4th Annual
Front Range Isotope Day

August 22, 2014

Program and Abstracts

Colorado School of Mines
Golden, CO
Welcome to Colorado School of Mines!

**Venue:**  CSM Student Center, Ballrooms B&C (2nd floor)

**Directions:**  
**Driving directions from Denver International Airport and/or from I-25:** Take I-70 west, exit Highway 58 to Golden. Exit Washington Street and turn left to enter into downtown Golden. Turn right on 13th Street and left on Maple to enter campus.

**From Denver:** Take 6th Avenue and head west into Golden. Turn right on 19th Street. Turn left on Elm Street to enter campus.

**From C-470 or I-70:** Head east to 6th Avenue. Follow the directions above from 6th Avenue.

**From Boulder:** Take Highway 93 into Golden. Turn left onto 19th Street. Turn left on Elm Street to enter campus.

**For Google Maps** or similar app, use 1500 Illinois St. to guide you to campus.

**Parking:**  
Visitors to campus during operational hours — Monday-Friday 7 a.m.-5 p.m. — should park in the General (blue) and Commuter (yellow) lots. All visitor parking areas have a pay and display parking meter. Please visit the pay stations to receive a parking permit. Pay station meter rates for General (blue) parking are $1.50 per hour or $8 daily; rates for Commuter lots are $1.25 per hour or $6 daily. Metered parking permits must be displayed on your dashboard. Click for a printable visitor parking map.

**Day/Time:**  
Friday, August 22 2014. 8:00AM until 4:00PM

Social time starting at 4:00PM at Golden City Brewery
Program and Oral Presentations

8:00 AM  Continental Breakfast

8:45 AM  Welcome and Introductions

9:00 AM  Chuck Douthitt - A cook’s tour of BSIA, EA, CSIA, GC, LC, MDF, MIF, MIMS, PSIA, ISP, DIF and more: not your grandfather’s isotopes

9:30 AM  Bob Dias - Normalization, standardization, and off-line corrections made to stable isotopic data: Are we all on the same page?

10:00 AM  Bruce Vaughan et al. - Ground based mobile methane measurements in the Front Range, Colorado: The Summer 2104 campaign with FRAPPE’, DISCOVER–AQ, and Air Water Gas Projects

10:30 AM  Break

11:00 AM  Cathy Stewart et al. - Switchgrass cultivars alter microbial contribution to deep soil C in Nebraska

11:30 AM  Evan Kipnis et al. - Stable isotope observations of seasonal snowpack development across forested mountain catchments

NOON  Lunch

1:00 PM  Owen Sherwood et al. - Nitrogen isotopic analysis of amino acids and the record of increasing N₂-fixation in the subtropical North Pacific Ocean

1:30 PM  Craig Barrie & Adrian Boyce - The life and times of a sulphide ore deposit – A tale of scale, isotopes and bugs…

2:00 PM  Josiah Strauss et al. - Stable isotopes of natural gas: Applications and potential effects of long-term storage

2:30 PM  John Humphrey et al. - Carbon and oxygen isotope studies in the late Cretaceous Niobrara Formation, Denver basin: Chemostratigraphy and diagenesis

3:00 PM  Breakout Sessions - Instrumentation/Standardization (Ballroom B) and Applications/Research Topics (Ballroom C)

4:00 PM  Social Time – Golden City Brewery (920 12th St., corner of 12th and Cheyenne)
Poster Presentations

Posters will be present throughout the day in Ballroom C

Erika Foster et al. - Determining fractionation during fungal respiration of C3 versus C4 sucrose: Results from the lab of the “Terrestrial Ecosystem Isotope Ecology” course

John Frank et al. - Does sublimation decline after a spruce beetle outbreak? The need to develop a realistic processed-based model

Sylvia Michel et al. - As methane concentration goes up, stable isotopes of methane go down: $^{13}$C implicates a microbial source across latitudinal gradients

Blake Osborn et al. - The legacy of Pleistocene glaciation on soil conditions and productivity of a Rocky Mountain conifer forest
Abstracts

Craig D. Barrie\(^1\) & Adrian J. Boyce\(^2\)

The life and times of a sulphide ore deposit – A tale of scale, isotopes and bugs…

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The Irish Midlands, in the Republic of Ireland, represent, per square km, the world’s largest known concentration of Zn. Here we present sulfur, iron & lead isotope results for both bulk mine concentrates and millimetre-scale layered sulfides from the Irish Midlands and Navan, the largest zinc deposit in Ireland. The concentrate samples, each representing up to a million tonnes of ore, show limited isotopic variation, with mean \(\delta^{34}\)S = -13.6 ± 2 per mil \((n = 20)\), and galena concentrate mean \(^{206}\)Pb/\(^{204}\)Pb = 18.19 ± 0.03 \((n = 7)\). Calculations suggest >90 percent of the Navan sulfides were derived through bacteriogenic reduction of Mississippian seawater sulfate, whereas metals were acquired from a local, orogenic crustal source beneath the orebody. The thin-section and hand-specimen samples of layered sphalerite display a remarkable range of isotopic variation \(\delta^{34}\)S = -30 to +10 per mil. The color, style, and scale of this layering show variations with chemical composition, but none of these correlations are consistent between samples. However, there are strong inter-sample correlations between the chemical and S-Fe-Zn isotope compositions. Analysis of sphalerite from the main Navan ore body demonstrates substantial Zn, Fe and S isotopic variation, with a positive correlation between \(\delta^{56}\)Fe and \(\delta^{66}\)Zn between samples. It is proposed that incoming metal-rich hydrothermal fluid at Navan had relatively light \(\delta^{56}\)Fe (< -0.3‰) and \(\delta^{66}\)Zn (< -2.2‰) but heavy \(\delta^{34}\)S (> +2‰) compositions. These values are short lived and rapidly underwent closed system kinetic fractionation to isotopically heavier Fe and Zn and lighter S. We conclude that the influx of deep metal-rich hydrothermal fluid, whose sulfur budget was minor, compared to the dominant bacteriogenic fluid, was an important trigger to sulfide mineralisation. Yet, bacterial activity, as clear from the concentrate results, was fundamental to ore deposition at Navan and the Irish Midlands in general: no bacteria, no economically viable mineralisation.
Normalization, standardization, and off-line corrections made to stable isotopic data: Are we all on the same page?

U.S. Geological Survey, Denver, CO 80225

With the proliferation of stable isotope ratio analysis in geological, biological, environmental, petrochemical and other fields of interest, increased sharing of analytical and instrumental methods across disciplines has resulted in general community-wide acceptance of best laboratory practices for generating stable isotopic data for C, H, N, O, and S. However, despite best efforts, not every isotope ratio monitoring system in every laboratory produces the exact same delta value for any given sample at any given time. Stable isotope analysis is governed by standardization and normalization to defined isotopic standards, regardless of analytical species. While we often find this task challenging, we are also plagued by the need to perform off-line corrections to isotopic data (usually in spreadsheets) to account for instrument linearity, sample-size effects, and time-dependent instrumental drift. This presentation will detail various methods of off-line data corrections, investigate the preferred ordering of these corrections, compare the use of delta values versus R in making corrections, and promote a discussion on best practices for off-line stable isotope data corrections.
Chuck Douthitt

A cook’s tour of BSIA, EA, CSIA, GC, LC, MDF, MIF, MIMS, PSIA, ISP, DIF and more: not your grandfather’s isotopes

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The development of the dual viscous flow inlet system in 1950 ushered in a period of systematic exploration of the distributions of the stable isotopes of CNHOS, which led to the identification and characterization of the major terrestrial reservoirs. It was during this time that the unique characteristics and conventions of IRMS were developed, those characteristics which make this field of mass spectrometry so distinct from other forms of mass spectrometry. The basic mass spectrometer used for TIMS was modified by addition of an electron impact ionization source, to make IRMS, and with static pumping, to make noble gas mass spectrometers, so all types of mass spectrometers used to measure isotope ratios started from the same basic design of Dempster and AO Nier.

In the 1980’s, the incorporation of gas chromatography columns into IRMS sample handling led to major changes in every aspect of what had been a stable and conservative instrument, where the major design changes to the IRMS were largely aimed at extending the reach and throughput of the dual inlet system by the addition of microvolumes and multiports. In time, “continuous flow” IRMS (CF-IRMS) emerged, in which the He carrier gas used in gas chromatography entrained the samples, which led to major expansion and diversification in the use of stable isotopes. At present, the three main divisions of CF-IRMS are 1) bulk stable isotope analysis, BSIA, in which an “elemental analyzer” (EA) is attached to an IRMS, referred to as EA-IRMS, 2) compound specific isotope analysis, CSIA, in which a capillary gas chromatograph (GC) is attached via microreactors to an IRMS, referred to as GC-IRMS generally, and 3) headspace sampling isotope analysis, where a GC column is attached directly to the IRMS, first used for measuring $^{13}$C in CO$_2$ in breath (for “breath testing” IRMS), but now extended to a diverse set of applications. The tool kit available for sample preparation and sample handling is now quite extensive, and the various modules of CF-IRMS can be quickly rearranged for novel measurements. The development of CF-IRMS led to considerable divergence of the IRMS from the previously closely-related TIMS and noble gas MS.

At the same time that all of these developments were going on, improvements to all components of the mass spectrometer have led to considerable extension to what could be measured with the IRMS. The IRMS was used to measure mass dependent fractionation, MDF, of singly substituted species, but the identification of mass independent fractionation, MIF, first in solid phases in meteorites and then in gas species in the Earth’s atmosphere, has greatly extended the field. Another relatively recent development has been the measurement of “clumped isotopes” in which variations in isotopes in two positions (double isotope substitution, DIS) are measured. There has been long standing interest in “intramolecular site preference” (IMS), to measure isotope distributions in isotopomers of a molecule but experimental difficulties largely left such measurements to NMR. Recent instrumental developments have made such measurements amenable to IRMS, and they are referred to as “position specific isotope analysis” (PSIA). It is important to note that MIF, DIS and, PSIA have been developed using the dual viscous flow inlet system, but these analyses are with time being implemented in CF-IRMS, while at the same time, changes being mass spectrometer design (ion optics, electronics, collector design) which were needed in order to make these difficult measurements are in fact leading to a reunification of the different types of isotope ratio mass spectrometry.
Erika J Foster, Jordan Allan, Derek Fedak, Timothy Fegel, Sarah Fulton-Smith, Carolina Gutierrez, Laurel Lynch, & Francesca Cotrufo

Determining fractionation during fungal respiration of C3 versus C4 sucrose: Results from the lab of the “Terrestrial Ecosystem Isotope Ecology” course

Colorado State University

Stable isotopes serve as an invaluable tool in biogeochemistry to track elements through a wide variety of ecosystems. This approach is essential in examining biotic interactions, particularly microbial processing of specific substrates. Often researchers implement natural abundance isotopic differences between C3 and C4 plants to monitor biogeochemical cycling. However, there is controversial evidence reporting the extent of fractionation during heterotrophic respiration and whether this differs between C3 and C4 substrates. To examine these dynamics, the Terrestrial Ecosystem Isotope Ecology Class at Colorado State University designed a short-term incubation experiment with C3 (beet $\delta^{13}C$ of $-27\%$) and C4 (cane $\delta^{13}C$ of $-12\%$) plant sucrose as substrate for fungal respiration. The research project allowed the graduate students to gain hands-on experience with the application of the isotopic mixing model and calculation of isotopic fractionation at natural abundance in soil isotope ecology. In this experiment, Saccharomyces cerevisiae (baker’s yeast) was incubated for 24 hours in a culture broth containing different ratios of the C3/C4 sucrose (i.e., 100%/0%, 75%/25%, 50%/50%, 25%/75% and 0%/100%). Headspace gas samples were collected from each vial and analyzed for carbon dioxide ($CO_2$) concentration using an Infrared Gas Analyzer (IRGA) and for $^{13}C$-$CO_2$ Gas Chromatograph-Isotope Ratio Mass Spectrometer (GC-IRMS). Additionally, all substrate mixtures were analyzed by Elemental Analyzer-IRMS (EA-IRMS). Application of the mixing model provided evidence of preferential substrate respiration by fungi. The results suggested that C3 plant sugars were fractionated more strongly than sugars derived from C4 plants, with the most fractionation occurring with the lightest substrate, the 100% C3 sucrose. This pattern emphasized that heterotrophic fractionation needs to be considered when studying the decomposition of substrates at different $^{13}C$ natural abundances. Furthermore, hands-on laboratory work provided valuable experience for students in an upper level isotope ecology class.
Does sublimation decline after a spruce beetle outbreak? The need to develop a realistic processed-based model

In the subalpine forests of southeastern Wyoming, sublimation can account for half of annual water vapor fluxes. Recent spruce beetle disturbances in these forests have caused significant mortality to the forested canopy, substantially affecting processes that control energy and mass exchange. While the loss of canopy allows more radiant energy into the understory, it also decreases snow interception. At the GLEES, WY AmeriFlux site, observations of winter sublimation appear to decrease coincident with the loss of the canopy following a spruce beetle outbreak. We hypothesize that in this subalpine forest the decrease in canopy interception of snow is the dominant process that drives changes in sublimation rates as the ecosystem responds to this disturbance. Testing this hypothesis will require development of a physically based process model to explain the patterns and magnitudes of sublimation. We use measurements of energy and mass exchange from eddy-covariance plus observations of the stable isotopes of snow water and atmospheric water vapor as tools to develop this model.
John D. Humphrey\textsuperscript{1}, Kazumi Nakamura\textsuperscript{1}, Lindsay Hefton\textsuperscript{1}, and K. Lyn Canter\textsuperscript{2}

**Carbon and oxygen isotope studies in the late Cretaceous Niobrara Formation, Denver basin: Chemostratigraphy and diagenesis**

\textsuperscript{1}Colorado School of Mines, Golden, CO
\textsuperscript{2}Whiting Petroleum, Denver CO

The late Cretaceous Niobrara Formation is a productive, unconventional resource play covering a large area of the Rocky Mountain region, including the Denver basin. A marine deposit of the Cretaceous Western Interior Seaway, the Niobrara Fm. is a mixed lithology unit comprised principally of pelagic coccolith chalks and marls. Throughout the Denver basin, chalk intervals are generally the producing intervals, while the marls typically represent intraformational source rocks.

Stable carbon isotopes of inorganic carbon derived from marine carbonate components can produce synchronous variations useful for stratigraphic correlations. This can be especially important in the Niobrara Fm., in which lithologic variability is visually subtle and biostratigraphic resolution is poor.

Traditional lithostratigraphic and biostratigraphic approaches have resulted only in a layer-cake understanding of Niobrara stratigraphic variability. This study uses a high-resolution carbon isotope chemostratigraphic approach to correlation of cores within the Denver basin, providing a basis for sequence stratigraphic interpretations. One “type core” was chosen and yielded a highly detailed chemostratigraphic profile from a 6-inch (15 cm) sampling density (678 samples). Beyond our correlations of Niobrara Fm. in the Denver basin, our stratigraphic analysis produced correlations to the Texas Comanche Shelf (Austin Chalk and Eagle Ford Shale), as well as to other global late Cretaceous carbon isotope excursions.

Chalks within in the Niobrara act as primary hydrocarbon reservoirs that have high porosities and low permeabilities. Controls on favorable reservoir properties of these chalks are principally diagenetic. Maximum burial depth is the main controlling factor in chalk alteration, followed by the chemical and biological composition, pore fluid chemistry, clay content, and other factors. Burial depth plays a significant role as a result of the unique composition of chalks, which are generally comprised entirely of very fine-grained carbonate remains of coccoliths, with lesser amounts of foraminifera and calcispheres.

Our diagenetic study focuses on a widely varied distribution of eight Niobrara cores that range from the deeper portions of the DJ basin (~7,500 ft) to an outcrop in eastern Kansas. The specific focus is on the B chalk and marl and the Ft Hays Member in each of the cores. A preliminary oxygen isotope analysis of four cores shows a progressive decrease in \( \delta^{18}O \) with depth (four cores at successively greater depths), likely indicating alteration of the oxygen values under increasingly deeper and higher-temperature conditions. Interestingly, the Fort Hays consistently has the heaviest values in each well. The marls tend to have more \(^{18}O\)-enriched values than the chalks.
Mountain landscapes have been previously investigated with regard to precipitation, sublimation, and melting of snow, yet predicting winter snowfall contribution to streamflow still remains highly uncertain. Understanding these hydrologic systems is important as winter dominated headwater catchments have grown more vulnerable to natural and anthropogenic disturbance. In Southeastern Wyoming the natural abundance of $\delta^2$H and $\delta^{18}$O is used to characterize the development of seasonal snowpack across multiple mountain watersheds. In this study, the relationship between elevation and vegetative cover are alongside stable isotope ratios to interpret relationships between landscape features and seasonal accumulation of snowpack. Preliminary results reveal some complexities in this system as elevation does not fully describe the isotope values in peak season snowpack. This work to characterize patterns of snow water isotopes in seasonal accumulation across forested mountain ecosystems will contribute towards improving future understanding of surface/atmosphere water fluxes and predicting future contributions of snowfall to streamflow.
Sylvia E. Michel, John B. Miller, Edward J. Dlugokencky, Bruce H. Vaughn, James W. C. White, Andrea L. Sack, and Owen A. Sherwood

As methane concentration goes up, stable isotopes of methane go down: $^{13}$C implicates a microbial source across latitudinal gradients

$^{1}$ INSTAAR, University of Colorado
$^{2}$ NOAA Earth System Research Laboratory

The mixing ratio of methane in the atmosphere has increased in recent years for reasons that are not completely understood. It is important to better understand this greenhouse gas in regard to our changing climate and its role in atmospheric chemistry. Stable isotopes allow us to elucidate sources of methane due to the relatively distinct isotopic signatures from fossil fuels, biomass burning, and biological sources. Here we examine a 15 year record of atmospheric methane to show that since 2007, atmospheric methane isotopes have decreased by an average of 0.15 permil. This decrease is evident at Arctic sites as well as in the mid-latitudes and the Southern Hemisphere. There has been no change in the inter-hemispheric difference of atmospheric methane isotopes, suggesting that the changes are occurring in both northern and southern regions. Likewise, Miller-Tans plots, which examine regional deviations from the background signal, show that sources of methane have become isotopically more depleted since 2007 across latitudes. This suggests stronger microbial emissions (such as wetlands) from tropical, temperate, and Arctic environments. We use a 2-box model to test the plausibility of increased sources of microbial methane across a latitudinal gradient, and to constrain possible additional contributions of fossil fuel and biomass burning sources to the observed variability.

Figure 1. Annual means of $\delta^{13}$C of CH$_4$ across sampling sites. Error bars represent the standard deviation in the data trend; seasons have been removed.
The legacy of Pleistocene glaciation on soil conditions and productivity of a Rocky Mountain conifer forest

University of Wyoming Department of Ecosystem Science and Management ¹, University of Wyoming Department of Botany ²

The interaction between soil conditions and climate variability plays a central role in the ecohydrological functions of montane conifer forests. Although soil moisture availability to trees is largely dependent on climate, the depth and texture of soil exerts a key secondary influence. We hypothesize that soil texture plays a more prominent role in the growth and photosynthetic function of lodgepole pine during dry rather than wet years, as the water holding capacity related to soil textural conditions will be most divergent during years with water scarcity. We have examined physiological and growth responses of lodgepole pine to interannual variation in precipitation across a chronosequence of Pleistocene glacial tills aged from 700k to 12k years before present (YBP). Soil textural differences across the glacial tills confirm the theory of different degrees of weathering with the most well developed soils occurring at the site of the oldest glacial event. Preliminary δ¹³C data, from 5 years of pine needles cohorts, indicate trees on well developed glacial tills allow for greater stomatal conductance than trees growing on younger, less developed glacial tills. Increased stomatal conductance is likely due to increased soil water content, as other environmental conditions such as relative humidity, temperature, and irradiance are the same across sites. The preliminary results are being explored further by looking at the tree ring δ¹³C and δ¹⁸O to determine whether differences in stomatal regulation are being amplified during drought years. Expanding this study to better understand the spatial variability of stomatal control during drought years will provide valuable information for the potential impact of climate change on montane conifer forests under future conditions.
Perennial cellulosic bioenergy crops such as switchgrass (Panicum virgatum L.) can improve marginally productive cropland and sequester C deep in the soil profile. While aboveground biomass production is well documented for switchgrass ecotypes (lowland, upland) and cultivars, there has been little focus on the impact of plant belowground productivity on microbial communities at subsurface soil depths. Phenotypic variability in switchgrass cultivars could impact belowground plant allocation, rooting characteristics and could influence the microbial community abundance and composition. We quantified microbial contributions to SOM over a growing season, to a depth of 150 cm using a pulse-chase $^{13}$C labeling experiment of two 3-yr old switchgrass cultivars, Kanlow and Summer. We measured total and relative abundance and $^{13}$C signatures of phospholipid fatty acids (PLFA). Total PLFA abundance decreased with soil depth and was greater for Kanlow compared to Summer over the entire year. Community composition and rhizodeposit C incorporation data will also be presented. For bioenergy production systems, variation between switchgrass ecotypes could impact C sequestration and storage as well as potentially other belowground processes by altering microbial communities.
The molecular and stable isotope composition ($\delta^{13}$C and $\delta^2$H) of low molecular weight (C$_1$-C$_6$) hydrocarbons (HC) are key parameters used to deduce the origin (i.e., thermogenic vs. bacterial) of natural gases and the maturity of oil and gas deposits. As a result, these data are critical components of oil and gas exploration and production as well as environmental assessment and remediation. Here we discuss the importance of standardized collection methods and laboratory timelines as well as a case study including production and groundwater samples collected from the Wattenberg field of Colorado. This demonstrates that with the proper collection and analytical protocols, stable isotopes can be a valuable tool that provides insight into groundwater and underlying petroleum systems and potential interactions between the two.

In the context of evaluating a petroleum system during the drilling of an oil or gas well, natural gases are samples mainly in two ways: as mud gases captured in cylinders and gases desorbed from drill cuttings immersed in water and stored in an airtight jar. Headspace gases in cuttings and water mixtures commonly exhibit greater molecular and stable isotopic variability compared with associated mud gases. To further understand this variability we investigated the degree, and manner in which, the molecular and isotopic composition of headspace gas varies temporally through a five-month monitoring period. Results showed headspace gas samples exhibit complex behaviors in molecular and stable isotope composition over the five month study interval, which can be attributed to several interconnected processes. These processes are ultimately dependent upon the availability of sufficient substrate for microbial methanogenesis (e.g., CO$_2$, acetate and formate) and possibly continued desorption of gas from drill cuttings. This study highlights the importance of implementing standardized collection methods and laboratory timelines and consistently utilizing a biocide when collecting drill cuttings for headspace gas analysis and provides a suite of parameters that can be used to assess the presence and origin of secondary methane production and desorption in natural samples.

The utility of these data can partly be explored through a case study using natural gas stable isotope data from production gas and groundwater samples in the Greater Wattenberg Area by the Colorado Oil and Gas Conservation Commission (COGCC). This study focused on an initial sampling and analysis of 73 producing gas wells in order to set a baseline for the different natural gas producing formations within Wattenberg. Subsequent samplings of groundwater wells within ½ mile are now required by the COGCC prior to and following the drilling of any new oil and gas wells in Colorado and the molecular and stable isotope composition data from dissolved natural gases in these samples were collected from the COGCC’s online GIS server. Dissolved natural gases in groundwater are analyzed using established headspace equilibration techniques in a manner similar that of the cuttings samples described previously. These samples therefore present similar analytical challenges as documented in the aforementioned experiment, namely the necessity for a biocide to prevent secondary methane generation and the complications arising from a two phase system. To identify methane sources, we focused on 112 out of 897 (12%) groundwater samples that exhibited elevated methane concentrations (>1mg L$^{-1}$). Within these wells, average methane concentrations from multiple sampling periods range
from 1.1 to 38 mg L$^{-1}$. Methane stable isotope data reveal the natural gas in 91 waters was of bacterial origin, while 12 wells contained thermogenic gas, and eight showed a bacterial-thermogenic mixture. No significant differences in average dissolved methane concentration between well waters affected by thermogenic and bacterial methane were observed. Water wells that showed elevated methane concentrations mainly occurred in the southern part of the Greater Wattenberg Area (GWA), however within that region no spatial significance was apparent for wells contaminated with thermogenic methane. Overall, this case study highlights the value of the COGCC baseline survey and groundwater monitoring tools for the GWA and Colorado.
Nitrogen isotopic analysis of amino acids and the record of increasing $\text{N}_2$-fixation in the subtropical North Pacific Ocean

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3 Institute for Marine Sciences, University of California, Santa Cruz
* Present address: Institute of Arctic and Alpine Research, University of Colorado, Boulder

Recent satellite data have shown that the ocean’s least productive waters – the vast, permanently oligotrophic, subtropical gyres – are expanding in size at the rate of 1 to 4 % per year. This raises important questions about the efficiency of oceanic uptake of CO$_2$ in a warming world. The North Pacific subtropical gyre (NPSG) is the largest of these subtropical gyres. Paradoxically, primary production in the NPSG has increased in recent decades despite a reduction in nutrient supply to surface waters. This is thought to be the result of a shift in plankton community structure from mostly eukaryotes to mostly dinitrogen-fixing prokaryotes. It remains uncertain, however, whether the plankton community domain shift can be linked to cyclical climate variability or a long-term global warming trend. Bulk and amino-acid-specific $^{15}$N/$^{14}$N isotopic ratios ($d^{15}$N) preserved in the skeletons of long-lived deep-sea proteinaceous corals collected from the Hawaiian archipelago serve as a proxy for the source of nitrogen-supported export production through time. These records show that the recent increase in nitrogen fixation is the continuation of a much larger, centennial-scale trend. After a millennium of relatively minor fluctuation, $d^{15}$N decreases between 1850 and the present. The total shift in $d^{15}$N of -2 per mil over this period is comparable to the total change in global mean sedimentary $d^{15}$N across the Pleistocene–Holocene transition, but it is happening an order of magnitude faster. In a steady-state model, isotopic mass balance between nitrate and nitrogen fixation implies a 17 to 27 per cent increase in nitrogen fixation over this time period. A comparison with independent records suggests that this increase might be linked to Northern Hemisphere climate change since the end of the Little Ice Age.
B.H. Vaughn¹, Owen Sherwood¹, Gabrielle Petron², and Chris Rella³


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Fugitive emissions of methane from the oil and natural gas industry have been investigated by different studies (eg. Karion et al., 2013, Allen et al., 2013, Petron et al., 2014) and emission estimates have varied significantly from each other as well as EPA or State estimates. New efforts are trying to reconcile bottom-up, or inventory-based, emission estimates of methane with top-down estimates based on atmospheric measurements from aircraft, towers, mobile ground based vehicles, and atmospheric models. Several non-methane hydrocarbons are also emitted by the O&G industry. They can act as precursors to ground level ozone formation. These emissions are not well understood either. The Denver Basin has been in non-attainment for the federal ozone 8-hr standard since 2007. VOC measurements in ambient air at the NOAA BAO tower, Erie, CO, suggest that VOC emissions from the O&G industry in the area play a substantial role in ozone formation Gilman et al. (2013).

In the summer of 2014, several projects have converged on the Denver Basin to make airborne and ground based measurements of methane, VOCs, NOx (nitrogen oxides), ozone and other chemical species. At INSTAAR, a light truck has been equipped with a cavity ring down laser spectrometer to measure methane and methane isotopes along with GPS position, wind speed and direction. The Mobile Methane Investigator has been deployed along the Front Range in the Denver Julesburg Basin, and yielded data that help constrain sources of methane emissions. In addition, continuous isotopic measurements were obtained using a MegaCore™, a 1500 ft tube that is filled continuously over a measurement path and subsequently analyzed at slower rates in the lab that yield meaningful isotopic information.

This effort was in conjunction with several major field campaigns, including FRAPPE’ (Front Range Air Pollution and Photochemistry Experiment), DISCOVER-AQ, and the Air Water Gas project at the University of Colorado. The mobile measurements on the ground were made in conjunction with four other mobile labs, and NASA, NSF/NCAR and NOAA airborne measurements.

