widely in Earth system modelling. Carbon isotopes differentiate and monitor biological and abiological sources and sinks of CO_2 and CH_4 (e.g. Ciais *et al.*, 1995) while the stable isotopes of water have been used to interpret long-term temperature trends since Dansgaard (e.g. Petit *et al.*, 1999). While early Global Climate Models (GCMs) were used to attempt to verify and interpret isotopic measurements (e.g. Joussaume *et al.*, 1984), more recent GCMs have challenged the simple correlations upon which ecosystem-based isotopic flux interpretation is founded (e.g. Noone and Simmonds, 2002). These contradictions present an opportunity for an isotopically capable EMIC (Earth-system Model of Intermediate Complexity) with which to investigate isotopes as indicators of ecosystem flux changes. We have added isotopic representation of ^{18}O and D in water to a DAFM (Dynamic Area Fraction Model) and hence assessed δD and $\delta^{18}\text{O}$ in precipitation as a function of local and global temperatures. In many situations, local relationships are developed between the isotopic composition of precipitation and the local mean temperature. Such relationships are then applied to palaeo-isotopic ratios derived from ice cores to develop palaeo-temperature datasets and are sensitive to other aspects of the climate system. In addition to the evaluation of this simple model for isotopic studies, this paper evaluates the dependency of δD and $\delta^{18}\text{O}$ enrichment/depletion on temperatures and the sensitivity to (i) local temperatures; (ii) moisture sources and transported distance; (iii) surface cover dynamics (i.e. ice, water, plants); (iv) the sensitivity of carbon pools; (v) biological and abiological sources over time; and (vi) modification of carbon sources and sinks as a function of climate.

B31E-0346 0830h POSTER

The D/H Ratio in Atmospheric Water Vapour: Continuous in situ Measurements of Soil-Plant-Atmosphere Exchange by Fourier Transform Infrared Spectroscopy

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The D/H ratio in atmospheric water vapour provides a valuable tracer for exchange and transport processes. We present a novel method for real-time, continuous, in situ field measurements of the D/H ratio of atmospheric water vapour, and illustrate the method with measurements of vertical profiles of both water content and $\text{HDO}/\text{H}_2\text{O}$ ratio over an agricultural pasture in SE Australia. We measured 7-point vertical profiles (0.5-22m) every 30 minutes continuously over a three week period in spring. The observed variations in the vertical profiles on diurnal and weekly timescales provide valuable constraints on the exchanges of water between atmosphere, soil and plants. The measurement technique used is Fourier Transform Infrared (FT-IR) spectroscopy. Whole air was drawn via a buffer volume into a multi-pass optical absorption cell from inlet lines on a 22m tower in the pasture paddock. The FT-IR absorption spectrum of the air was recorded with a Bomem MB100 FTIR spectrometer at 1 cm^{-1} resolution, typically for 2 minutes per sample. Each of the 7 inlets was sampled twice per half hour to provide 30 minute average vertical profiles. Precision in δD is around 1-2 per mil. The instrument can be fully automated, and is mobile and suitable for field measurements.

B31E-0347 0830h POSTER

A Non-steady-state Analytical Model to Compute the Stable Isotope Enrichment of Leaf Water at the Evaporative Sites Under Field Conditions

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The $^{18}\text{O}/^{16}\text{O}$ ratio of leaf water is a useful signal, notably because it affects the oxygen isotopic composition of atmospheric CO_2 which thereby gives rise to the possibility of assessing terrestrial gross primary productivity at different spatial scales. It is now established that this ratio is governed by two competing effects which are the isotopic enrichment of leaf water during transpiration and the back-diffusion of the heavy water from the sites of evaporation into the xylem. In most studies, measurements are made in the laboratory with controlled environment and saturating light, so that leaf transpiration is at its maximum and steady-state conditions are reached. However, in a natural and varying environment, where leaves are not light-saturated, we expect non-steady-state effects to be strong. Indeed 2-3 h are usually needed for the steady-state to be reached while environment variables are known to change significantly over a time step of only 30 min. For this reason we developed a non-steady-state model that allows to compute the $^{18}\text{O}/^{16}\text{O}$ ratio of leaf water between the xylem and the evaporative sites in a varying and not light-saturated environment. Under realistic field conditions the deviation from the steady-state values can be as great as $10\text{--}15^\circ/\text{oo}$ at the evaporative sites after 1 h. This demonstrates the importance of considering the non steady-state when studying the $^{18}\text{O}/^{16}\text{O}$ ratio signal in the natural environment. When the initial conditions for the $^{18}\text{O}/^{16}\text{O}$ ratio are assumed to vary exponentially from the leaf xylem to the evaporative sites, the model has an analytical solution which makes its use possible also for larger scale studies.

B31E-0348 0830h POSTER

Preliminary Measurements of Oxygen-18 and Hydrogen-2 in Water Samples Collected from a Cloud Forest in Monteverde, Costa Rica

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We collected water samples in August, 2003 from a cloud forest in Monteverde, Costa Rica. This forest is inundated frequently by orographic clouds formed during rapid uplift of trade winds along the Cordillera de Tilaran. Climate observations at Monteverde suggest an overall warming along with intensification of the January-April dry season when convective storms are minimal and orographic cloudwater inputs are most important for the forest ecosystem. This intensification may be driven by uplift of the orographic cloud base above the forest elevation. In order to assess how such changes affect the forest ecosystem, we collected samples during a convective rainstorm, from orographic clouds flowing over the forest, from canopy mosses, and from stream water. The long-term objective of this research is to quantify the influence of orographic clouds on the ecological functioning of this forest. This will include an assessment of cloud water usage by the vegetation using isotopic tracers. We will take advantage of the isotopic offset between cloudwater and convective precipitation to partition water usage by forest vegetation into cloudwater and precipitation inputs on seasonal and interannual bases.

B31E-0349 0830h POSTER

Description and Preliminary Results From an On-Line Method of Analysis of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2

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At the Biosphere 2 Center in Oracle, Arizona we have developed a continuous flow analysis method to measure in "real-time" the concentration, $^{13}\text{C}/^{12}\text{C}$, and $^{18}\text{O}/^{16}\text{O}$ of CO_2 in air. CO_2 isotope analysis in air samples is crucial for the partitions of the net ecosystem flux into its net assimilation and respiration components. Previous analysis techniques depend on having many glass flasks and transporting the flask samples to the lab for analysis. Our technique transports gas using 1/4 inch tubing from various sampling points in Biosphere 2 Center to an on-site laboratory, which houses the on-line discrimination stable isotope mass spectrometer (O.L.D.S.I.M.S.). OLDSIMS is a system designed to combine a Licor 6262 gas analyzer (Lincoln, NE) for instant CO_2 concentration values, a SIRA (Stable Isotope Ratio Analyzer, VG-Micromass, UK), and a Process Control computer for peripheral system control and coordination with the SIRA. The stable isotope and concentration analysis of one sample as well as a know reference gas currently takes OLDSIMS 12.4 minutes to run. Results from a diurnal run of a standard CO_2 tank are: $[\text{CO}_2] = 998.7 \pm 0.45$ ppm, $\delta^{13}\text{C} = -3.34 \pm 0.098^\circ/\text{oo}$, $\delta^{18}\text{O} = -11.75 \pm 0.108^\circ/\text{oo}$ vs PDB. During our presentation we will show this and other data collected at the Biosphere 2 Center tropical rainforest biome to demonstrate the capabilities of this "real-time" technique.

B31E-0350 0830h POSTER

Source Contributions to the Carbon Isotopic Signature of Ecosystem Respiration in a Northern Deciduous Forest Ecosystem

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Respiratory carbon (R_c) losses from forests are large and may account for regional differences in annual carbon sequestration. In addition, different sources of R_c respond differently to temperature, soil moisture, and current photosynthesis. One of our objectives at the UMBS Forest Carbon Cycle Research Program in northern lower Michigan USA (45.6° N, 84.7° W) is to partition ecosystem respiration (R_e) among major contributing fluxes and to account mechanistically for annual and interannual variation in R_e . Previous work based on analyses of the temperature and moisture dependencies of soil, leaf, and bole respiration suggested that over three years (1999-2001), soil respiration contributed ~ 70% of R_e , with leaves and boles contributing 11% and 19% respectively. With the installation of a ThermoFinnigan Delta^{Plus} XL isotope ratio mass spectrometer at UMBS in early 2003 we have expanded our analyses of R_e to include partitioning the isotopic signature of R_e into that contributed by the autotrophic and heterotrophic components of soil respiration, and by leaves, branches, and coarse woody debris. Results from Keeling plots taken mid-summer 2003 at 2.5 m above the soil surface showed an ecosystem $\delta^{13}C$ of -24.5‰/‰. Soil respiratory $\delta^{13}C$ taken from soil cuvettes was very similar, at -24.7‰/‰. Cortical photosynthesis in *Populus*, the dominant canopy species, caused a shift in branch respiratory $\delta^{13}C$ from -21.5‰/‰ in the dark to -15.2‰/‰ in the light. Respiratory $\delta^{13}C$ from coarse woody debris varied with decay class, but averaged ~ -26‰/‰. Leaf organic matter $\delta^{13}C$ varied with canopy position and species, from ~ -27‰/‰ at the top of the canopy to ~ -30‰/‰ in the shrub layer. We will use these observations as an independent check against our partitioning of R_e based on measured component fluxes and to facilitate interpretation of the responses of these ecosystem components to changing environmental conditions.

B31E-0351 0830h POSTER

Variation in ^{13}C abundance in Respiration Among Ecosystem Components: Implications for Flux Partitioning

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Contrary to the longstanding notion of isotopic equilibrium among ecosystem respiration components, we found significant variation in the carbon isotope ratio of CO₂ respired from leaves, stems, roots and soil microorganisms in five contrasting ecosystems along a climate gradient in California (redwood forest, chaparral, grassland, oak savanna, ponderosa pine plantation). The largest differences were observed between leaf and microbial respiration (5.84 per mil +/- 1.58 per mil; mean +/- SD) with the signature of ecosystem respiration always lying between that of leaves and microbes (leaves < ecosystem < microbes). Based on these differences, we determined that ecosystem respiration comprised an average of 25% microbial and 75% plant respired CO₂ (+/- 10%). Further study is underway to determine the underlying cause of these isotopic differences.

B31E-0352 0830h POSTER

Measurement of Discrimination Against ^{13}C During Photosynthesis ($\Delta^{13}C$) and Quantification of the Short-Term Variability of $\Delta^{13}C$ Over a Diurnal Cycle

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We measured the net fractionation of photosynthesis ($\Delta^{13}C$) for a slash pine (*Pinus elliotii*) through the analysis of eight consecutive air samples collected from a closed system while foliage contained within the system was undergoing photosynthesis. A model was applied to the series of samples to calculate the isotopic composition of the carbon removed and the resulting $\Delta^{13}C$. Raleigh distillation equations were built into the model to correct for the closed-system isotopic-dilution effects, and the results were compared to other techniques for calculating $\Delta^{13}C$. This technique was found to have higher resolution than the two-endmember models and provided the necessary tools for investigating short-term variability. Consecutive measurements

were made over one daylight cycle to test the hypothesis that the observed variation in $\Delta^{13}C$ would exceed the variation predicted by the established and frequently modeled relationship between c_i/c_a and $\Delta^{13}C$ because of the draw down of CO₂ concentrations at the chloroplast when photosynthetic rates are elevated. The results from this study show a good correlation between predicted $\Delta^{13}C$ values from the c_i/c_a model and the measured values except when photosynthetic rates were near the daily minimums and maximums, with the predicted value underestimating $\Delta^{13}C$ when rates were very low and overestimating $\Delta^{13}C$ when rates were high. Measurements of foliage-respired CO₂ $\delta^{13}C$ were also made, and the values are consistently ^{13}C depleted relative to the fixed carbon $\delta^{13}C$ values, but show a mid-day ^{13}C enrichment indicating recently fixed carbon as the major substrate for respiration.

B31E-0353 0830h POSTER

Carbon cycling in an old growth forest

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Currently ocean and terrestrial biosphere are significant sinks for atmospheric carbon dioxide. The partitioning of the sink into these two reservoirs can be constrained by observations of the mass and ^{13}C isotope balance of CO₂ of the atmosphere, as uptake by the terrestrial biosphere discriminates more against ^{13}C than does ocean uptake. A large uncertainty in the equations used for the ^{13}C mass balance of the atmosphere is the isotopic disequilibrium that results from secular changes in the $\delta^{13}C$ of atmospheric CO₂ that have occurred since the beginning of the industrial revolution. The atmosphere has become more enriched in $^{12}CO_2$. Because there is a time delay of several years in the cycling of fixed carbon through terrestrial ecosystems, the isotopic composition of CO₂ released by respiration from the ecosystem can be more enriched in ^{13}C than that which is currently being fixed. This disequilibrium of the land carbon fluxes accounts for about 20% of the total isotope balance of atmospheric CO₂, and this term has been difficult to measure. We have constructed an integrated land surface and carbon cycle model that explicitly treats the dynamics of carbon movement through (and the isotopic composition of) multiple carbon pools. We have used this model to simulate carbon cycling, the isotope ratio of major carbon pools and the isotopic disequilibrium in this ecosystem as forced by measured changes in the concentration and isotopic composition of CO₂ over the past 400 years. We compare these simulations to observations of the present carbon isotopic composition of carbon in various pools in the ecosystem, to independent estimates of the turnover times of these pools, and to rates of net CO₂ exchange by the ecosystem. We discuss the constraints that these observations provide on the isotopic disequilibrium flux from this ecosystem and the possible use of this model for estimating the global terrestrial ^{13}C -disequilibrium.

B31E-0354 0830h POSTER

A model simulation of carbon dioxide and stable carbon isotope exchange between the atmosphere and terrestrial biosphere: Is the terrestrial $\delta^{13}C$ discrimination effect decreasing?

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Terrestrial ecosystems exchange a huge amount of carbon with the atmosphere, causing seasonal, interannual, and even long-term variability in atmospheric CO₂ concentration. They also affect stable carbon isotope composition of atmospheric CO₂, because of photosynthetic discrimination against heavier stable carbon isotope (^{13}C). In this study, atmosphere-biosphere exchange of CO₂ was simulated with a process-based terrestrial carbon cycle model (Sim-CYCLE), including stable carbon isotopic features. The fractionation factor is affected by a couple of factors: photosynthetic pathway (C3/C4), stomatal gas diffusion, and recycling of respired CO₂ within canopy. A long-term simulation

from AD 1901 to 2000 suggested that average discrimination effect would be -16.5 per mil, including -1.8 per mil by canopy recycling. Apparently, C3 species had larger (more negative) discrimination effects than C4 species. It was remarkable that the discrimination factor became gradually small (less negative), from -16.65 per mil in 1900s to -16.40 per mil in 1990s. The decline of the discrimination effect was mainly attributable to stomatal response to elevated atmospheric CO₂ concentration, reducing the ratio of intercellular (Ci) to ambient CO₂ concentration (Ca). This stomatal response exceeded the competitive responses of C3/C4 composition and canopy recycling, both of which lead to larger discrimination effects. Importantly, the temporal change in the discrimination factor could induce an isotopic disequilibrium of the atmosphere-biosphere CO₂ exchange, in addition to the disequilibrium induced by fossil fuel combustion (^{13}C Suess effect). Including this factor, isotope-based analyses of the global carbon budget would be more or less amended.

B31E-0355 0830h POSTER

Analysis of Southern African Aerosols Using Bulk Stable Isotope Analysis

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In southern Africa, emissions from industrial fossil fuel combustion, extensive biomass burning, as well as eolian dust and marine aerosols affect biogeochemical processes. Chemical characterization of aerosols is crucial to understanding their role in nutrient cycling. This study analyzed the organic carbon, nitrogen and sulfur bulk stable isotope compositions of total suspended particulate aerosols as a function of geographical and diurnal differences for sites throughout southern Africa. A regional approach showed isotopic differences in the aerosols collected in different seasons, where primarily C₃ vegetation influenced dry season aerosol compositions and C₄ vegetation influenced wet season aerosol samples. Dry season samples showed a significant enrichment of $\delta^{13}C$ and $\delta^{15}N$ with increasing mean annual precipitation (MAP). Wet season samples showed a significant depletion in ^{15}N with increasing MAP. These results were related to the relative contributions of C₃ and C₄ vegetation to aerosols at each site and to changes in the isotopic signature of nitrogen source pools. These results further suggest that location specific processes drive aerosol production in the wet season, whereas regional processes contribute more importantly in the dry season.

B31E-0356 0830h POSTER

The global iron budget: estimates of isotopic composition and elemental fluxes

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Recent advances in the field of Fe isotope geochemistry show that isotope fractionation occurs under controlled conditions as a result of reduction, organic complexation, aqueous speciation, and/or hydroxide precipitation. These processes are integral to weathering, and are especially important for mobilizing Fe in an oxidizing environment. Our measurements of the Fe isotopic composition of soils, rivers, and marine sediments demonstrate significant isotopic variations (ca. 4‰/‰ in $^{56}Fe/^{54}Fe$) due to continental weathering. Based on these measurements, we hypothesize that dissolved Fe in rivers is variable but may be up to 3‰/‰ lighter than igneous rocks. The flux and isotopic composition of dissolved riverine Fe could significantly affect the $\delta^{56}Fe$ of the ocean over geologic time, indicating changes in the productivity of the terrestrial biosphere or oxidation state at the Earth's surface. A preliminary global Fe budget is constructed for the modern oxidized surface Earth based on studies of global Fe fluxes in the literature. The total Fe flux to the modern ocean is dominated by riverine material, but the flux of dissolved Fe is roughly equally partitioned between atmospheric, riverine, and hydrothermal sources. There may be a significant diagenetic Fe flux to the water column from marine sediments, which we hypothesize has an Fe isotope composition that is substantially lighter than igneous rocks. A diagenetic Fe flux may be especially important in high productivity regions, such as the coastal ocean and enclosed near-shore basins, and

during periods in Earth history when large portions of the ocean turn anoxic. The Fe isotopic signals of the diagenetic and riverine Fe fluxes, if preserved in the geologic record, may be useful for characterizing changing levels of biological productivity and oxidation state at the Earth's surface through time.

B31E-0357 0830h POSTER

N₂O production pathway change during drought and following wet-up in a controlled rainforest at Biosphere 2 Center

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N₂O is the fourth most important greenhouse gas and it leads to ozone destruction in the stratosphere. Rainforests account for ~ 20% of global N₂O emissions. In soils N₂O can be produced through hydroxylamine oxidation by methanotrophs, nitrification, nitrifier denitrification, and denitrification. The former two processes occur under aerobic and the latter two under anaerobic conditions. During a drought, soils are expected to change from more anaerobic to more aerobic conditions, thus leading to a change in N₂O production pathway.

To test this we conducted a 37-day drought in a controlled rainforest mesocosm at Biosphere 2 Center. Three times during the drought and immediately after wet-up, we collected air and soil samples to determine the N₂O isotope changes. Top 10 cm soil Water Filled Pore Space (WFPS) decreased from ~ 60 to 20% and WFPS below 50 cm decreased from ~ 50 to 40% during the drought. Meanwhile the whole system N₂O flux decreased from 120±4 to 41.5±2.6 µg-N/m²/hr. δ¹⁵N, δ¹⁸O, and site preference of N₂O increased by 7, ~2, and ~2.5‰, respectively. Immediately following wet-up a pulse of N₂O was released with δ¹⁵N, δ¹⁸O, and Site preference 15, 3 and 15‰ lower than before.

We will present evidence to support that the stable isotope increase with soil water loss can be explained by an increase in contribution of hydroxylamine oxidation by methanotrophs. Whereas the isotopic change following wet-up is due to increased contribution from nitrifier-denitrification to the overall N₂O flux.

B31E-0358 0830h POSTER

Methane Production Pathways in a California Rice Paddy: Isotopic Evidence for Substantial CO₂ Reduction as Cause for Isotopically Light Emitted CH₄ Carbon

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We report measurements of δ¹³C of emitted CH₄ and sediment CH₄ and CO₂ during the 1999 rice-growing season near Maxwell, CA. Two treatments, one with rice straw incorporated from the previous season and one without rice straw were studied. The δ¹³C value of emitted CH₄ was consistently lighter isotopically (-67‰ to -83‰ throughout the season) in both straw incorporated and straw removed (burned) plots than in fields we have studied in Texas, Kenya, and Japan. Measured isotopic values of the production zone CH₄ were compared to a two-point mixing curve representative of isotopic CH₄ produced from either pure methyl-group fermentation or CO₂ reduction pathways to partition the production pathways and to track seasonal changes in the production processes.

Our sediment CH₄ and CO₂ isotope data indicate that fermentation was rarely the dominant methanogenic pathway - on the contrary CO₂ reduction with H₂ was more prevalent than fermentation methanogenesis throughout most of the season. The relatively isotopically light CH₄ emitted by the paddy fields is also a product of oxidation and stem-transport processes which have isotopic effects of their own. These effects are discussed in context with the methanogenic isotope effects to provide a complete picture of the paddy field CH₄ carbon isotope system.

B31E-0359 0830h POSTER

Effect of CH₄ and O₂ variations on rates of CH₄ oxidation and stable isotope fractionation in tropical rain forest soils

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Methane-oxidizing bacteria are the primary sink for CH₄ in reduced soils, and account for as much as 90% of all CH₄ produced. Methanotrophic bacteria strongly discriminate against the heavy isotopes of carbon, resulting in CH₄ emissions that are significantly more ¹³C-enriched than the original source material. Previous studies have used an isotope mass balance approach to quantify CH₄ sources and sinks in the field, based on the assumption that the fractionation factor for CH₄ oxidation is a constant. This study quantifies the effect of systematic variations in CH₄ and O₂ concentrations on rates of CH₄ oxidation and stable isotope fractionation in tropical rain forest soils. Soils were collected from the 0-15 cm depth, and incubated with varying concentrations of CH₄ (100ppmv, 500 ppmv, 1000 ppmv and 5000 ppmv) or O₂ (3%, 5%, 10% and 21%). The isotope fractionation factor for CH₄ oxidation was calculated for each incubation using a Rayleigh fractionation model. Rates of CH₄ oxidation varied significantly between CH₄ treatments, with the 100 ppmv CH₄ treatment showing the lowest rate of CH₄ uptake, and the other 3 treatments showing similar rates of CH₄ uptake. Rates of CH₄ oxidation did not vary significantly between the different O₂ treatments. The fractionation factor for CH₄ oxidation varied significantly between the different CH₄ treatments, with the 5000 ppmv CH₄ treatment showing the largest ¹³C-enrichment of residual CH₄. In treatments where CH₄ concentration was not rate-limiting (>500 ppmv CH₄), the fractionation factor for CH₄ oxidation was negatively correlated with CH₄ oxidation rate (P<0.003, r² = 0.86). A multiple regression model that included initial CH₄ concentration and CH₄ oxidation rate as independent variables accounted for 94% of the variability in the isotope fractionation data, suggesting that both factors are important in determining the extent of isotopic fractionation (P<0.002, r² = 0.94). The fractionation factor for CH₄ oxidation did not vary significantly between the different O₂ treatments. These results challenge the assumption that the isotope fractionation factor for CH₄ oxidation remains constant, regardless of metabolic activity or CH₄ pool size.

B31E-0360 0830h POSTER

Seasonal Effects on the Carbon Stable Isotope Compositions of Natural gas Subjected to Microbial Oxidation in Soils Near Leaking oil Wells in Western Canada

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The molecular and carbon stable isotope compositions of leaking natural gas in the unsaturated zone near oil wells in Saskatchewan have been monitored for 12 to 20 months. Leaking gas originates in the Upper Cretaceous Colorado Group shales and is a mixture of bacteriogenic and incipient thermogenic gas that consists of more than 99 percent methane, 2400 ppm ethane, and lesser propane, butane, and pentane. Long term monitoring of soil gas concentrations and stable isotopic compositions demonstrates that microbial oxidation reduces hydrocarbon gas concentrations at the soil surface to less than 1000 ppm and results in the production of large volumes of carbon dioxide with significantly depleted in ¹³C carbon stable isotope signature. Rapidly dropping natural gas concentrations, rising carbon dioxide concentrations, and elevated carbon, nitrogen, and sulphur soil contents at depths of 100 to 150 cm indicate that microbial oxidation is confined to a relatively narrow zone around the well bore. The δ¹³C of light hydrocarbon gases and carbon dioxide collected from a soil gas probe installed at 100 cm depth and 50 cm distance from well bore exhibit significant seasonal variance. Hydrocarbon gases generally have lower δ¹³C during the summer and higher δ¹³C during the winter whereas CO₂ exhibits the opposite trend. Kinetic fractionation factor associated with the microbial oxidation of methane estimated from carbon isotope measurements of CH₄ and CO₂ varies from 8 per mil during the summer to 28 per mil during the winter. Soil temperatures at 100 cm depth vary from 1.7°C in March to 17.3°C in late August and exhibit significant negative correlation (R² = 0.89) with the estimated kinetic fractionation factor. The negative correlation likely reflects higher methane consumption rates during the summer and lower rates during the winter. Lower oxidation rates in the winter may be related to environmental stress associated with the formation of a several tens of centimeters thick frozen layer in the upper soil horizon from November to April or May. The frozen layer may obstruct oxygen and natural gas transport thereby affecting the openness of the system.

B31E-0361 0830h POSTER

Stable Carbon Isotopic Signatures and Fractionations Occurring During Fungal Biosynthesis of Methyl Chloride

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Methyl halides are responsible for approximately 25% of the equivalent chlorine involved in stratospheric ozone depletion, yet quantitative understanding of their atmospheric budgets is still incomplete. The use of an isotopic mass balance to constrain these budgets is currently being investigated. The utility of this approach will depend not only on being able to measure the source signatures and loss kinetic isotope effects contributing to their atmospheric budgets, but also in our ability to assess the variability in these terms. Natural methyl halide sources and sinks due to microbial cycling, combined with their large and variable associated isotopic effects, should have discernable effects on the global atmospheric signature of these gases. Thus, we have begun investigating the isotopic signatures of methyl halides produced by fungi, and the fractionations occurring during their biosynthesis, using controlled laboratory cultures. Measurements of the stable carbon isotopic signatures of growth medium, biomass, respired CO₂, CH₃Cl, and the carbon mass balance were made over the growth cycle of *Inonotus andersonii*, a wood-rot fungus previously shown to emit methyl halides. Resulting CH₃Cl δ¹³C signatures were enriched by approximately 10‰/‰ as compared to those previously reported for *Phellinus pomaceus*, another wood-rot species¹. Fractionations between substrate and biomass {ε_{s-b}}, as well as biomass and gases {ε_{b-g}}, were nearly constant during exponential and early stationary phase growth. Biomass was depleted by 1‰/‰ compared to the ¹³C malt extract medium, and CH₃Cl and CO₂ were depleted by up to 5‰/‰ compared to the biomass, implying the bulk of the final CH₃Cl signature is determined during CH₃Cl synthesis and not during uptake of the carbon substrate. However, the magnitude of these fractionations, and the direction of ε_{s-b}, probably depends on the complexity of the substrate. Additionally, a survey of

isotopic signatures of CH_3Cl produced by several fungal species on C3 and C4 substrates was begun to quantify likely variability in the natural source signature.

¹ Harper, DB., R.M. Kalin, J.T.G. Hamilton, and C. Lamb, Carbon Isotope Ratios for Chloromethane of Biological Origin: Potential Tool in Determining Biological Emissions, *Environ. Sci. Technol.*, 35, 3616-3619, 2001.

B31E-0362 0830h POSTER

Degradation of Methyl Bromide and Methyl Chloride in Soil Microcosms: Use of Stable C Isotope Fractionation and Stable Isotope Probing to Identify Reactions and the Responsible Microorganisms

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Methyl bromide (MeBr) and methyl chloride (MeCl) are important atmospheric trace gases that contribute directly to stratospheric ozone depletion. These compounds have natural and anthropogenic sources and sinks in both aquatic and terrestrial environments. Soils comprise the largest known sink for MeBr on the Earth's surface and are also a large sink for MeCl. However, the processes that influence the flux of these compounds from air to soil or soil to air are poorly understood at present. Bacteria in soil microcosm experiments oxidized both MeCl and MeBr, the former compound more rapidly than the latter. MeBr was also removed by chemical reactions while MeCl was not. Chemical degradation of MeBr accounted for more than half of its total loss. We applied new techniques to determine if different bacteria were responsible for degrading MeBr and MeCl. Stable isotope probing revealed that different populations of soil bacteria assimilated added ^{13}C -labeled MeBr and MeCl. Soil bacterial oxidation of MeBr and MeCl was characterized by different kinetic isotope effects (KIEs). The KIE for MeBr oxidation by bacteria was $22 \pm 5 \text{ ‰}$ and the KIE for MeCl oxidation was $56 \pm 3 \text{ ‰}$, suggesting that different bacteria were responsible for degrading each compound. The identity of the active MeBr and MeCl degrading bacteria in soil was determined by analysis of 16S rDNA sequences amplified from ^{13}C -DNA fractions. The diverse population of active bacteria was reflected by the range of sequences found for the *cmuA* gene, which codes for the enzyme that catalyzes the initial step in the oxidation of MeBr and MeCl. The diversity and number of different bacteria actively degrading MeBr and MeCl in the soil and the number of bacteria identified that contain the enzyme capable of degrading methyl halides were in contrast to the limited number of methyl halide degrading bacteria that have been isolated thus far from soil and aquatic environments; thus suggesting that the extant degraders represent only a subset of the natural diversity of methyl halide degrading bacteria.

B31E-0363 0830h POSTER

Changes in Carbon Isotope Composition of Methyl Halides Resulting from Biological and Chemical Degradation

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Methyl bromide (MeBr), methyl chloride (MeCl) and methyl iodide (MeI) are reactive trace gases that are produced and released to the atmosphere at the Earth's surface. These methyl halides have the potential to influence ozone levels in the stratosphere. Current estimates of the relative contributions of natural and anthropogenic sources of these methyl halides are the subject of considerable debate. In addition, there is uncertainty in the magnitude of some of the largest sinks for these compounds. Hence, the atmospheric budgets of MeBr, MeCl and MeI, while uncertain at present, may be better constrained using stable isotope ratio ($^{13}\text{C}/^{12}\text{C}$) mass balances of sources and sinks. Our work has focused on characterizing the effects upon $\delta^{13}\text{C}$ values of methyl halides released after

reactions which discriminate in favor of ^{12}C during removal processes. Previously, we determined very large fractionations of carbon isotopes by pure cultures of soil bacteria. Further, we have documented large fractionations (kinetic isotope effects or KIEs) of methyl halides in live soils. In the case of MeBr and MeI, substantial fractionation also occurred in heat-killed soil, suggesting that chemical degradation resulted in a shift in the stable isotopic composition. At elevated concentrations, for instance during agricultural soil fumigations, the $\delta^{13}\text{C}$ value of MeBr or MeI released from soil can be determined by flux measurements or soil profiles. However, more information is needed regarding the processes responsible for isotope fractionation to be able to extrapolate to areas where the concentration is low or direct measurement is not otherwise possible. We report here on measurements of the fractionation of carbon isotopes in methyl halides during degradation by chemical processes that are likely to occur in soil or seawater. These processes include aqueous hydrolysis and halide exchange and the methylation of organic matter using humic acid as the model methyl acceptor. Results are compared with fractionation achieved during the uptake of methyl halides by live and heat-killed soils.

B31E-0364 0830h POSTER

Quantifying Reemission Of Mercury From Terrestrial And Aquatic Systems Using Stable Isotopes: Results From The Experimental Lakes Area METAALICUS Study

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This study represents the first attempt to directly quantify the re-emission of deposited Hg. This is crucial for understanding the sources of Hg emitted from natural surfaces as being of either geological origin or through re-emission of recently deposited Hg. Three stable Hg isotopes are being added experimentally to a headwater lake, wetlands, and its watershed in a whole-ecosystem manipulation study at the Experimental Lake Area in Canada. Our overall objective is to determine the link between atmospheric deposition and Hg in fish, but numerous aspects of the biogeochemical cycling of Hg are being addressed during METAALICUS (Mercury Experiment to Assess Atmospheric Loading in Canada and the U.S.), including Hg re-emission. Pilot studies in 1999-2000 applied enriched 200Hg to isolated upland and wetland plots, and to lake enclosures. Fluxes were measured with dynamic chambers for several months. The 200Hg spike was quickly detected in ground-level air (e.g. 5 ng/m³) suggesting rapid initial volatilization of the new Hg. Initial 200Hg fluxes > ambient Hg, but emissions of 200Hg decreased within 3 months to non-detects; about 5% of the applied 200Hg spike was emitted from uplands and about 10% from wetlands. The 200Hg spike (representing new deposition) was generally more readily volatilized than was ambient (old) Hg in both sites. Mercury evasion to the atmosphere from a lake enclosure was also measured and compared with the flux estimated from measured dissolved gaseous mercury (DGM). The introduction of the tracer spike was followed by increased concentrations of DGM and higher fluxes to the atmosphere. In some cases, the observed and calculated fluxes were similar; however, it was common for the observed flux to exceed the calculated flux significantly under some conditions, suggesting that DGM concentration alone in the water column is a poor predictor of gaseous mercury evasion. A substantially larger fraction of the newly deposited Hg was re-emitted from the lake than from wetlands or from upland soils. The whole-ecosystem manipulation is now underway at ELA Lake 658. Addition of 200Hg (to uplands), 202Hg (lake), and 199Hg (wetlands) commenced in 2001 and was completed in June 2003. These data are now being analyzed, and appear to support the behavior seen in the pilot studies; final results will be presented.

URL: <http://www.esd.ornl.gov/people/lindberg/lindberg.html>

B31E-0365 0830h POSTER

Stable Isotope Analysis of Extant Lamnoid Shark Centra: A New Tool in Age Determination?

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The oxygen isotopes of fourteen vertebral centra from ten extant lamnoid sharks (including *Carcharodon carcharias* [great white], *Isurus paucus* [longfin mako], and *Isurus oxyrinchus* [shortfin mako]) were sampled and measured along the growth axis to determine the periodicity of incremental growth represented in the centra. As part of the internal (endochondral) skeleton, shark centra are composed initially of hyaline cartilage, which then secondarily ossifies during ontogeny forming calcified hydroxyapatite bone. The incremental growth of shark centra forms definite growth rings, with darker denser portions being deposited during slower growth times (i.e., winter) and lighter portions being deposited during more rapid growth (i.e., summer). Thus, shark centra, whether they are extant or extinct, are characterized by clearly delineated incremental growth couplets. The problem with this general rule is that there are several factors in which the growth of these couplets can vary depending upon physical environment (including temperature and water depth), food availability, and stress. The challenge for paleobiological interpretations is how to interpret the periodicity of this growth. It can generally be assumed that these bands are annual, but it is uncertain the extent to which exceptions to the rule occur. Stable isotopic analysis provides the potential to independently determine the periodicity of the growth increments and ultimately the ontogenetic age of an individual.

B31E-0366 0830h POSTER

Growth versus metabolic tissue replacement in mouse tissues determined by stable carbon and nitrogen isotope analysis

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Stable isotope analysis is becoming an extensively used tool in animal ecology. The isotopes most commonly used for analysis in terrestrial systems are those of carbon and nitrogen, due to differential carbon fractionation in C3 and C4 plants, and the approximately 3‰ enrichment in 15N per trophic level. Although isotope signatures in animal tissues presumably reflect the local food web, analysis is often complicated by differential nutrient routing and fractionation by tissues, and by the possibility that large organisms are not in isotopic equilibrium with the foods available in their immediate environment. Additionally, the rate at which organisms incorporate the isotope signature of a food through both growth and metabolic tissue replacement is largely unknown. In this study we have assessed the rate of carbon and nitrogen isotopic turnover in liver, muscle and blood in mice following a diet change. By determining growth rates, we were able to determine the proportion of tissue turnover caused by growth versus that caused by metabolic tissue replacement. Growth was found to account for approximately 10% of observed tissue turnover in sexually mature mice (*Mus musculus*). Blood carbon was found to have the shortest half-life (16.9 days), followed by muscle (24.7 days). Liver carbon turnover was not as well described by the exponential decay equations as other tissues. However, substantial liver carbon turnover was observed by the 28th day after diet switch. Surprisingly, these tissues primarily reflect the carbon signature of the protein, rather than carbohydrate, source in their diet. The nitrogen signature in all tissues was enriched by 3 - 5‰ over their dietary protein source, depending on tissue type, and the isotopic turnover rates were comparable to those observed in carbon.