

# 45<sup>th</sup> Annual Graduate Student Colloquium



*photo by Kiya Riverman*

Sponsored by Shell  
Hosted by the Department of Geosciences

March 15-16, 2013

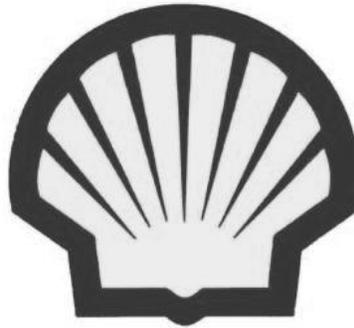


# 45<sup>th</sup> Annual Graduate Student Colloquium

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March 15-16, 2013

The Graduate Student Colloquium is a forum where students present their research or research proposal to faculty, friends, and peers. The Colloquium is hosted by the Department of Geosciences and is open to graduate students involved in geosciences research. The colloquium format stimulates research discussion, allows students to practice for national meetings, and helps students improve their presentation skills. The Colloquium assists both the Department and Penn State in maintaining and strengthening their reputations for giving high quality talks and poster presentations at national and international meetings.

The Graduate Colloquium Committee wishes to thank the students for sharing their work and the faculty for providing constructive feedback. The Committee also wishes to thank the Shell People Services division of Shell Oil Company for their generous financial support, and the Department of Geosciences for hosting this Colloquium.



## Schedule of Events

<i>Event</i>	<i>Date and Time</i>	<i>Location</i>
Poster Viewing	March 15, 6:30-8:30 March 16, 8:30-4:00	EES Atrium
Poster Session 1	March 15, 6:30-7:30	EES Atrium
Poster Session 2	March 15, 7:30-8:30	EES Atrium
Oral Session 1a – Rock Mechanics/Petrology	March 16, 8:30-10:30	114 EES
Oral Session 1b - Biogeochemistry	March 16, 8:30-10:30	116 EES
Break	March 16, 10:30-11:00	
Oral Session 2 - Paleobiology	March 16, 11:00-11:45	114 EES
Lunch	March 16, 11:45-12:45	EES Atrium
Oral Session 3 – Isotope Geochemistry	March 16, 12:45-2:45	114 EES
Break	March 16, 2:45-3:15	
Oral Session 4 - Astrobiology	March 16, 3:15-4:30	114 EES
Entropy Pep Rally and Chili Cook-off at the Marone's	March 16, 6:30	591 E. Shadow Lane, State College

Graduate Student Colloquium  
Committee Members  
2013

Jamie Brainard, Chair  
Lauren Milideo, Chair

Matt Gonzales  
TJ Deane  
Anna Wendt  
Florence Ling  
Marsella Kachingwe  
Leah Tsao  
Kiya Wilson

# The Peter Deines Lectureship

The first place award for an oral presentation by a post-comprehensive Ph.D. student is designated the Peter Deines Lectureship for the following academic year.

This award was started in 2004 to represent the tremendous amount of respect and admiration the graduate students in the Department of Geosciences had for Dr. Peter Deines, who that year was stepping down from the position of Graduate Program Chairman. Recipients of the honor are invited to give a departmental colloquium talk during the proceeding academic year.

The department and the world lost a great man and wonderful person when Peter passed away on February 2, 2009. It is with great pride that the Graduate Student Colloquium continues the tradition born in 2004.

## Past Recipients:

2012-2013 Elizabeth Herndon

2011-2012: Bryan Kaproth

2010-2011: Tim Fischer

2009-2010: Aaron Diefendorf and Bryn Kimball

2008-09: Daniel Hummer

2007-08: Gavin Hayes

2006-07: Christina Lopano

2005-06: Shawn Goldman and Courtney Turich

2004-05: Margaret Benoit

# The Peter Deines Lectureship



Peter Deines (4/02/36 - 2/02/09) earned a Geologen Vordiplom at the Rheinsche Friedrich Wilhelms Universitaet, Bonn, Germany in 1959, an M.S. (1964) and a Ph.D. (1967) in Geochemistry and Mineralogy from Penn State University. Since 1967, and after 2004, as an Emeritus Professor, he was a member of the Geological Science Faculty of the Pennsylvania State University. He earned an international reputation for his geochemical research, teaching, and science administration. Recognition came in teaching awards, election to the University Senate, in which he served for 24 years, and election especially to Treasurer of the International Geochemical Society. In that office, he was so effective that he was awarded a unique Honorary Life Membership for his financial management of the society. He was a principal organizer of that Society's primary international meetings, the famous Goldschmidt Conferences.

With his gift for organization, he also served the Department of Geosciences on most of its committees and he served as its Graduate Program Chairman, while also administering committees for the College of Earth and Mineral Sciences, primarily for Scholarships. Most important was his commitment to the University Academic Senate, in which he served in 28 committee posts, including its Chair for 1990-91; and to the University, on 34 committees and commissions, including University Ombudsman since 2006. He also was elected President of the Faculty-Staff Club. Dr. Deines' research centered on precise explanations of natural variations in stable isotope abundances as means of understanding geologic processes. Results were presented in lectures throughout the world and in over 60 published papers. His illustrated book, "Solved Problems in Geochemistry," was polished by his teaching of eight graduate courses and is available on the web especially for graduate students.

A 40-year member of the Nittany Valley Symphony, Peter will be missed for his finesse with violin and viola.

# Poster Session One

Friday, March 15  
6:30-7:30pm, EES Atrium

Poster #	Presenter	Advisor	Title
1	Beth Meyers	Kevin Furlong	Surface and Subsurface Fault Displacements from the September 2010 Darfield (Canterbury) Earthquake
3	Florence Ling	Peter Heaney	Sorption of contaminant lead with birnessite
5	Max Christie	Mark Patzkowsky	Contrasting Taxonomic and Ecological Change Across the Mid-Late Devonian Interval
7	Yipeng Zhang	Demian Saffer	Induced Seismicity in Crystalline Basement Rocks by Fluid Injection into Basal Reservoirs
9	James Cederberg	Rudy Slingerland	River delta response to forced regression: A quantitative morphologic and stratigraphic assessment
11	Xin Gu	Susan Brantley	Nano-to-Micrometer Size Pores in Marcellus Shale Matrix: A Neutron Scattering Study
13	Roman Olson	Klaus Keller	What is the effect of internal climate variability on climate sensitivity estimates?
15	John Fegyveresi	Richard Alley	A closer look at the total air content record from the WAIS Divide (WDC06A) ice core, West Antarctica
17	Katelynn Olcott	Demian Saffer	Constraints on in situ stress across the shallow megasplay fault offshore the Kii Peninsula, SW Japan from borehole breakouts
19	Xuhua Shi	Eric Kirby	Weak middle crust beneath central Tibet: constraints from shoreline deformation around Siling Co
21	Brian Culp	Eric Kirby	Using an Elastic Half Space Model to Test the Dynamics of the Hunter Mountain Fault System in the Eastern California Shear Zone
23	Marsella Kachingwe	Andrew Nyblade	Preliminary Results for Crustal Structure in Southeastern Africa from P-wave Receiver Functions
25	Halldor Geirsson	Peter LaFemina	Multidisciplinary observations of the 2011 eruption of Telica volcano, Nicaragua: implications for the dynamics of low-explosivity eruptions

# Surface and Subsurface Fault Displacements from the September 2010 Darfield (Canterbury) Earthquake

**Beth Meyers**  
M.S. Student

**Advisor: Kevin Furlong**

Gavin Hayes, National Earthquake Information Center, USGS  
Matthew Herman, Pennsylvania State University  
Mark Quigley, University of Canterbury, New Zealand

On September 3, 2010 a Magnitude 7.1 earthquake struck near Darfield, New Zealand. This was to be the first earthquake in an ongoing, damaging sequence near the city of Christchurch. The earthquake produced a surface rupture with measurable offsets of up to 5.3m along a 30km surface fault system. The spatial pattern of slip during this rupture has been determined by various groups using a range of approaches and several independent data sets. Surface fault rupture was measured in the field and fault slip at depth has been inferred from a seismologic finite fault model (FFM) and various geodetic observations including GPS and InSAR. Here we compare the observed segmented surface displacements with fault slip inferred from the other data.

Measurements of the surface rupture show segmented faulting consistent with subsurface slip in the FFM. In the FFM, the main slip patch near the hypocenter can be directly correlated to the region of maximum surface displacement. The FFM and some evidence in the InSAR data also indicate that the Greendale fault system, the structure responsible for the bulk of the rupture, continues at depth closer towards Christchurch than is seen in surface rupture patterns. There is an additional 20km long patch with up to 3m of modeled slip seen in the eastern end of the inverted fault, offset to the south from the Greendale fault trace. This additional fault segment is consistent with a zone of aftershock activity of the main Darfield event, and with local patterns of strong motion. It thus appears that slip recorded at the surface does not describe the entire fault system. This eastward extension of the September rupture means that there is only a short segment of unruptured crust remaining along the entire fault system involved in the Canterbury earthquake sequence.

# Sorption of contaminant lead with birnessite

**Florence Ling**

Ph.D. Student, Pre-comps

**Advisor: Peter Heaney**

Lead (Pb) contamination in soils remains a problem, largely due to past use of leaded gasoline.<sup>1</sup> Birnessite, a manganese oxide, can potentially remediate Pb. Its crystal structure of layered octahedral sheets allows for a high cation exchange capacity, enabling the exchange of many metals into the interlayer including Ba, K, and Cs.<sup>2</sup> Birnessite is known to sorb Pb, although the sorption mechanism remains unclear. Pb may be sorbing to either the surface or within the interlayer. In addition, the phase of birnessite may affect whether Pb can be effectively sequestered. Each phase differs in crystal structure, and phase transformations often occur due to changes in pH. For this project, time-resolved x-ray diffraction (TRXRD) was used to examine the sorption of Pb with several varieties of birnessite in a series of flow-through experiments. The XRD patterns are will hopefully elucidate structural changes in birnessite at varying pH, determine the location of Pb atoms after sorption, and clarify differences in Pb sorption between various birnessite phases. Understanding these aspects of Pb sorption to birnessite will provide further insight into Pb remediation.

## References:

<sup>1</sup>Filippelli, G., Laidlaw, M. (2008) Resuspension of urban soils as a persistent source of lead poisoning in children: A review and new directions. *Applied Geochemistry*. Vol. 23. 2021-2039.

<sup>2</sup>Lopano, C., Heaney P., Bandstra, J., Post, J., Brantley, S. (2011) Kinetic analysis of cation exchange in birnessite using time-resolved synchrotron X-ray diffraction. *Geochimica et Cosmochimica Acta*. Vol. 75. 3973-3981.

# **Contrasting Taxonomic and Ecological Change Across the Mid-Late Devonian Interval**

**Max Christie**

Ph.D. Student, Pre-comps, Not Petroleum Related

**Dr. Mark Patzkowsky**

Steven M. Holland, The University of Georgia

Andrew M. Bush, The University of Connecticut

The Mid-Late Devonian was an interval of elevated faunal turnover culminating in the Frasnian/Famennian mass extinction. In addition to the severe taxonomic changes that occurred during this time, communities also experienced severe ecological changes.

We investigate patterns of taxonomic and ecological change through the Mid-Late Devonian interval using faunal counts from bulk samples in New York State. Taxonomic and ecological changes are measured by classifying organisms into genera and ecological lifestyles, a method of grouping organisms by their role in an ecosystem regardless of their evolutionary history. Two-way cluster analyses and ordinations were used to analyze samples across the Givetian/Frasnian and Frasnian/Famennian boundaries.

A two-way cluster analysis of samples and genera from each stage shows several distinct biofacies identified by previous studies. When samples are coded for these biofacies they describe a depth gradient along axis 1 of a DCA ordination for the Givetian and Famennian stages, and axis 2 of the Frasnian stage. When these depth zones are considered for ecological communities, Givetian samples show little differentiation according to depth; however, Frasnian and Famennian communities show distinct separation by biofacies. This suggests that while similar Givetian ecological communities could exist along a depth gradient, Frasnian and Famennian ecological communities changed as water depth increased.

When the data for each stage is combined, ordination among genera shows progressively smaller groups for the Givetian through Famennian, suggesting communities become increasingly similar. Givetian samples separate primarily along axis 2, possibly representing a depth gradient. Frasnian samples also separate along axis 2, albeit to a lesser degree, likely representing a depth gradient. Famennian samples cluster closely, with no clear distinction of depth. When considering the entire data set for ecological communities, no distinction is seen along axes 1 or 2 in terms of depth. Instead, samples separate based on the abundance of the two primary lifestyles, surficial-attached-suspension feeders and surficial-unattached-suspension feeders, with communities becoming predominantly surficial-attached-suspension feeders by the Famennian.

# Induced Seismicity in Crystalline Basement Rocks by Fluid Injection into Basal Reservoirs

**Yipeng Zhang**

Ph.D. Student, Pre-comps

**Advisor: Dr. Demian M. Saffer**

Mark A. Person, Earth and Environmental Sciences Department, New Mexico Tech

John Rupp, Indiana Geological Survey, Indiana University

Michael A. Celia, Department of Civil Engineering, Princeton University

Carl W. Gable, Earth and Environmental Sciences Department, Los Alamos National Laboratory

Brenda B. Bowen, Department of Geology and Geophysics, University of Utah

Peter Mozley, Earth and Environmental Sciences Department, New Mexico Tech

James Evans, Department of Geology, Utah State University

Thomas A. Dewers, Geomechanics Department, Sandia National Laboratory

A series of M3.8-M5.5 induced seismic events during the past decade due to unconventional oil and gas development across the midcontinent USA have raised concern regarding regulations for hazardous waste injection. Here we present a hydrogeologic-geomechanical sensitivity study using a hybrid analytic-numerical cross-sectional model to assess a wide variety of possible failure scenarios within crystalline rocks. The hydrostratigraphic framework model we used in this study is based on the geology of the Illinois Basin. The model includes 2.8 km thick Paleozoic sedimentary aquifers and confining units underlain by 4 km of bedrock. We represented injection at 5451 m<sup>3</sup>/day into a basal sandstone aquifer (Mt. Simon) as well as the overlying carbonate and siliciclastice reservoirs (middle aquifer: Knox limestone, St. Peter sandstone, upper Ordovician carbonates). In some scenarios, we included high/low permeability vertical and sub-horizontal thrust faults. Deviatoric pore pressures from the model were used to estimate failure along critically stressed faults within the bedrock. For a basement permeability between 10<sup>-15</sup> m<sup>2</sup> to 10<sup>-16</sup> m<sup>2</sup>, injection into the basal aquifer (Mt. Simon) resulted in a failure envelope within the crystalline basement to depths of about 1.4-4 km and extending laterally up to 6 km. Including a transmissive vertical normal fault increased the depth of the failure envelope to 4 km below the base of the sedimentary pile. If a 10<sup>8</sup> order-of-magnitude permeability contrast exists between the thrust fault (10<sup>-10</sup> m<sup>2</sup>) and basement rocks (10<sup>-18</sup> m<sup>2</sup>) with the fault width being constant, then pore pressures can propagate along the sub-horizontal fault about 12 km from the injection well. For middle-aquifer injection, the presence of a bottom seal (Eau Claire shale) had a prophylactic effect, preventing the build up of deviatoric pressures into the basement. Thus we propose that injecting hazardous waste in basal aquifers is not an optimal solution and should be replaced by middle-aquifer-injection scenario.

# **River delta response to forced regression: A quantitative morphologic and stratigraphic assessment**

**James Cederberg**

M.S. Student

Petroleum related

**Advisor: Rudy Slingerland**

Other authors each on a separate line:

Doug Edmonds, Indiana University

Dan Parsons, University of Hull

Jim Best, University of Illinois

Andrew McGuffin, Penn State

Alex Burpee, Penn State

Jordan Royce, University of Hull

Rebecca Caldwell, Indiana University

Austin Nijhuis, Boston College

**Purpose:** This project aims to quantitatively connect the sedimentology and geomorphology of deltas experiencing relative sea level fall, or forced regression, to their stratigraphy in a sequence stratigraphic framework.

**Regional Context:** This study will focus on consists of two field locations. The first is the modern Goose River Delta in Labrador, Canada which is currently experience in a fall in relative sea level. The second location is the ancient Panther Tongue Delta Complex in Utah which is widely interpreted as being deposited during a drop in relative sea level.

**Methods:** A series of numerical models will be run with a range of rates of relative sea level fall. Different basin geometries will be cross-tested with these models to control for the anticipated effects of basin depth. These models will be calibrated to the stratigraphic and morphologic data gathered from the modern Goose River Delta using outcrop analysis, ground penetrating radar, seismic data, coring, real-time kinematic GPS data, and hydraulic measurements. Outcrop data from the ancient Panther Tongue Delta Complex will be collected in the field and well-log and seismic data will be gathered from the literature. Plugging this data into the numerical models, the predicted results for the Panther Tongue's rate of relative sea level fall and basin geometry will be compared to the interpretations made in the current literature.

**Scientific Importance:** Little work has been done to quantitatively link the sedimentology of a modern delta experiencing forced regression to an ancient system despite the fact that forced regression is commonly attributed to many ancient deltas. The predictive model developed in this project will fill this gap in knowledge and aid the sequence stratigraphic community in its quest to better understand petroleum systems.

# **Nano-to-Micrometer Size Pores in Marcellus Shale Matrix: A Neutron Scattering Study**

**Xin Gu**

Ph.D. Student, Pre-comps

**Advisor: Susan Brantley**

Currently, the production of natural gas from black shale has increased dramatically due to the development of hydraulic fracturing techniques which significantly increase the porosity and fracture network of shales. As a result, the pore structure of black shale is an active area of study as it is highly relevant to hydrocarbon storage and the gas pathway through the rock formations. In this study, we focus on the microstructures of the black shale ranging from approximately 0.7 nm to several micrometers in dimension: fractal dimensions, internal specific surface area, porosity, and pore size distribution in the silicate matrix by using combined Ultra Small Angle Neutron Scattering (USANS) and Small Angle Neutron Scattering (SANS). Deep core samples were collected from the economically important Union Springs member of the Marcellus formation from a drill core in Howard, PA. We find the nano-pores probed in Marcellus shale are isotropic when neutrons are scattered from thin sections cut in the plane of bedding but anisotropic from sections cut from other planes. In addition, the smaller, more anisotropic pores are connected. The porosities in the sections cut perpendicular to bedding are much higher than those in the plane of bedding. Neutron scattering reveals the complex structure of the matrix porosity at scales that are hard to interrogate using other techniques.

# What is the effect of internal climate variability on climate sensitivity estimates?

**Roman Olson**

Ph.D. Student, Post comps

**Advisor: Klaus Keller**

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Nathan M. Urban, Los Alamos National Laboratory

Klaus Keller, Penn State University, and Earth and Environmental Systems Institute

Climate sensitivity is defined as the rise in global mean near-surface temperatures following the doubling of atmospheric CO<sub>2</sub> concentrations. Climate sensitivity is an important climate property that affects future climate projections, and many recent studies have attempted to estimate it. A common methodology is to fuse observations of recent warming with Earth system Models of Intermediate Complexity (EMICs). Despite this effort, climate sensitivity has remained consistently uncertain. Moreover, the effects of internal climate variability on these estimates have not received thorough attention. Here we evaluate the role of climate variability in contributing to this uncertainty.

Using observation system simulation experiments, we find that internal climate variability may play a key role in climate sensitivity uncertainty. Our methodology involves simulating many realizations of possible observations of upper ocean and surface warming given a “true” climate sensitivity, and then re-estimating the climate sensitivity using the observations, and a parameter estimation method. We find that a single realization of internal climate variability can introduce a considerable (up to several deg. C) bias into the estimates. This opens a possibility that recent climate sensitivity estimates derived from EMICS and global datasets might be systematically biased. The effects of internal climate variability warrant further investigation with other climate models and/or different observational datasets.

# **A closer look at the total air content record from the WAIS Divide (WDC06A) ice core, West Antarctica**

**John M. Fegyveresi**

Ph.D. Student, Post comps

**Advisor: Richard B. Alley**

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Total gas content, or air content ( $V$ ), is a measurement of the total air trapped in polar ice. This air initially becomes trapped during the transformation of snow into ice by way of packing and sintering firnification processes. At pore close-off depth, the air trapped in spaces (pores) between grains, becomes pinched-off and is no longer free to reach a pressure equilibrium with the surface atmosphere. This closure of pore space can be complicated, however, by the effects of seasonality upon the snow surface and upon the density of various layers within the firn. Despite these complications, air content of ice has been used as a fairly accurate “paleo-barometer” and thereby as a sensitive indicator of the past elevations of ice sheets.

The total air content record from the WAIS Divide, WDC06A ice core, was measured along the entire length of the core below pore close-off (~75 - 3300 meters). The results show an overall long-term trend consistent with measured stable isotope values, the timing of recent glaciation events, and with known paleo-elevation data for the site. Variations seen on smaller scales may be indicative of changes in the pore volume at the pore close-off depth brought on by seasonality-induced metamorphism of the surface snow that is being preserved at depth. Additionally, the results are compared with optical, dust, and major ion data sets from the core to determine potential correlations.

The air content values fall within an expected range of 0.095 and 0.12 cm<sup>3</sup> g<sup>-1</sup> and show a noticeable decrease in volume as the samples pass below the Holocene transition. These results have been corrected for the effects of cut bubbles, bubble compression, and gas solubility. The timing of crust and surface hoar formation in relation to the local seasonal cycle at WAIS Divide and to measured gas content, may help to identify any correlations of statistical significance between seasonality and the trapping of gases during the close-off process. Specifically, visible crust data (formation and frequency) will be compared to the entire total air content record at various spacings above and below each measured gas sample. If a surface pressure history for WAIS Divide can be independently acquired or estimated using recent elevation models, then a more accurate reconstruction for pore close-off volume ( $V_c$ ) could be calculated that might allow for a realistic parameterization of the seasonal influences. Lastly, it is hoped that spectral analysis work will help to elucidate possible low and high-frequency signals in the data.

# Constraints on in situ stress across the shallow megasplay fault offshore the Kii Peninsula, SW Japan from borehole breakouts

**Katelyn Allison Huffman Olcott**

Ph.D. Student, Pre-comps

**Advisor: Demian Saffer**

The orientation and magnitude of stress in active tectonic settings, and in the vicinity of active faults, are important toward understanding faulting and earthquake mechanics. In areas where boreholes have been drilled, stress magnitude can be quantified by combining observations of compressional borehole breakout (BO) widths with estimates or measurements of unconfined compressive rock strength (UCS). Here, we estimate stress at Integrated Ocean Drilling Program (IODP) Sites C0004 and Site C0010, drilled into the accretionary prism offshore the Kii Peninsula, SW Japan, as part of the IODP NanTroSEIZE project. These sites penetrated the shallow portion of the megasplay fault, a major out of sequence thrust fault that cuts the accretionary prism and branches from the master décollement ~55 km from the trench. Drilling at Site C0004 included logging while drilling (LWD) and coring to a total depth (TD) of ~399 m. Drilling at Site C0010, located ~3.5 km along strike, included LWD to a TD of 555 mbsf. The megasplay fault is marked by a 60-m wide fractured zone at Site C0004, whereas at Site C0010 it is defined by a sharp contact between the overriding thrust wedge and footwall sediments. At Site C0010, the hole was temporarily suspended for 3 days due to weather conditions, and ~70 m of the hanging wall and the upper portion of the footwall were relogged after re-entry and prior to continued drilling. We measure BO width from LWD resistivity-at-the-bit (RAB) images, and estimate a range of UCS values from existing experimentally-derived relations between P-wave velocity ( $V_p$ ) and UCS. Under the assumption that stresses at the edge of BO are in equilibrium with the rock strength, we quantify far field horizontal stresses  $SH_{max}$  and  $SH_{min}$  as a function of depth at each drillsite. Our results indicate that stresses at both Site C0004 and Site C0010 define a thrust-faulting regime, in both the hanging wall and footwall of the fault. This implies that stress is not decoupled across the shallow megasplay. Computed horizontal stress magnitudes are generally similar at both Sites, with  $SH_{max}$  referenced to the seafloor ranging from 7.4 - 8.5 MPa at ~250 mbsf and 11.5-11.9 MPa at ~350 mbsf. There is a distinct shift to lower estimated stress magnitudes over the 150 m below the megasplay at Site C0010, but not at Site C0004, based on narrower observed breakouts in the footwall at Site C0010. The relogged portion of Site C0010 also presents a unique opportunity to explore the possibility that BO grow through time as formation pore pressure and thus rock strength equalize after drilling. BO appear to have grown by as much as  $60^\circ$  between the first and second logging runs. This growth corresponds to an increase in computed horizontal stress of ~2 MPa. If this process is common, it implies that stresses computed from BO width in low-permeability sediments may under-estimate the true in situ stress magnitude.

# Weak middle crust beneath central Tibet: constraints from shoreline deformation around Siling Co

**Xuhua Shi**

Ph.D. Student, Pre-comps

**Advisor: Eric Kirby and Kevin Furlong**

Whether the deep crust beneath the Tibetan Plateau is weak enough to flow on geologic timescales remains a central point of debate. Here we attempt to constrain the effective elastic thickness ( $T_e$ ) by exploiting the flexural deformation of highstand shorelines around the Siling Co, central Tibet, in response to climatically-induced lake recession. Extensive flights of well-preserved paleo-shorelines are distributed around the lake, and extend up to 100 m above present day lake level. In this study, we examined the highstand shoreline (~4594 m a.s.l.) in an effort to ascertain whether it is deflected. This highstand shoreline is characterized by obvious constructional features (beach ridges, benches, spits, bars and cusps) that continuously connect to wave-cut scarps which define a clear geomorphic boundary between an older landscape characterized by dissected alluvial gullies and a lower one characterized by younger, recessional shorelines. The age of relict shorelines was determined by OSL (optically stimulated luminescence) and of cosmogenic  $^{36}\text{Cl}$  depth profiles. The OSL ages for four samples from the highstand complex range from ~ 8 ka to ~ 4 ka, suggesting a relatively stable lake level during this time and the timescale of the lake unloading of the Siling Co, ~ 10 ka. Flights of shorelines below this highstand show ages younger than 3.3 ka, while degraded, relict shorelines above the highstand are significantly older; OSL ages range from ~ 18 – 43 ka and two  $^{36}\text{Cl}$  depth profile yield ages of 113 ka and 178 ka.

Comparing observed shoreline deflections with models of elastic deformation in response to removal of a 3D load, we find that the effective elastic thickness of central Tibetan crust is relatively thin ( $T_e \sim 13 \pm 2$  km), suggesting that most of the mechanical strength of the crust resides in the upper crust. The timescale of lake recession (~ 10 ka) implies strain rates on the order of  $\sim 10^{-16} \text{ s}^{-1}$ , which, when combined with existing constraints on the thermal and seismic velocity structure of the crust in central Tibet, allow us to place bounds on the range of probable viscosity beneath central Tibet. Assuming a simple, two-layer model with a viscous layer beneath the elastic upper crust implies viscosity on the order of  $\sim 10^{19} \text{ Pa s}$ . A more comprehensive consideration of possible strength profiles consistent with available seismic and thermal data is consistent with a significant reduction in effective viscosity below depths of ~ 20 – 40 km. In this treatment, viscosities above this level range from  $10^{20} - 10^{22} \text{ Pa s}$ , while viscosities at depth range from  $10^{18} - 10^{21} \text{ Pa s}$ . Collectively, our findings of thin elastic upper crust and a reduction in viscosity at depth suggests that the middle and lower crust beneath central Tibet is likely relatively weak at timescales of  $10^4 - 10^5$  yr. However, a more definitive determination awaits a refined understanding of lake loading history.

# **Using an Elastic Half Space Model to Test the Dynamics of the Hunter Mountain Fault System in the Eastern California Shear Zone**

**Brian M. Culp**

M.S. Student

**Advisor: Eric Kirby, Ph.D.**

Kevin Furlong, Ph.D., Penn State University

While most of the motion accommodated between the North American and Pacific Plates is on the well-known San Andres Fault, nearly 25% is accommodated across the Eastern California Shear Zone (Dokka et al., 1990). The Eastern California Shear Zone is composed largely of a network of normal and strike-slip faults. Understanding the dynamics and development of these systems has been a focus among researchers for decades, but despite much progress, we lack a complete understanding of the apparent differences between displacement rates over different timescales. One idea is that the measured geodetic rates (eg., Insar, GPS) are too focused to compare to the long term geologic rates. Alternatively, the measured geodetic rates could be a result of numerous faults interacting, giving the appearance that measured rates are actually higher than the real rate. Focusing on the Hunter Mountain Fault System, bounded to the South by Panamint Valley and to the North by Saline Valley, this study will test the variability of displacement rates using an Okada Half Space Model, developed by Matt Herman. Recent estimates of slip on the Hunter Mountain Fault system using Insar, estimate that current slip is on the order of 5-6 mm/yr (Gourmelen et al., 2011). Conversely, geologic and GPS methods have estimated slip on the order of 3-4 mm/yr (Oswald, 1998). By adding the surrounding fault systems to the elastic half space model, one can test the impact that they have on the measured rates across the Hunter Mountain Fault System.

# **Preliminary Results for Crustal Structure in Southeastern Africa from P-wave Receiver Functions**

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D. Wiens, Washington University in Saint Louis  
J. Julia, Universidade Federal de Rio Grando do Norte

The crustal structure of southeastern Africa is investigated by modeling P-wave receiver functions, using H-k stacking and joint inversion methods. P-wave receiver functions are obtained beneath 29 broadband seismic stations in Zambia, Malawi and Mozambique. Estimates for the Moho depth and Poisson's ratio, are determined from H-k stacking, and estimates for the shear wave velocity are determined by the joint inversion of receiver functions and surface wave dispersions. Preliminary results show that Moho depths beneath southeastern Africa range from 32 km to 51 km. Thicker crust is found in Proterozoic terrains, such as the Irumide Belt, while thinner crust is found in reworked Archean terrains, such as the Bangweulu Block. These results are consistent with previous studies and global averages for Precambrian terrains. The preliminary results also show a range of Poisson's ratios from 0.2 to 0.3. These new results for southeastern Africa are being combined with similar results from elsewhere in eastern and southern Africa to improve our understanding of African crustal structure.

# **Multidisciplinary observations of the 2011 eruption of Telica volcano, Nicaragua: implications for the dynamics of low-explosivity eruptions**

**Halldor Geirsson**

Ph.D. Student, Post comps

**Advisor: Peter C. LaFemina**

Mel Rodgers, University of South Florida, Tampa, FL, USA

Diana Roman, Carnegie Institution of Washington, Washington, D.C., USA

Molly Witter, The Pennsylvania State University, University Park, PA, USA

Maureen D. Feineman, The Pennsylvania State University, University Park, PA, USA

Tanya Furman, The Pennsylvania State University, University Park, PA, USA

Angelica Muñoz, Instituto Nicaraguense de Estudios Territoriales, Managua, Nicaragua

Julio Alvarez, Instituto Nicaraguense de Estudios Territoriales, Managua, Nicaragua

Vladimir Conde Jacobo, Chalmers University of Technology, Gothenburg, Sweden

Daniel Nilsson, Chalmers University of Technology, Gothenburg, Sweden

Bo Galle, Chalmers University of Technology, Gothenburg, Sweden

The driving mechanisms for small, mostly non-magmatic, explosive eruptions are uncertain in terms of whether, why, and where pressure builds up before the eruption, and the involvement of meteoric water through phreatomagmatic interactions. We present multidisciplinary observations of the March-June 2011 eruption of the basaltic-andesitic Telica volcano, Nicaragua. A dense network of seismic and GPS instruments in addition to ash analysis, visual observations, plume SO<sub>2</sub> measurements, and temperature measurements within the active vent and fumaroles near the vent comprise our data-set. The 2011 eruptive episode consisted of discrete explosions with maximum ash plume height of ~2 km above the crater rim and total volume of ash less than ~10<sup>5</sup> m<sup>3</sup>. The ash mainly consisted of reworked, hydrothermally altered andesite, but there may be up to 25% juvenile ash. Fumarole temperatures outside the crater, as well as temperatures within the crater decreased before the main phase of the eruption and increased as the eruption progressed. Likewise, SO<sub>2</sub> emissions were at a minimum before the eruption. The number of seismic events per day decreased to a minimum over a period of a few months before the eruption. Seismicity then increased as the eruption intensified and reached a maximum near the end of the eruption. Continuous GPS measurements from a ten-station network in the area show no deformation associated with the eruption. The 2011 eruption was Telica's most explosive since 1999; however, it was less energetic than the 1982 eruption. Our observations of subdued pre-eruptive seismicity, SO<sub>2</sub> emission, and fumarole temperatures indicate that the eruption dynamics were controlled by temporary closure of the otherwise open-vent degassing system, facilitating pressure build-up and subsequent explosions when the conduit system was re-opened.

# Poster Session Two

Friday, March 15  
7:30-8:30pm, EES Atrium

Poster #	Presenter	Advisor	Title
2	Rosie Oakes	Tim Bralower	Phosphorus cycling in the Early Aptian
4	Piyali Chanda	Matthew Fantle	The study of marine carbonate dissolution using Mg isotopic composition of foraminiferal calcite and the methods for measuring Mg isotopes using MC-ICPMS
6	Will Ethier Colon	Hiroshi Ohmoto	Molybdenum Adsorption on to Hydrothermally Produced Fe(oxyhydr)oxides: Constraining the Molybdenum Cycle
8	Ellen Chamberlin	Liz Hajek	Multistory sand bodies: evaluating process interpretations and estimating preservation potential
10	Nate Wysocki	Liz Hajek	Fine sediment deposition and storage in sandy fluvial systems
12	Nooreen Meghani	Eric Kirby	Erosion and Uplift in the Sub-Himalaya
14	Kiya Riverman	Sridhar Anandakrishnan	GPS Measurements of Ice Velocity and Strain on the Northeast Greenland Ice Stream: Implications for Long-Term Stability of the Ice Sheet
16	Bryan Kaproth	Chris Marone	Silent laboratory earthquakes with elastic wave speed precursors
18	Christine Regalla	Don Fisher	Kinematic evolution of the NE Japan convergent margin and implications for plate boundary dynamics
20	Matt Herman	Kevin Furlong	Using Regional Moment Tensors to Constrain the Kinematics and Stress Evolution During the 2010-2012 Canterbury, New Zealand, Earthquake Sequence
22	Robert Valdez	Demian Saffer	Permeability and Consolidation of sediments from the underlying accretionary prism in the Kumano Basin, SW Japan
24	Cristo Ramirez	Andrew Nyblade	Estimates of Crustal Structure in Antarctica from S Waves Receiver Functions
26	Leah Tsao	Jennifer Macalady	Assessing the Correlation between Dissolved Sulfide to Oxygen Ratios and the Abundance of a Sulfur Oxidizing Bacterium

# Phosphorus cycling in the Early Aptian

**Rosie L. Oakes**

Ph.D. Student, Pre-comps

**Advisor: Tim Bralower**

Maria Dittrich, Department of Physical & Environmental Sciences, University of Toronto

Ulrich G. Wortmann, Department of Earth Sciences, University of Toronto

Phosphorus is an essential nutrient for living organisms. It is vital for the formation of ATP, the energy store in cells, and is needed for DNA synthesis. Seawater phosphorus concentration therefore plays a critical role in controlling marine productivity on geological timescales. The majority of research on the P cycle focuses on modern lacustrine and marine settings. This follows the necessity to gain a further understanding on the effects of agricultural fertilisers on nutrient cycling; in particular on the mechanisms which lead to eutrophication. These studies use sequential extraction to determine the speciation of P. The results suggest that bottom sediments can act as both a source and a sink of phosphorus; the role they assume depends on range of factors including bottom water oxygen concentrations, sedimentation rate and the concentration of iron.

This study applies a sequential extraction method developed in modern sediments to sediments from the Early Cretaceous, specifically the Early Aptian. During this time, globally synchronous oceanic anoxic events (OAE's) appear in the rock record. It has been suggested that these events represent an increase in marine productivity combined with bottom water anoxia. Our study investigates whether the speciation of sedimentary phosphorus can be used to reconstruct P cycling at this time. Our samples are taken from pre-, syn- and post-OAE1a but are not from the organic matter rich layers. Our results show that the original fractions of phosphorus have been altered during diagenesis with the majority of phosphorus now being preserved as either apatite (Ca-P) or phosphorus in organic matter (Porg). The dominance of Ca-P is expected as it is thought that redox-sensitive forms of P undergo 'sink switching' during diagenesis and are preserved as Ca-P. The high concentration of Porg however, differs from previous studies which generally find that Ca-P or iron (oxyhydr)oxide associated phosphorus (Fe-P) are dominant depending on deposition conditions. We find that during the anoxic event Ca-P preservation is enhanced, a trend which is not mirrored by an increase in total phosphorus concentration. This suggests that the formation of authigenic apatite via sink switching may have been enhanced during OAE1a. This agrees with the findings of a modern field and lab based study which proposes that more P is fixed than regenerated under anoxic conditions but contradicts earlier studies which suggest that more P will be refluxed from sediments under anoxic bottom water conditions.

# The study of marine carbonate dissolution using Mg isotopic composition of foraminiferal calcite and the methods for measuring Mg isotopes using MC-ICPMS

**Piyali Chanda**

Ph.D. Student, Pre-comps

**Advisor: Dr. Matthew Fantle**

Dissolution is one of the most important processes in marine carbonate diagenesis. A significant portion of marine biogenic carbonate comprises foraminiferal tests that are very susceptible to dissolution. Foraminiferal tests lose about 50% of their weight during dissolution and the decrease of foraminiferal Mg/Ca ratios with depth due to dissolution are also reported in previous studies [1]. Therefore, the question arises whether this substantial amount of loss of carbonate takes place due to dissolution within the seawater column while settling or the dissolution occurs mostly in the sediment deposited on the seafloor. Additionally, intra-test heterogeneity of Mg/Ca ratio in foraminiferal calcite is also observed for some of the species [2]. Since the presence of Mg in calcite increases the dissolution susceptibility of the calcite, the Mg-rich part of the foraminiferal tests are more prone to the preferential dissolution compared to the low-Mg portion of the tests. On the other hand, the  $\delta^{26}\text{Mg}$  of foraminiferal tests are found to be in the range of -3.0 to -5.7‰ compared to the DSM3 reference. A few studies on Mg isotopic composition ( $\delta^{26}\text{Mg}$ ) of various biogenic carbonates indicate that Mg-rich calcites are less depleted in heavier isotope ( $^{26}\text{Mg}$ ) compared to the calcite with lower Mg content. Therefore, the question arises: how does the preferential dissolution of Mg-rich part of the calcitic tests influence the  $\delta^{26}\text{Mg}$  of the foraminiferal tests? Here, I present the design of the experimental approach to study the effect of partial dissolution on foraminiferal  $\delta^{26}\text{Mg}$  and the methods developed for accurate and precise measurement of Mg isotopic composition of natural samples using Thermo-Scientific Neptune Plus Multi-collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) in the Metal Isotope Laboratory at Penn State.

Since, accurate and precise measurement Mg isotopes requires near quantitative chemical purification of Mg from the multi-element matrix a method has been developed to separate Mg from natural samples. This method includes the ion-exchange chromatography using 2 ml of Bio-Rad AG50W X-8 (200–400 mesh) cation exchange resin to separate pure Mg from samples consists of Ca, Na, Mg, K and Sr. 1N ultrapure HCl acid is used to elute the Mg fraction from a sample. The method developed for Mg isotope measurement in Neptune Plus ICPMS with Apex HF desolvating nebulizer involves sample-standard bracketing (SSB) technique for mass bias drift correction using DSM3 as the reference standard.

[1] Brown, S.J., and Elderfield, H., 1996. Variations in Mg/Ca and Sr/Ca ratios of planktonic foraminifera caused by postdepositional dissolution: Evidence of shallow Mg-dependent dissolution. *Paleoceanography*, 11(5), 543-551.

[2] Eggins, S. M., Sadekov A. Y., and Deckker P. De, 2004. Modulation and daily banding of Mg/Ca in *Orbulina universa* tests by symbiont photosynthesis and respiration: A complication for seawater thermometry? *Earth Planet. Sci. Lett.*, 225, 411 – 419.

# Molybdenum Adsorption on to Hydrothermally Produced Fe(oxyhydr)oxides: Constraining the Molybdenum Cycle

**William C. Ethier Colon**  
M.S. Student

**Hiroshi Ohmoto**

Molybdenum has several characteristics suitable for geochemical studies of ocean paleoredox conditions including a long ocean residence time of 800 kyr, being the most abundant trace metal in the ocean at 105 nm, but most importantly, isotopic fractionates through as it cycles. The current focus of our research attempts to constrain the isotopic mass balance of Mo. In the literature, it is already known that Fe (oxyhydr)oxides play a key role in Mo adsorption. However, it is ambiguous whether oxic sediments act as either a sink or a site of Mo recycling, and producing a false isotopic signal. We believe we can test their role in the Mo cycle by looking at low temperature ridge flank hydrothermal systems. As ferrous iron is expelled from hydrothermal vents and reacts with the overlying deep ocean oxic waters to form goethite, FeOOH, molybdate will have the opportunity to adsorb and form a stable iron molybdate species.

However, we attempt to recreate the process of Mo adsorption through the simulation of an actual hydrothermal vent, letting ferrous bearing hydrothermal fluid react with “overlying” oxic seawater laden with  $\text{MoO}_4^{2-}$  and later test the crystal structures of the produced solids. This method of approach will more accurately depict the process at hand; under open system conditions wherein these types of experiments are unprecedented.

We hope to infer a reaction mechanism by characterizing an immobile Mo species. From that, we can then calculate the stability and thusly constrain the role of adsorption on metal oxides in the overall Mo cycle. The implications of this study are pertinent when employing Mo as a proxy for inferring paleoredox conditions.

Initial experiments have been undertaken without the addition of molybdate to constrain the minimum threshold of dissolved  $\text{O}_2$  required for reaction (1) to take place under geologically important conditions. Further studies will involve varying pH of both the starting solution as well as the reservoir, varying ionic strength to more accurately model seawater, and mediate dissolved  $\text{O}_2$  levels to better control the rate of Fe oxidation. We hope that our research will give further incite towards explaining the isotopic mass balance of Mo.

# **Multistory sand bodies: evaluating process interpretations and estimating preservation potential**

**Ellen Chamberlin**

Ph.D. Student, Pre-comps, Petroleum related

**Advisor: Liz Hajek**

The architecture of amalgamated channel sand bodies, or multistory sand bodies (MSBs), is a key control on reservoir quality and connectivity in many fluvial formations, and interpreting MSB origin can provide important information about long time-scale river behavior, paleo-environmental conditions, and sedimentation and subsidence patterns in alluvial basins. Interpreting MSB origin and predicting subsurface sand-body connectivity is difficult because a variety of alluvial processes can build amalgamated sand bodies. To characterize and improve uncertainty associated with process interpretations of MSBs, we review published interpretations of MSBs and present results from an object-based basin-filling model. Overall we identify three main process that control MSB formation: 1) intra-channel-belt processes, 2) channel-belt avulsions that reoccupy previous channel sites, and 3) changes in basin boundary conditions. Within this framework, field evidence is used to constrain the uncertainty with which various process interpretations can be extrapolated from field data, and model results demonstrate how different processes influence channel body preservation potential.

Based on a literature review of 75 published interpretations of MSBs, and based on work in the Williams Fork Formation (Cretaceous, Colorado, USA) we evaluate the confidence of MSB-origin interpretations from field evidence. Two pieces of field evidence are high-confidence indicators of unique process origins: the shape and scale of the basal MSB bounding surface, and the geometry and amount of paleosol development within and surrounding the MSB. Other types of field evidence that are widely used to interpret MSB origin (such as variable paleocurrent directions between stories or high MSB width:thickness ratios) are shared between multiple MSB process origins. Interpretations made from solely these shared characteristics have high uncertainty.

We test the statistics of channel body preservation in different settings using an object-based geometric model with varying avulsion types, channel incision and floodplain aggradation rates, lateral channel mobilities. Preliminary results suggest that without floodplain aggradation, the channel incision:aggradation ratio is the first-order control on channel preservation, while lateral channel mobility and avulsion style have relatively minor effects. In model runs with floodplain aggradation, the spatial distribution and rate of floodplain aggradation is a first order control on channel body preservation. Model results suggest that, given an understanding of basin boundary conditions, we can predict the formation, preservation, and connectivity of MSBs within a given basin.

# **Fine sediment deposition and storage in sandy fluvial systems**

**Nathaniel Wysocki**

M.S. Student, Petroleum related

**Advisor: Liz Hajek**

Sandy fluvial deposits are important reservoir units for hydrocarbons and aquifers. However, they can be difficult to predict and efficiently produce due to particle-size heterogeneity ranging from the grain to basin scale. Fine sediment (silt and clay) is transported as suspended load and is either bypassed through the system as wash-load or is deposited and stored in the channel or on the floodplain. These deposits can cause porosity and permeability reduction at the pore scale as well as reservoir compartmentalization due to baffles and barriers to flow at the reach scale. In order to improve interpretation of fine sediment in ancient fluvial deposits, a better understanding of the conditions controlling when and where fine sediment accumulates and is stored in sandy fluvial systems is needed. It is possible that the properties of the suspended sediment load (composition and concentration) are a primary control the amount of fine sediment deposited in the channel. Here we present preliminary analysis of sediment data from two sandy rivers and propose field research and physical experiments to study the conditions that control the amount of fine sediment stored in fluvial deposits.

The White River in South Dakota and the Niobrara River in Nebraska afford the opportunity to study the influence of suspended-sediment load on fine sediment deposition because, although they have similar discharges and bed material grain-size, the suspended sediment concentrations (SSC) are drastically different. The Niobrara River has an average SSC of 1500 mg/l while the White River has a much higher average SSC of 9500 mg/l (<http://co.water.usgs.gov/sediment/>). Based on preliminary analysis of limited sediment data from the USGS, the White River also has a smaller median grain size of the suspended load than the Niobrara River. However, there is evidence that flocculation of grains plays a significant role in the White River which may enhance fine sediment deposition.

We will collect field data from these two rivers and physical experiments will be conducted to test the relationship between suspended-sediment composition and concentration and the degree to which fine sediments are deposited in active beds. Field data will also be used to evaluate the influence of reach-scale topography on fine-sediment deposition. We plan to collect bed material and suspended-sediment load samples from both physical experiments and modern rivers for use in grain size analysis which will allow us to model statistical relationships between the grain size distributions of bed material and suspended load samples. Linking these grain size distributions will provide a powerful tool in reconstructing the paleo-suspended sediment load from ancient bed load deposits.

# Erosion and Uplift in the Sub-Himalaya

**Nooreen A. Meghani**  
M.S. Student

**Advisor: Eric Kirby**

One of the most active plate margins in the world, the Himalayas take up more than 40 mm/yr of shortening between the Indian and Eurasian plates. Nearly half of this shortening is accommodated along active fault systems in the Himalayan foreland, though how the shortening is distributed among individual faults is poorly constrained. However, as there is a component of vertical motion, topography develops along these faults.

Of particular interest is the Siwalik Hills, a young hill-front developing along the Main Frontal Thrust (MFT). This growing topography records information about fault motion at depth. In turn, stream channels developed above growing folds in the Siwaliks incorporate signatures of topographic changes that can be identified through analysis of longitudinal channel profiles. In this region it has been suggested that the stream channels are adjusted to the differential rock uplift, and that one can use this as a guide to mapping patterns of active deformation within regions of consistent lithology (eg. Kirby and Whipple, 2012).

The relationship developed by Kirby and Whipple (2012) is limited to a single section of the Siwaliks SE of Kathmandu. By combining stream channel analyses and uplift rates determined with fluvial terraces, GPS data, and balanced cross sections, this correlation can be expanded and then applied to regions within the Siwaliks for which there are no uplift rates. This will give us a better understanding of shortening within the Sub-Himalaya, as well as regional implications for uplift rates across the Himalaya.

Kirby, E., & Whipple, K. X. (2012). Expression of active tectonics in erosional landscapes. *Journal of Structural Geology*, 44(C), 54–75.

# GPS Measurements of Ice Velocity and Strain on the Northeast Greenland Ice Stream: Implications for Long-Term Stability of the Ice Sheet

**Kiya Riverman**

Ph.D. Student, Pre-comps

**Advisor: Sridhar Anandakrishnan and Richard Alley**

Knut Christianson, St. Olaf College

Leo Peters, Penn State University

The North East Greenland Ice Stream (NEGIS) is a region of fast-flowing ice that initiates near the ice divide and extends to the coast, some 700 km to the northeast. As the ice stream drains an estimated 8% of the ice sheet, describing its current and future stability is important for understanding the potential dynamics of the Greenland Ice Sheet under a changing climate regime. Despite NEGIS' potential influence on Greenland Ice Sheet mass balance, no prior ground-based fieldwork has been conducted to understand its flow patterns or any potential instability.

Here we present the results of the first ground-based GPS data collected on the NEGIS. A 9-station GPS strain grid was deployed approximately 150 km upstream of the initiation of fast-flow and ran continuously for three weeks in the summer of 2012. GPS results are presented in the context of the overall structure of the ice stream, including shear margin location and basal topography, as interpreted from 3 MHz ice-penetrating radar data. We observe that GPS flowlines across NEGIS support the Christianson et al. (2013) hypothesis that steep marginal hydropotential barriers act as a barrier that prevent extensive ice entrainment.

Christianson, K., Alley, R., Anandakrishnan, S., Jacobel, R., Riverman, K., Muto, A. 2013. Self-stabilizing ice-stream flow in Northeast Greenland. *Geophysical Research Letters*, submitted.

# Silent laboratory earthquakes with elastic wave speed precursors

**Bryan Kaproth-Gerecht**

Ph.D. Student, Post comps

**Advisor: Chris Marone**

Slow earthquakes and earthquake precursors are relatively new discoveries with significant implications for earthquake prediction. Seismologists have made rapid progress to observe, characterize and understand these phenomena, and recent models emulate these observations well. Experiments have unfortunately lagged behind these discoveries, as slow-slip and precursors have remained elusive in the lab, until now. We have recently observed highly repeatable, long duration, stick-slip events in the laboratory, many of which follow long duration precursors. We observe 60+ earthquakes per experiment on powdered serpentine, with slip durations ranging from 1-50 seconds. We also observe precursor changes in ultrasonic velocity up to 100s prior to rupture. These experiments were conducted under direct shear in the biaxial load frame at Penn State with continual active-seismic measurements ( $\sigma_n = 1$  MPa; far-field velocity = 1-30  $\mu\text{m/s}$ ). An essential ingredient for these experiments is that force was applied by a spring in the shear direction. We suggest that slow slip in these experiments is modulated by the interplay of shear stress applied by the spring (K) and gouge strength (Kc), modulated by rate and state friction during fault slip. In particular, it is likely that rapid fault slip is modulated by an evolution from rate-weakening to rate-strengthening at higher velocities. Additionally, we suggest that precursor changes in velocity are likely due to very small preseismic slip at the gouge layer. Indeed, acoustics may produce a stronger signal of microstrain than any direct strain measure.

# **Kinematic evolution of the NE Japan convergent margin and implications for plate boundary dynamics**

**Christine Regalla**

Ph.D. Student, Post comps

**Advisor: Don Fisher and Eric Kirby**

Kevin Furlong

Tectonic erosion along convergent plate boundaries, whereby removal of upper plate material along the subduction zone interface drives mass loss and subsidence of the outer forearc, has been invoked to explain the geologically recent evolution of nearly half the world's subduction margins. However, the mechanisms that initiate and sustain forearc subsidence are not well understood. We provide new analyses of the kinematic evolution of the northeast Japan margin, considered a type example of erosive margins, that demonstrate that vertical motions of the outer forearc are coincident with changes in upper plate kinematics and lower plate convergence rate. New constraints on the timing and kinematics of deformation along inner forearc faults indicate Plio-Quaternary inversion of Miocene extensional structures. The initiation of reverse slip along the inner forearc Futaba (5.6 to 3.9 Ma), Oritusme (5.9 to 4.8 Ma), and Noehij (Pliocene) faults are constrained by new U-Pb ages from tephra in growth strata. The initiation of an earlier phase of extension along the Oritusme and Futaba faults is identified from thick sequences of Miocene rift-related sediments in the hanging walls that are absent in the footwalls. Existing biostratigraphic and geochronologic ages near the base of the syn-extensional sequences constrain the initiation of extension to 23.9-21.0 and ~20.8 Ma for the Futaba and Oritusme faults, and cross sections across these structures require nearly complete thrust inversion of Miocene extensional displacement. A regional synthesis of deformation demonstrates that the timing and kinematics of forearc deformation are contemporaneous with previously documented Miocene extension and Plio-Quaternary inversion in the backarc. Moreover, reconstructions of Pacific-Honshu convergence rates indicate that 1) the initiation of forearc subsidence and upper plate extension is coincident with a two to three fold increase in margin-perpendicular convergence, and 2) the onset of arc-normal shortening and increased frontal accretion occurred during a period of relatively constant convergence rate. The temporal correlation between deformation along upper plate faults, forearc subsidence, and lower plate convergence rates at the Northeast Japan margin suggests that the vertical motions of the forearc are likely governed by changes in lower plate kinematics. We hypothesize that an acceleration in plate convergence drives changes in slab geometry at shallow depths that allows for subsidence of the forearc, and suggest that a portion of the subsidence record previously interpreted as tectonic erosion instead reflects an upper plate response to plate boundary dynamics.

# Using Regional Moment Tensors to Constrain the Kinematics and Stress Evolution During the 2010-2012 Canterbury, New Zealand, Earthquake Sequence

**Matthew W. Herman**

Ph.D. Student, Pre-comps

**Advisor: Kevin P. Furlong**

Robert B. Herrmann, Saint Louis University

Harley Benz, National Earthquake Information Center, USGS

On September 3, 2010, a MW7.0 (USGS moment magnitude) earthquake ruptured a ~40 km long fault approximately 100 km southeast of the Alpine Fault across the Canterbury Plains in South Island, New Zealand. Since then, over 10,000 aftershocks, including three destructive ~MW6.0 earthquakes near Christchurch have been recorded (Geonet NZ). Prior to September 2010, there were no active tectonic structures visible at the surface or recorded earthquakes larger than ~MW4.5 in the general vicinity of the earthquake rupture. Here we treat the Canterbury earthquake and its aftershocks as an intraplate sequence and consider its behavior to reflect characteristics of intraplate earthquake systems. We determined source depths, moment magnitudes, and double-couple focal mechanisms for 144 earthquakes larger than MW3.7 in the Canterbury sequence using waveforms observed at GEONET stations in South Island, New Zealand. The majority (120) of these solutions have strike slip focal mechanisms, with right lateral slip on ENE trending fault planes or left lateral slip on SSE trending fault planes. Based on surface deformation and aftershock locations, we interpret these as dominantly right lateral. The remaining focal mechanisms mainly show reverse faulting, with the exception of only two normal faulting events. The strike slip segments of the Canterbury earthquake sequence have compatible orientations for slip in a stress field with horizontal  $\sigma_1$  oriented ~N115E, and horizontal  $\sigma_3$ . P- and T-axes determined from the double couple solutions are inferred to reflect the orientations of the stress field driving the events. Despite variations in slip direction and faulting style, and the occurrence of several large earthquake ruptures, these stress orientations remained unchanged throughout the Canterbury earthquake sequence (in both space and time). This implies that the regional state of stress has also remained unchanged throughout this sequence.

# **Permeability and Consolidation of sediments from the underlying accretionary prism in the Kumano Basin, SW Japan**

**Robert D. Valdez II**

Ph.D. Student, Pre-comps

**Advisor: Demian Saffer and Chris Marone**

Hiroko Kitajima, AIST, Tsukuba, Japan

Fluid pressures play an important role in the nature of faulting within subduction zones by modifying effective stress conditions. The role of permeability is important in controlling the magnitude of excess pore fluid pressure buildup resulting from compaction processes. We conducted uniaxial and triaxial consolidation experiments on six whole-round core samples in order to quantify the permeability and degree of consolidation. Specimens were collected during the drilling of site C0009A as part of the Integrated Oceanic Drilling Program (IODP) Expedition 319 from Nankai Trough Seismogenic Zone Experiment (NanTroSEIZE). The samples were chosen from the underlying accretionary prism cored by IODP in the Kumano Basin in order to (1) define mechanical and hydraulic properties of the sediments and (2) estimate the in-situ effective stress conditions.

Samples exhibited similar fluid flow properties with in-situ intrinsic permeability generally being  $<10^{-16} \text{m}^2$ , with values ranging from  $\sim 4.54 \times 10^{-17} \text{m}^2$  to  $2.53 \times 10^{-17} \text{m}^2$ . We used the work-stress and Casagrande method to find the pre-consolidation pressures ( $P_c$ ) for each sample. Using the pre-consolidation pressure and the in-situ stress calculated from the shipboard data, the overconsolidation ratios (OCR) of the samples were estimated. All of the CRS experiments gave an OCR  $> 1$  ranging from 1.02-1.60. These results reinforce the notion that Expedition 319 did in fact drill into the underlying accretionary prism and not just in the overlying Kumano basin sediment, something the drilling team was uncertain about at the time of drilling.

# **Estimates of Crustal Structure in Antarctica from S Waves Receiver Functions**

**Cristo Ramirez**

Ph.D. Student, Pre-comps

**Andrew Nyblade**

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In icecap regions, reverberations of the ice layer can mask the crust-mantle boundary P-to-S (Ps) conversion, and special modeling of the ice layer is necessary to properly analyze P-wave receiver functions. S-wave receiver functions (SRFs) that take advantage of S-to-P (Sp) conversions provide an alternative method for estimating crustal structure. We analyzed broadband seismic data from AGAP and Polenet icecap-sited stations in Antarctica. SRFs have been obtained from 22 stations in east Antarctica belonging to the AGAP/GAMSEIS network and 16 stations of west Antarctica from the ANET/POLENET network. Moho Sp arrivals are clearly seen at ~6-8 sec for the AGAP stations and at 3-4 sec for the ANET stations. The difference in Moho Sp arrival times between stations in east vs west Antarctica is indicative of previously reported differences in crustal thickness of 10-20 km between these two regions of the continent. Constraints from SRFs will be combined with Rayleigh wave phase and group velocities to invert for details of crustal Vs structure. Additional forward modeling and misfit analysis was conducted in the AGAP/GAMSEIS stations to more reliably determine crustal Vs structure.

# Assessing the Correlation between Dissolved Sulfide to Oxygen Ratios and the Abundance of a Sulfur Oxidizing Bacterium

**Leah Tsao**

Ph.D. Student, Pre-comps

**Advisor: Jennifer Macalady**

Irene Schaperdoth, The Pennsylvania State University

The Frasassi Caves in Italy are a hypogenic limestone cave system with sulfide entering from groundwater and oxygen entering from the cave atmosphere and downward percolating meteoric water. The presence of an electron donor, sulfide, and a terminal electron acceptor, oxygen, has allowed for a rich microbial ecosystem dominated by bacteria which oxidize hydrogen sulfide ( $\text{H}_2\text{S}$ ) to elemental sulfur ( $\text{S}^0$ ) or sulfate ( $\text{SO}_4^{2-}$ ), depending on sulfide and oxygen concentrations. Previous work showed that the niches of the most dominant bacteria within the cave are bound by dissolved sulfide to oxygen ratios. However, fluorescent in-situ hybridization results from this study show that the abundance of *Thiobacillus baregensis*, a widespread and abundant bacterial population, is not correlated with dissolved sulfide to oxygen ratios. Determining the factors which control the abundance of *T. baregensis* is important for understanding the accumulation of  $\text{S}^0$  used for anthropogenic applications, and whether or not microbial sulfide oxidation is the main factor contributing to karst corrosion.

# Oral Session One A: Rock Mechanics/Petrology

Saturday, March 16  
8:30-10:30, 114 EES

Time	Presenter	Advisor	Title
8:30	John Leeman	Chris Marone	Electrical Anomalies Observed During Failure in Granular Materials
8:45	Marco Scuderi	Chris Marone	Fluid Pressure and Effective Normal Stress During the Seismic Cycle of Stick-Slip Frictional Sliding
9:00	Mike Cleveland	Charles Ammon	Precise Relative Earthquake Location Using Surface Waves
9:15	Yunhui Tan	Terry Engelder	Characterization of Hydraulic Fracturing in the Marcellus Shale using Microseismic Data
9:30	Jennifer Alpern	Chris Marone	Experimental Analysis of the Effects of Fluid Properties on Hydraulic Fracture and Fracture Complexity
9:45	Alicia Cruz-Urbe	Maureen Feineman	Geodynamic kinetics: Metamorphic reaction rates and their application to subduction zone settings
10:00	TJ Deane	Maureen Feineman	$fO_2$ Control on Equilibrium Partitioning of Li between Mantle Minerals
10:15	Nick Hoschuh	Richard Alley	Inferring Bed Topography in West Antarctica through Ice Surface Inversion

# Electrical Anomalies Observed During Failure in Granular Materials

**John R. Leeman**

Ph.D. Student, Pre-comps

**Advisor: Chris Marone & Demain Saffer**

Marco Scuderi, Penn State University

Reported electromagnetic anomalies associated with earthquakes include electrical discharges known as earthquake lights, low frequency electromagnetic waves, and electrical resistivity changes in the rock surrounding the faults. Despite the number and variety of natural observations, the origin of electromagnetic anomalies and their connection to tectonic faulting is poorly understood.

We present data from double direct shear experiments on granular synthetic fault gouge (glass beads) in which the electrical potential difference between the gouge layers and system ground was monitored with a no-contact electrostatic voltmeter. Data were obtained for different humidity conditions, loading velocities, and particle size distributions. A normal stress of 4 MPa was maintained with load point velocities of 1, 30, and 100  $\mu\text{m/s}$ .

We find that electrical potential varies systematically during repetitive stick-slip frictional sliding. Voltages rise rapidly after shearing begins, peaking at potentials of up to several hundred volts as the material reaches a steady-state frictional behavior. Subsequently, the potential slowly relaxes as slip continues. Electrical anomalies associated with stick-slip events are superimposed on this long-term trend.

Upon a stick-slip event, electrical potential is observed to increase co-seismically at low shear strain, transitioning to co-seismic potential drops as shear strain increases. At slip velocities of 1-30  $\mu\text{m/s}$  potential changes are on the order of volts, increasing to tens of volts at shear velocity of 100  $\mu\text{m/s}$ . A positive correlation is also observed between co-seismic slip duration and potential change, with longer sliding times leading to higher charging rates. The change of the sign of electrical anomaly coincides approximately with attainment of steady-state mechanical (frictional) behavior.

The observed variations of electrical potential with slip velocity suggests that a triboelectric charging mechanism may be responsible for electronic transfer/expulsion. Dickinson *et al.* (1983) observed the emission of charged particles, excited neutrals, and photons from a solid during tensile fracture, a process referred to as fractoemission. A similar process may be occurring during granular failure, potentially explaining the observed dynamic surface charge.

# Fluid Pressure and Effective Normal Stress During the Seismic Cycle of Stick-Slip Frictional Sliding

**Marco Maria Scuderi**

Post comps

**Advisor: Chris Marone**

Carpenter B.M., Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma 1, Via di Vigna Murata 605, 00143 Roma, Italy

Many seismological observations have reported aseismic creep during the inter-seismic phase of the seismic cycle. However, the role that pore fluid pressure plays during creep (pre-seismic slip) and earthquake nucleation remains poorly understood. Dilation associated with aseismic creep may cause changes in mechanical and frictional properties of fault gouge, which may induce changes in pore fluid pressure and modify the stress state within the fault. Increases in pore pressure associated with compaction can reduce effective normal stress and destabilize slip or cause dynamic weakening and abet propagation of dynamic rupture. In order to investigate the evolution of pore fluid pressure during the pre- and co-seismic stages of the earthquake cycle, we performed laboratory experiments on synthetic fault gouge in the stick-slip regime. We sheared layers of soda-lime glass beads of known initial grain size (dia. 105-149  $\mu\text{m}$ ) in a double-direct shear configuration within a pressure vessel. Effective normal stress ( $\sigma'_n = \sigma_n - P_p$ ) was kept constant throughout the experiments at values of 5 and 10 MPa. Initial layer thickness was chosen as 5 mm for each  $\sigma'_n$ , and variations were monitored continuously via an on board displacement transducer across the sample assembly. Shear stress was applied via a constant displacement rate at the layer boundaries, and shearing velocity was increased stepwise from 1 to 300  $\mu\text{m/s}$ . Variations in pore fluid pressure and pore water volume during shearing were measured under undrained and drained conditions respectively. Our experiments under undraining loading conditions show that during a given stick-slip event, as shear stress builds, the creation of new pore space associated with gouge dilation causes a decrease in pore pressure. Upon stick-slip failure, the gouge compacts and pore pressure increases rapidly. We find that frictional strength and pore pressure evolution are intimately related with both initial applied stress and the hydrological state of the gouge layers. For undrained conditions at  $\sigma'_n = 5$  MPa, we document a decrease in pore fluid pressure with shearing, causing  $\sigma'_n$  to increase, hence resulting in dilatancy hardening and higher frictional strength compared to the drained case. On the other hand, at higher normal stress (10 MPa) undrained shearing results in a rise in pore pressure, which lowers frictional strength in comparison to the drained case. We find that the amount of pre-seismic dilation (i.e. increase in porosity) is bigger at  $\sigma'_n = 5$  MPa than at  $\sigma'_n = 10$  MPa, suggesting that elasto-plastic water-activated processes act at the grain junctions controlling the evolution of real area of contact during shear.

# Precise Relative Earthquake Location Using Surface Waves

**K Michael Cleveland**

Ph.D. Student, Post comps

**Charles J. Ammon**

Earthquake locations provide a fundamental tool for seismological investigations. While dense seismic networks can provide robust locations, accuracy and precision of these locations suffer outside dense networks. This is particularly true in offshore areas, where location analysis relies heavily on distant seismic observations. We present a method for estimating precise relative seismic source epicentroid locations using surface waves. Several reasons, including lower velocities and strength of the signal at distance, make use of surface waves for event location appealing. We focus on the Panama Fracture Zone region and relocate 81 strike-slip earthquakes to produce tectonically consistent epicentroid locations. The resulting pattern of earthquakes more clearly delineates recently active regional structures than original body-wave locations. The mean shift between the USGS NEIC epicenter and our epicentroids is about 14 km (the median is about 11 km), and typical origin time changes are generally less than  $\pm 2$  s. We find that north of  $6.5^\circ\text{N}$ , the plate boundary motion is split across two roughly north-south striking structures, the Panama and Balboa Fracture zones. For the last 36 years, slip along these two structures roughly matches slip along the Panama Fracture Zone to the south (from  $4.5^\circ\text{N}$  to  $6.25^\circ\text{N}$ ), but the Balboa Fracture zone has roughly three times the moment than the northern Panama Fracture Zone. Our analyses show that observed Rayleigh-wave signal-to-noise ratios for moderate-to-large shallow earthquakes are suitable for applying the procedure and that Rayleigh-wave observations form a self-consistent set of constraints on the relative location of earthquake centroids.

# Characterization of Hydraulic Fracturing in the Marcellus Shale using Microseismic Data

**Yunhui Tan**

Ph.D, pre-com and petroleum related

**Advisor: Terry Engelder**

Rongmao Zhou, Microseismic Inc.

Terry Engelder, Penn State University

Shawn Maxwell, Schlumberger

Mike Mueller, Microseismic Inc.

Mike Thornton, Microseismic Inc.

The objective of this study is to understand and characterize hydraulic fracturing at the Marcellus level through detailed analysis of microseismic events during hydraulic fracturing of four laterals drilled in southwest Pennsylvania. The technique for this analysis was the inversion and decomposition of the seismic moment tensor for the larger microseismic events. 34 out of the 50 largest events identified from a downhole linear array of Schlumberger accelerometers were processed by Microseismic Inc. using data from their surface array. Lower frequency and better spatial coverage made surface array data a better source for performing moment tensor inversion. Inversion was done based on a linear relationship between seismic moment tensor and P-wave first motion using a L2-norm inversion algorithm.

11 of the 34 events took place on subvertical plane with a subvertical slip vector. The average strike of the nodal planes from these subvertical events was N49°E. Some of these subvertical events had a relatively large volumetric component whereas other events were mainly double couple. Dip-slip motion is consistent with the majority of regional stress data from the eastern edge of the North American continental lithosphere. The subvertical orientation of these brittle fractures is most consistent with the J1 joint set populating black shale of the Appalachian Basin.

# **Experimental Analysis of the Effects of Fluid Properties on Hydraulic Fracture and Fracture Complexity**

**Jennifer Alpern**

M.S. Student

**Advisor: Chris Marone**

We investigate the optimal conditions for the development of an open, complex fracture network to increase hydrocarbon recovery through hydraulic fracture. Hydrocarbon recovery is potentially maximized with a complex fracture network of large surface area to volume ratio that penetrates the reservoir. The larger the surface area created by fractures in a finite space, the higher the capability of the system to recover hydrocarbons through the flow channels produced within the fracture network. To better understand how hydraulic fracture networks initially develop, we focus our study on fracturing transparent, homogenous cubes of Polymethyl methacrylate (PMMA) that contain model boreholes, and introducing a pore pressure to overpressurize the borehole at a controlled rate. By using fracture-driving fluids that have a large distribution of physical properties, we study how different fluid characteristics manipulate fracture development. We measure PMMA breakdown pressure, physical characteristics of resulting fractures, and how these results vary between fluid types and experimental conditions. Results show a correlation between fracture complexity and breakdown pressure as a result of the physical state of the fluid at the time of rupture. Further research extends these experimental methods to materials that contain natural bedding surfaces of different lithologies and levels of anisotropy.

# Geodynamic kinetics: Metamorphic reaction rates and their application to subduction zone settings

**Alicia Cruz-Uribe**

Ph.D. Student, Post comps

**Advisor: Maureen Feineman**

Thomas Zack, University of Gothenburg

The ability to quantify the rates at which metamorphic reactions occur is critical to assessing under what circumstances equilibrium thermodynamics are applicable to geologic problems in metamorphic settings. Here we investigate the kinetics of rutile replacement by titanite during amphibolite-facies overprinting of eclogite, garnet amphibolite, and anorthosite from Catalina Island, CA, the Tromsø nappe, Norway, the North Qaidam terrane, China, and the Guichicovi Complex, Mexico. Trace element concentration profiles across rutile rimmed by titanite, as determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), reveal Nb zoning in rutile that we interpret as the result of Nb back-diffusion into rutile from the rutile-titanite boundary.

We present new field-based reaction rates calculated from grain boundary velocities, which in turn were calculated using a 1-D diffusion model for Nb back-diffusion into rutile during titanite replacement over the temperature range 670 – 771° C. Our data are consistent with previous studies of field-based reaction rates for regional metamorphism, and suggest a relationship between net reaction rate ( $R_{\text{net}}$ , g/cm<sup>2</sup>/a) and temperature (° C) according to the following rate law:

$$\log R_{\text{net}} = 0.0077T - 12.1.$$

To consider the application of these reaction rates to prograde subduction zone settings, we model the extent to which reactions may go to completion within a dynamic subduction setting by combining reaction rates with thermal models of cold subduction zones. These models provide a context for examining the kinetic environment of a cold subducting slab and suggest that in order to create the assemblages found in subduction channels (e.g., blueschist, eclogite) and the corresponding dehydration reactions, either (1) grain sizes must be very small; for instance, on the order of 100 μm or less, or (2) the kinetic environment of the subduction channel is fundamentally different than in other regional metamorphic settings. If (2) is the case, we propose that the dynamic nature of subduction zones (high dT/dt) results in conditions that are far from equilibrium (large  $\Delta G_{\text{rxn}}$ ) and that reaction rates in these systems respond quickly in order to reach equilibrium. This would allow for the production of blueschist and other low temperature assemblages within the thermal and temporal constraints of cold subduction zones.

# **$fO_2$ Control on Equilibrium Partitioning of Li between Mantle Minerals**

**James A. Deane Jr.**

M.S. Student

**Advisor: Maureen Feineman**

The lithium isotope system holds great potential as a tracer of recycled subducted materials in the Earth's interior due to the striking isotopic contrast between lithium at the Earth's surface and that in the mantle. While it is convenient that Li is present in measurable quantities in mantle minerals, measurements of lithium isotope ratios in mantle xenoliths have proven difficult to interpret. Mantle xenolith data compiled from samples worldwide have revealed that lithium elemental and isotopic distribution between olivine and clinopyroxene is highly variable. At high temperatures such as those found in the mantle, the isotopic fractionation factor  $\alpha_{ol/cpx} [=(^{7}Li/^{6}Li)_{ol}/(^{7}Li/^{6}Li)_{cpx}]$  is expected to approach 1, and experimental constraints on equilibrium partitioning show that the partition coefficient ( $D_{ol/cpx}^{Li}$ ) is between 1.5-2. Many xenolith samples exhibit this equilibrium behavior with respect to both isotopic fractionation and equilibrium partitioning, but some samples do not. Xenoliths with apparent  $D_{ol/cpx}^{Li} < 1$  trend toward isotopically lighter Li in clinopyroxene relative to olivine, with  $\delta^7Li_{ol-cpx} [= \delta^7Li_{ol} - \delta^7Li_{cpx}]$  ranging from 3 - 25‰. A physical process explaining this relatively extreme isotopic fractionation between co-existing mantle phases has yet to be satisfactorily demonstrated. One proposed hypothesis to explain the apparent Li isotopic disequilibrium in mantle xenoliths is that upon exhumation, closed system redistribution of Li between mantle minerals occurs as a function of changing physical or chemical conditions, meaning the partition coefficient is dependent upon specific environmental conditions. Richter et al. (2003) have shown potential for considerable kinetic isotopic fractionation of Li during diffusion. Thus if Li is redistributed under dynamic conditions preceding or concurrent with eruption, kinetically driven isotopic fractionation might be "locked in" to the mantle minerals upon reaching closure conditions. Previous piston cylinder experiments have shown that the equilibrium partition coefficient is independent of temperature – removing cooling upon exhumation as a cause for this closed system Li redistribution. Mantle olivine contains some amount of iron (~10% FeO\*), and the ambient  $fO_2$  controls the relative amount of  $Fe^{+2}/Fe^{+3}$ . Variation in the amount of  $Fe^{+3}$  could potentially influence the incorporation of  $Li^+$  into the octahedral site of olivine by providing a charge-balancing mechanism potentially allowing for a redistribution and isotopic fractionation of Li in response to changing  $fO_2$ . We have developed a method of running piston cylinder experiments under prescribed and controlled  $fO_2$  conditions. Experiments at 900°C and 1.0 GPa with solid state  $fO_2$  buffers of Re-ReO<sub>2</sub>, Fayallite-Magnetite-Quartz, Magnetite-Wustite, and Mo-MoO<sub>2</sub> are currently underway to determine whether oxygen fugacity plays a role in controlling Li partitioning.

[1] Richter et al. (2003) *Geochimica et Cosmochimica Acta* **67**, 20, 3905–3923.

# Oral Session One B: Biogeochemistry

Saturday, March 16  
8:30-10:30, 116 EES

Time	Presenter	Advisor	Title
8:30	Laurence Bird	Katherine Freeman	Coenzyme F430, quantification and isotope analysis from the Eel River Basin California
8:45	Christine Doman	Katherine Freeman	Fire as a driver of C4 grassland evolution using polycyclic aromatic hydrocarbons as fire proxies
9:00	Elizabeth Denis	Katherine Freeman	A Fiery Investigation of the Paleocene-Eocene Thermal Maximum (PETM) using Polycyclic Aromatic Hydrocarbons (PAHs): Preliminary Results
9:15	Christy Grettenberger	Jennifer Macalady	Composition and Functional Diversity of Subsurface Microbial Communities at an Acid Mine Drainage Site
9:30	Amanda Martino	Christopher House	Microbiology of the Costa Rica Margin Subseafloor: Working Around Drilling-Induced Contamination in Deep Cores
9:45	Leah Brandt	Christopher House	Investigating the microbial diversity in the deep, hot biosphere of the Okinawa backarc basin
10:00	Ashlee Dere	Sue Brantley	A Tale of Two Shale Catchments
10:15	Heather Graham	Kate Freeman	Preservation of the Carbon Isotope “Canopy Effect” in Fossil Leaves and Sediments

# Coenzyme F430, quantification and isotope analysis from the Eel River Basin California

**Laurence Robert Bird**

Ph.D. Student, Pre-comps AND Petroleum related

**Katherine H. Freeman**

James M. Fulton, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

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Large amounts of methane are oxidized by communities of methanotrophic archaea and sulphate-reducing bacteria, preventing this greenhouse gas from reaching the atmosphere [1,2]. Methyl-coenzyme M reductase, an enzyme associated with methanogenesis, has recently been linked to the anaerobic oxidation of methane suggesting methane oxidation follows a pathway similar to reverse methanogenesis. Coenzyme F430, a tetrapyrrole-nickel complex within the active site of methyl-coenzyme M, is used in methanogenesis and is hypothesized to play a key role in archaeal methanotrophy [2].

We recently developed a method to extract and isolate F430 from natural sediments for carbon and nitrogen isotope analysis. Sediment samples are first extracted by sonicator probe in water (pH 7), then twice in formic acid (pH 3). An F430 containing fraction is isolated using Sephadex and Amberlite column chromatography. Further purification is performed using two dimensions of HPLC, first with a C-18 column followed by a Hypercarb column (ThermoFisher). F430 is then quantification using a diode array detector with fractions collected for isotope analysis via a nano-scale elemental analyzer isotope ratio mass spectrometer [3].

Here, we report F430 concentrations and isotopic data determined from active seep sediment cores from the Eel River Basin (California), a site where the anoxic oxidation of methane occurs. A spike in the concentration of F430 is observed at the 3-6 cm depth horizon of the core, which corresponds to peak abundance in ANME-2 aggregate counts. Carbon isotope values of F430 are significantly more enriched in  $^{13}\text{C}$  (-23‰ to -26‰) than published diphytanyl glycerol diether archaeal lipids and cell clusters. Our observations indicate F430 in this methanotrophic sediment is not uniquely associated with methanotrophs. However, the enriched signal reported here could also be due to another carbon source for the ANME in the sediment, which needs to be further explored.

[1]Orphan (2001) *Science* **293** 5529 484 [2]Scheller (2010) *Nature* **465** 7298 606 [3] Polissar (2009) *Analytical chemistry*, **81**

# **Fire as a driver of C4 grassland evolution using polycyclic aromatic hydrocarbons as fire proxies**

**Christine E. Doman**

Masters Student

**Advisor Katherine Freeman**

The C4 photosynthetic pathway existed for nearly fifteen million years before it came to dominate grassland ecosystems. These ecosystems emerged globally three to five million years ago indicating climatic or other environmental changes that made room for this new type of ecosystem. Past work on this subject has produced conflicting theories that taken as whole fail to adequately explain how this important biome emerged and what the environmental factors leading to the transition were. Modern C4 grasses thrive in warm, high light and semi-arid ecosystems. Paleoclimate data for North America indicate a shift to a cooler and wetter climate at the same time as the evolution of the C4 grass biome. The phylogeny of C4 grasses shows that many arose from shade-tolerant lineages despite their modern preference for sunny environments. To make sense of these contradictory climatic and evolutionary data we must consider other environmental factors that could have resulted in a shift to C4 dominated grasslands.

Fire plays an essential role in the maintenance of modern grasslands by preventing the establishment of woody plants. The workings of the modern ecosystem give clues to the functioning and development of their ancient counterparts. If fire is an integral part of modern grassland ecology then it is likely that it played a key role in its evolution as well. Keeley and Rundell (2005) present paleosol carbonate data that shows C4 expansion into wetter soils more frequently associated with wooded areas. The authors also compile charcoal data that shows evidence for fires at the same time as the expansion of C4 grasslands. In addition to these empirical data Scheiter et al. (2012) published an extensive model that shows fire's ability to open canopy and allow for the expansion of savannah like environments. More evidence is needed to link fires to the expansion of C4 grasslands. Charcoal records provide solid evidence for fire but they are notoriously incomplete and spatially limited. Other proxies have been developed using polycyclic aromatic hydrocarbons (PAH's) as markers of fire. A suite of PAHs only formed by fires can be analyzed to give information about approximately how hot the fire was and what was burning. Few studies have been done linking the charcoal record with the PAH record and even fewer have been done linking the charcoal and PAH records with historical records of fires. We have abundant samples at our disposal with which to test this method. Specially a set of Miocene paleosols from the Meade basin, KS, USA. Applying this technique to these well-studied time periods can provide new data on the evolution of C4 grasslands.

# **A Fiery Investigation of the Paleocene-Eocene Thermal Maximum (PETM) using Polycyclic Aromatic Hydrocarbons (PAHs): Preliminary Results**

**Elizabeth H. Denis**

Ph.D. Student, Pre-comps

**Advisor: Katherine H. Freeman**

Scott L. Wing, Department of Paleobiology, Smithsonian Institution, Washington, D.C.  
Bighorn Basin Coring Project (BBCP) Science Team

The Paleocene-Eocene Thermal Maximum (PETM) coincided with a global negative carbon isotope excursion, suggesting a massive perturbation to the global carbon cycle and a large release of  $^{13}\text{C}$ -depleted carbon to the atmosphere, oceans and biosphere. Several proposed sources of this carbon include ocean-floor methane clathrates, thermogenic methane, permafrost oxidation and burning of peat or shallowly buried coal, but the exact source(s) remain unknown. The Paleocene was a time of extensive terrestrial organic carbon burial and some authors have suggested that a change in climate induced burning of the  $^{13}\text{C}$ -depleted carbon deposits. In this study a diverse suite of polycyclic aromatic hydrocarbons (PAHs), organic compounds produced as aerosols during combustion, were characterized and quantified in order to investigate evidence for fire during the PETM. We sampled intervals of cores from Basin Substation, Bighorn Basin, Wyoming, USA, collected as part of the Bighorn Basin Coring Project (BBCP). PAHs were evaluated using gas chromatography-mass spectrometry (GC-MS) in selective ion monitoring (SIM) mode. We found a range of two- to seven-ring PAHs from naphthalene to coronene. For all samples the abundances of individual PAHs range from 0.1 – 100 ng/g dry sediment. Total PAH abundance (sum of 16 PAHs) is reduced in samples from the body of the PETM carbon isotope excursion relative to samples from the latest Paleocene (300 ng/g and 40 ng/g, respectively), although there is a spike in total PAH concentration (2300 ng/g) before the onset of the PETM. The stratigraphic pattern of PAH abundance is consistent with a peak in wildfires before the onset of the PETM, followed by a decrease in the body of the PETM, but also may reflect decreased preservation of organic matter during the hotter and more seasonally dry climate that this region experienced during the PETM. The latter explanation is consistent with a general decrease in organic matter preservation during the PETM interval in this core. Higher relative abundance of high molecular weight PAHs in PETM samples suggests hotter fire temperatures at that time, regardless of fire occurrence. A literal interpretation of the PAH record from the Basin Substation core would suggest more intense burns but less wildfire activity during the PETM, but the effect of changes in organic matter preservation must be eliminated before this interpretation can be accepted.

# **Composition and Functional Diversity of Subsurface Microbial Communities at an Acid Mine Drainage Site**

**Christy Grettenberger**  
Ph.D. Student, Pre-comps

**Advisor: Jennifer Macalady**

Lance Larson, Department of Environmental Engineering, The Pennsylvania State University  
Bill Burgos, Department of Environmental Engineering, The Pennsylvania State University

Acid mine drainage (AMD) is “the most important and widespread industry related pollution problem.” (California Mining Water Study, 1988). The northern Appalachian Plateau in the eastern United States has widespread damage with 8,000 km of streams polluted by AMD. Biological passive treatment using acidophilic bacteria is a promising alternative to the traditional treatment systems. Toward this end, many studies have examined surface microbial communities at AMD sites. However, few have examined the role subsurface communities play in biogeochemical cycling at these sites. In order to develop efficient biological treatment systems it is necessary to understand the role of both surface and subsurface microbial communities.

Brubaker Run is a highly acidic, metal laden stream located near Ashville, PA. The majority of water at this site follows subsurface paths. Therefore, the evolution of water chemistry downstream is affected by both surface and subsurface microbial communities. Understanding the roles microbes are playing in the subsurface, and how it differs from surface communities is extremely important in understanding the system as a whole. We investigated the microbial community composition, functional diversity, and metabolic potential of surface and subsurface microbial communities using 16S clone libraries and GeoChip gene assays. A total of five samples have been investigated using 16S clone libraries. Forty-two samples were investigated with Geochip gene assays. Preliminary results suggests that surface microbial communities are distinct when compared to subsurface communities. This suggests they may differ in their metabolic potential and, therefore, in their influence on AMD water chemistry.

# **Microbiology of the Costa Rica Margin Subseafloor: Working Around Drilling-Induced Contamination in Deep Cores**

**Amanda Martino**

Ph.D. Student, Post comps

**Advisor: Christopher House**

The deep subsurface biosphere represents a frontier for the discovery of new life, and for investigations of the extent, versatility and perseverance of life on earth. Ocean drilling programs, as well as other types of oceanographic expeditions, have yielded many successful studies of deeply buried microbes. To date, however, most microbiology work in marine subsurface sediments has been focused in the upper 100-200 meters of sediment. This is because the switchover from advanced piston coring to extended core barrel coring generally occurs around this depth, which leads to large increases in drilling-induced contamination. Molecular studies in deeper samples are greatly hindered by interference from these contaminating microbes. Here I have utilized a strategy of separating sequence information originating from drill-fluid contamination, from that which represents the indigenous microbial communities of the sediments. Deep 16S rRNA sequencing using next-generation sequencing technology has permitted a characterization of both sediment microbial communities and drilling-fluid communities that is thorough enough to confidently show the differences in both communities. Examination of the results suggest that sequences originating from drilling fluid may be only a minor portion of the data obtained from even the deepest XCB cores examined, and that due to the greatly different community composition of the drilling fluid, it should be possible to at least some extent to subtract out contaminating lineages from the analysis. In collecting this data, I will also show an extensive community composition analysis of 9 samples from each of two sites on the Costa Rica Margin, which has not been explored for microbiology to date.

# Investigating the microbial diversity in the deep, hot biosphere of the Okinawa backarc basin

**Leah D. Brandt**

Ph.D. Student, Pre-comps

**Advisor: Christopher House**

The IODP Expedition 331 to the Okinawa backarc basin provided a unique opportunity to study the deep, hot subvent biosphere—the subsurface environment surrounding an active vent hypothesized to host an active microbial ecosystem despite the high temperature hydrothermal conditions. The sediment profile is not only influenced by laterally migrating hydrothermal fluid, but is also geographically located within a continental margin setting. Site C0014 in the Iheya North Field has a low surface temperature (5°C) and a temperature gradient of ~3°C/m. Analyzing DNA from sediment horizons with depth has the potential to reveal new and interesting information regarding how microbial communities either shift toward better-adapted organisms (*e.g.* thermophiles), or adapt to the increasing hydrothermal conditions. DNA has been extracted, amplified, and sequenced from the top 45 meters; however, shipboard and land-based biogeochemical data indicate that the habitable biosphere occurs above a caprock layer (top ~10 m), which may have protected the upper sediments from an inundation of hydrothermal fluid. Further RNA analyses will be used to identify the active microbial community members within the subvent biosphere and determine the horizon at which life can no longer survive.

# **A Tale of Two Shale Catchments**

**Ashlee Laura Denton Dere**

Ph.D. Student, Post comps

**Advisor: Sue Brantley and Tim White**

Elizabeth Herndon, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Brian Reynolds, Centre for Ecology and Hydrology, Wales, United Kingdom

In an effort to quantify the influence of climate on shale weathering rates, a transect of study sites has been established on Silurian shales along a climatic gradient in the northern hemisphere. One site is the Susquehanna Shale Hills Critical Zone Observatory (SSHO), a 9 ha first-order catchment in central Pennsylvania dominated by mixed deciduous forest. This catchment has been monitored since the 1970s, including weekly stream and precipitation chemistry since 2007. The most northerly site of this transect is the Hafren catchment in the headwaters of the River Severn, at Plynlimon, Wales, UK. This 357 ha catchment is 70% covered by Sitka spruce plantation forestry and has been extensively studied with continuous measurements of precipitation and runoff since 1968 and weekly monitoring of rain and stream water chemistry since 1983. Both catchments are underlain by the same iron-rich, organic-poor Silurian shale and provide abundant stream chemistry and discharge data to compare shale weathering processes in two different catchments.

At SSHO and Plynlimon, major rock-derived elements in the stream, including Na, K and Mg, show chemostatic behavior such that elemental concentrations remain constant with increasing discharge. Other elements, including Mn, Al (Plynlimon), Fe (SSHO) and dissolved organic carbon (DOC), exhibit non-chemostatic behavior, with concentrations increasing then decreasing with higher discharge. Finally, Ca and Si (Plynlimon) show dilution behavior where concentration decreases with increasing discharge. This spectrum of behavior, ranging from dilution to chemostatic, suggests there are organically-controlled (Mn, Al, Fe) and nonorganically-controlled (Na, K, Mg, Ca, Si) weathering-derived species in these catchments. However, the spatial distribution of the organic matter that is driving the organically-controlled weathering differs between the two catchments, resulting in different elemental loads under different discharge conditions. At SSHO, stream chemistry contains relatively high DOC during low flow, when organic-rich swales are contributing water to the stream and there is little contribution of water from other parts of the catchment. The opposite is true at Plynlimon, however, where the stream chemistry is DOC-rich at high flow when peat at the top of the catchment is contributing water to the stream. The observation that elemental behavior is driven by the presence and distribution of organic matter in both catchments will help us understand hydrologic connectivity in the catchments and lead to better quantification of weathering in shale catchments.

# Preservation of the Carbon Isotope “Canopy Effect” in Fossil Leaves and Sediments

**Heather Graham**

Ph.D. Student, Post comps

**Advisor: Kate Freeman**

Mark Patzkowsky, Pennsylvania State University

Scott Wing, Smithsonian Institution

Paleoecologists and paleoclimatologists alike are interested in the geological history of closed-canopy forests because of their evolutionary and climatic significance. In order to develop chemical tools for inferring closed-canopy forests in the geological record we have studied the relationships among foliar carbon isotope compositions ( $\delta^{13}\text{C}$ ), litter flux, and leaf-wax properties in the context of environmental gradients (light, moisture,  $\text{CO}_2$ ) within extant forest canopies.

A survey of leaves in an extant tropical closed-canopy forest exhibits a greater range of vertical isotopic enrichment (10‰), or “canopy effect”, when compared with a similarly sampled temperate open-canopy forest (~6‰). We used these data and a statistical resampling (bootstrap) method to form expectations for isotopic variation in fossil leaf assemblages and sediments that form in different forest types. According to this model, there is a robust likelihood of identifying canopy closure by isotopic analysis of as few as 50 fossil leaves selected randomly. We test this by analyzing the bulk carbon isotope composition of 210 fossil leaves from three fossil localities. The sampled assemblages date from the Maastrichtian through the Middle and Late Paleocene. Family-level community identification of these flora suggests that two are from a closed-canopy forest and one is an open-canopy. The range of carbon isotope expression in these leaves confirms the closed-canopy signature of one Paleocene forest and the open-canopy signature of the oldest forest.

By sampling many thousands of leaves, our model estimates the influence of leaf biomass on organic matter in ancient soils and other terrestrial archives. The model predicts that soil organic matter arising from leaf material in a tropical closed-canopy will be ~1‰ more depleted than in a temperate open-canopy forest. Modeled closed-canopy litter coincides with observed  $\delta^{13}\text{C}$  values for litterfall and humic soils in the tropical forest. Therefore, in addition to analyzing fossil leaves we also analyze the bulk carbon isotope composition of their rock matrix. Organic carbon preserved in the rock matrix can be analogous to the soil organic carbon that forms in soils but it will also represent the non-leaf carbon inputs as well as the fractionation of organic material during degradation. By comparing the isotopic range of the fossil leaves and the isotopic composition of the fossil matrix we can better understand the influence of leaf flux from various forest canopy types on the organic sedimentary record.

# Oral Session Two: Paleobiology

Saturday, March 16  
11:00-11:45, 114 EES

<b>Time</b>	<b>Presenter</b>	<b>Advisor</b>	<b>Title</b>
11:00	Lauren Milideo	Russ Graham	Taphonomic Differences Between Fox and Wolf Dens
11:15	Jon Scheuth	Tim Bralower	Modeling the Uncertainty of True Origination and Extinction Time in the Nannofossil Record
11:30	Michael Donovan	Peter Wilf	Novel insect leaf mining at Mexican Hat, Montana (early Paleocene) and the demise of Cretaceous leaf miners

# Taphonomic Differences Between Fox and Wolf Dens

**Lauren Milideo**

Ph.D. Student, Post comps

**Russ Graham**

Russ Graham, Penn State University

Interpretation of paleontological sites is dependent upon understanding the ways in which bone accumulations form. Workers wishing to extract paleoecological information from fossil bone assemblages must first determine the temporal and spatial scales that they represent (Behrensmeyer, 1978; Shipman, 1981). For example, the degree of time-averaging may indicate the temporal precision of paleoecological information contained in an assemblage (Behrensmeyer 1978). Many taphonomic processes, including transport of partial or complete carcasses, bone weathering, or density-mediated bone destruction, all may remove elements from the original bone assemblage, yielding fossil materials that may reflect their ecosystem only in part (Shipman 1981, Behrensmeyer, 1978). Site formation processes are therefore an essential component of a rigorous understanding of vertebrate assemblages and subsequent paleoecological study.

Modern dens, including hyena den sites have been studied as possible proxies for fossil bone accumulation localities (Kuhn, 2005). Here, we present a comparison of fox (*Vulpes vulpes*) and wolf (*Canis lupus*) den assemblages from Nunavut, Canada. We statistically compare bone damage (particularly processes reflecting carnivore consumption), bone weathering, and the identities and quantities of elements and taxa present. Additionally, we employ GIS software to examine differences in spatial statistical patterns. This study, part of a larger ongoing actualistic taphonomic project, has identified several patterns in the taphonomy of these different den types. These include divergence in taxa types and sizes present, as well as spatial differences between the bone distributions at each den. Such data will aid interpretations of fossil localities, yielding a means of understanding the processes in effect, and accounting for the taphonomic alterations that these processes create.

Behrensmeyer, A.K., 1978. Taphonomic and Ecologic Information from Bone Weathering. *Paleobiology* 4 (2): 150-162.

Kuhn, B., 2005. The Faunal Assemblage and Taphonomic Signatures of Five Striped Hyena (*Hyaena hyaena syriaca*) Dens in the Desert of Eastern Jordan. *Levant* 37: 221-234.

Shipman, P., 1981. Life history of a fossil: an introduction to taphonomy and paleoecology. Harvard University Press. 222 pages.

# **Modeling the Uncertainty of True Origination and Extinction Time in the Nannofossil Record**

**Jon Schueth**

Ph.D. Student, Post comps

**Advisor: Tim Bralower**

Klaus Keller, Mark Patzkowsky

All species are very rare close to their true times of origination or extinction. This makes these rare species more likely to avoid preservation and evade detection by a paleontologist. Preservation can vary significantly between environments or locations, and there is observational error present in all paleontological data. Paleontologists therefore can often misinterpret patterns in first/last occurrences between locations. It is possible that an observed globally synchronous evolutionary event or extinction may be only representing chance differences or variation in preservation. We have developed a new method to account for these errors that combines paleontology with the statistical approaches used in building climate model uncertainty. This method uses a model of the preservation and detection processes that lead from original abundance of a species in its environment to detection by a paleontologist. The model is completely parameterized on experimental data to eliminate the use of assumptions that many other methods are required to make. Monte Carlo simulations of the model are used to determine the total range in uncertainty in the relationship between original and detected abundance. The model is then inverted with nannofossil count abundance data and the Monte Carlo results to determine the total estimate of uncertainty for the original abundance of the species through time. With the original abundance estimate, we then build a probability density function for the original time of first or last appearance. This resulting probability density function is then used to compare the timing of origination or extinction between locations. Our modeled uncertainty approach provides a reliable and fairly simple way to separate between-site differences in preservation and paleontological counting errors from true evolutionary or biological events. It addresses a significant paleontological problem in a new way and also eliminates many assumptions that are made or required in other techniques. While we developed this method with nannofossils it should be simple to modify it for any type of fossil data.

# Novel insect leaf mining at Mexican Hat, Montana (early Paleocene) and the demise of Cretaceous leaf miners

**Mike Donovan**

M.S. Student

**Advisor: Peter Wilf**

Conrad Labandeira, Smithsonian National Museum of Natural History

Kirk Johnson, Smithsonian National Museum of Natural History

Plant and associated insect-damage diversity in the western U.S.A. decreased significantly at the Cretaceous-Paleogene (K-Pg) boundary. However, Mexican Hat, a fossil plant locality in southeastern Montana with a typical, low-diversity "disaster flora," uniquely exhibits high damage diversity compared to more than 100 other Paleocene sites. The locality is part of the Lebo Member of the Fort Union Formation ( $^{40}\text{Ar}/^{39}\text{Ar}$  ages ca. 64.0-64.7 Ma), and the flora is dominated by four widespread species that show minimal damage elsewhere: *Platanus raynoldsii*, *Juglandiphyllites glabra*, *Zizyphoides flabella*, and *Cercidiphyllum genatrix*. We tested whether the high insect damage diversity at Mexican Hat was related to the survival of Cretaceous insects from refugia or an influx of novel Paleocene taxa by comparing damage from Mexican Hat to that in the terminal Cretaceous Hell Creek flora from nearby southwestern North Dakota. Over 9000 Hell Creek leaf fossils were observed for insect damage to analyze potential links with Cretaceous insects, and a supporting data set of over 9000 early and late Paleocene leaf fossils from the Fort Union Formation of North Dakota, Montana, and Wyoming was also observed for comparison with local and regional post-extinction floras. We focused on leaf mines because they are typically host-specialized and preserve a number of morphological features on compression fossils, including oviposition site, variation in length and width, and frass characteristics that allow for detailed comparisons and potential identification of mining culprits. We also assessed whether plant families that crossed the K-Pg boundary provided refuge for Cretaceous insects by comparing damage on Cretaceous species of Platanaceae and Cercidiphyllaceae to damage on *P. raynoldsii* and *C. genatrix*. Eight mine morphotypes from three orders of insects are found at Mexican Hat and are all unique to the site except for one, a lepidopteran mine also found on *C. genatrix* at late Paleocene Wyoming sites. Mines unique to *P. raynoldsii* at Mexican Hat include sawfly, microlepidopteran moth, and agromyzid fly mines, and one microlepidopteran mine is unique to *C. genatrix*. None of the mines found on Cretaceous Platanaceae or Cercidiphyllaceae are found at Mexican Hat or other local or regional Paleocene localities, suggesting that these plant families did not provide a refuge for Cretaceous leaf miners. There is no evidence linking any Cretaceous mines with those found at Mexican Hat, and no conclusive evidence for the survival of any Cretaceous leaf mines over the K-Pg boundary regionally. Overall, comparisons to Hell Creek insect damage more strongly supports the high damage diversity on the depauperate Mexican Hat flora as being caused by an influx of novel insect herbivores during the Paleocene, and drastic extinction rather than survivorship of Cretaceous insect taxa from refugia.

# Oral Session Three: Isotope Geochemistry

Saturday, March 16  
12:45-2:45, 114 EES

<b>Time</b>	<b>Presenter</b>	<b>Advisor</b>	<b>Title</b>
12:45	Matt Gonzales	Matthew Fantle	Exploring the Presence and Influence of Precursor Mineral Phases on the Final Ca Isotopic Composition of Calcium Carbonates
1:00	Andrew Chorney	Hiroshi Ohmoto	Anomalous isotope fractionation of sulfur (AIF-S) during thermochemical sulfate reduction by solid organic matter
1:15	Angela Chung	Katherine Freeman	The relationship between sedimentary processes and organic matter preservation: Studying the PETM
1:30	Ying Cui	Lee Kump	Initial assessment on the carbon emission rate and climatic consequences during the Permian-Triassic mass extinction
1:45	Jason Boettger	James Kubicki	CO <sub>2</sub> hydration: The origin of carbonate kinetic isotope effects
2:00	Heather Tollerud	Matt Fantle	The temporal development of surface roughness and its relationship with evaporite mineralogy and water in a playa dust source
2:15	Paul Grieve	Susan Brantley	Contamination in private water wells related to Marcellus Shale drilling
2:30	Anna Wendt	Mike Arthur	Geochemistry of the Union Springs Member of the Marcellus Formation

# Exploring the Presence and Influence of Precursor Mineral Phases on the Final Ca Isotopic Composition of Calcium Carbonates

**Matthew Scott Gonzales**  
M.S. Student

**Advisor: Matthew Fantle**

Over the past decade the Ca isotopic compositions of calcium carbonate ( $\text{CaCO}_3$ ) minerals such as calcite have become popular proxies for global weathering fluxes, changes in ocean chemistry, and climate on million year timescales. Despite this use of the Ca isotope system, the manner in which the geochemical signals are stored in  $\text{CaCO}_3$  remains poorly understood. Without sufficient knowledge of these mechanisms, geochemical records can be misinterpreted. Experimental calcite precipitation studies have shown that the Ca isotope fractionation factor is susceptible to kinetic effects such that it scales with the mineral precipitation rate. However, these experiments have yielded opposing trends such that the fractionation factor increases with precipitation rate in one set of experiments while it decreases in another set. This suggests that precipitation rate is not the dominant control on the Ca isotope fractionation factor.

The work presented here is designed to investigate why there are two trends in the relationship between Ca isotope fractionation and precipitation rate. One possibility is that experiments which produce calcite that is less fractionated at higher precipitation rates tend to precipitate  $\text{CaCO}_3$  from more saturated solutions. Higher saturation states may give rise to alternative precursor phases which partition Ca isotopes differently than calcite. In particular, it is thought that amorphous calcium carbonate (ACC) is more prominent in the early stage of precipitation or crystalline phases such as vaterite form initially which later give way to calcite. Using x-ray diffraction and optical microscopy, the development and persistence of non-calcite carbonates is observed in batch reactions where  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  solutions are mixed in varying degrees of supersaturation similar to those observed in previous Ca isotope studies. Thus far, it has been observed that amorphous materials, likely ACC, with regular dendritic macrostructure, forms initially which quickly coalesces into bulbous spherical masses. A small amount of calcite crystals also form initially which continue to grow in volume over the course of several weeks. These observations suggest that calcite formation may be preceded by other carbonate phases that could impart a unique isotopic signature onto a mature calcite crystal.

# Anomalous isotope fractionation of sulfur (AIF-S) during thermochemical sulfate reduction by solid organic matter

**Andrew Chorney**

M.S. Student

**Advisor: Hiroshi Ohmoto**

Yumiko Watanabe, Penn State University

AIF-S is defined by  $\Delta^{33}\text{S}$  ( $=\delta^{33}\text{S} - .515*\delta^{34}\text{S}$ ) and  $\Delta^{36}\text{S}$  ( $=\delta^{36}\text{S} - 1.89*\delta^{34}\text{S}$ ) values having greater than  $\pm 0.2$  and  $\pm 0.4\%$ , respectively. Many researchers believe that the AIF-S signatures observed in Archean age rocks were created by the photolysis of volcanic  $\text{SO}_2$  gas by UV light in an oxygen poor atmosphere. However, recognizing that the samples with large  $\Delta^{33}\text{S}$  values are typically kerogen- and pyrite-rich black shales that were deposited during times of large scale hydrothermal activity, some researchers suggested the possibility that the AIF-S signatures were created during high-temperature fluid-organic-mineral reactions in sediments. This suggestion was supported by the results of thermochemical sulfate reduction (TSR) experiments with glycine and alanine by Watanabe et al. (2009) and Oduro et al. (2011). They found that while alanine did not produce significant AIF-S signatures, glycine was able to produce  $\text{H}_2\text{S}_{(\text{g})}$  with  $\Delta^{33}\text{S}$  values between 0 and  $+1.2\%$  and  $\Delta^{36}\text{S}$  values between  $-1.26$  and  $1.06\%$  and organic-bound S  $\Delta^{33}\text{S}$  values between 0 and  $13\%$  and  $\Delta^{36}\text{S}$  values between  $-1$  and  $.1\%$ .

We have conducted additional TSR experiments using a mixture of alanine and glycine and  $\text{Na}_2\text{SO}_4$ , and also using simple amino acids and sulfuric acid. We have found a significantly increased range of AIF-S in  $\text{H}_2\text{S}$  from experiments with the glycine and alanine mixture ( $\delta^{34}\text{S} = -10.6$  to  $+15.5$ ,  $\Delta^{33}\text{S} = +.5$  to  $+2.3$ ,  $\Delta^{36}\text{S} = +.4$  to  $+1.4$ ). These data suggest that high temperature polymerization reactions of simple organic matter have played an important role in creating the AIF-S signatures in Archean sedimentary rocks. Variations in the  $\Delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values among the volatile-S, organic-bound S, and residual  $\text{SO}_4^{2-}$  measured in experiments using amino acids and sulfuric acid appear to depend on the degree of polymerization/dehydration of the organic matter, which affect its surface characteristics.

Our experimental data, as well as the recent findings of distinct AIF-S signatures in Phanerozoic-age sedimentary rocks in natural gas fields (Bontagnali et al., 2012) provide strong evidence that most (if not) all AIF-S signatures in geologic samples were generated by TSR, rather than by atmospheric UV reactions.

Watanabe et al. (2009) *Science* 324, 370-373.

Oduro et al. (2011) *Proceeding National Academy of Science* 108, 17635-17638.

Bontagnali et al. (2012) *Proceeding National Academy of Science* 109, 15146-15151

# The relationship between sedimentary processes and organic matter preservation: Studying the PETM

**Angela Chung**

M.S. Student

**Advisor: Katherine Freeman**

Elizabeth Hajek, Department of Geosciences, Pennsylvania State University

Preliminary total organic carbon content (TOC) and organic carbon isotope values from paleosols in the Wasatch Formation are reported. The Wasatch Formation of Piceance Creek Basin, Colorado, represents Paleocene and early Eocene deposition. The global warming event during the Paleocene-Eocene transition (PETM) is marked with a negative carbon isotope excursion. This investigation seeks to delineate that record for terrestrial organic carbon and establish a relationship between sedimentary processes and organic carbon preservation.

Preservation of organic carbon strongly influences the carbon isotope record, which is used in paleoenvironment studies. Well-preserved organic carbon lends reliable isotope readings. It is therefore imperative to understand the factors affecting preservation. Organic matter that eludes decomposition is buried and preserved in sediments. Previous studies have investigated factors influencing preservation in the marine realm. The debate for marine sediments revolves around the amount of oxygen exposure. However, there is little headway on the organic carbon subject in the terrestrial setting.

To study organic carbon degradation on land, this research looks at channel deposits and paleosols of the Wasatch Formation. How the TOC and carbon isotope values of these samples correspond to grain size and paleosol development is the main focus. Looking at the basin deposits further investigates how organic matter attenuates through time. Mechanisms of sediment deposition play a role in how sediments are preserved. On land ancient alluvial basins provide continuous records in sediments. In alluvial basin filling avulsion is a dominant depositional processes (Jones and Hajek, 2007). Avulsion is the rapid shift of a river from an old channel to a newly formed one (Slingerland and Smith, 2004). Studying this particular sedimentary process will help gain insight into how sediments are deposited and how it affects the organic carbon record. This study aims to construct a spatial and temporal relationship of organic carbon isotopes and depositional environment.

## References

- Jones H. L. and Hajek E. A. (2007) Characterizing avulsion stratigraphy in ancient alluvial deposits. *Sedimentary Geology* **202**, 124-137.
- Slingerland R. and Smith N. D. (2004) River avulsions and their deposits. *Annual Review of Earth and Planetary Sciences*. **32**. 257-285.

# **Initial assessment on the carbon emission rate and climatic consequences during the Permian-Triassic mass extinction**

**Ying Cui**

Ph.D. Student, Post comps

**Advisor: Lee Kump**

Andy Ridgwell, University of Bristol

Numerous lines of geochemical and stable isotopic evidence indicate that the end-Permian mass extinction is tied to abrupt climate change induced by CO<sub>2</sub> addition. Catastrophic end-Permian Siberian volcanism may have released large amount of CO<sub>2</sub> into the atmosphere and pushed the Earth's system beyond a critical threshold, causing the mass extinction. However, the injection rate, total amount and source of CO<sub>2</sub> are largely unknown. We conducted a suite of simulations using the newly published carbon isotope records and U-Pb age from Meishan section in Zhejiang province, China. An Earth System Model of Intermediate Complexity (EMIC) (Genie-1; <http://www.genie.ac.uk>) was used to extract the pattern of CO<sub>2</sub> release needed to replicate the observed carbon isotope excursion across the Permian-Triassic boundary. This analysis leads us to suggest that the source of CO<sub>2</sub> must have been significantly heavier than typical biogenic or thermogenic methane to explain the significant warming that occurred during and after the extinction event. As with the Paleocene-Eocene Thermal Maximum, end-Permian rates of CO<sub>2</sub> addition are small compared with modern fossil-fuel burning, but considerably more protracted, such that the likely total CO<sub>2</sub> emitted significantly exceeded the modern fossil-fuel reserves.

# CO<sub>2</sub> hydration: The origin of carbonate kinetic isotope effects

**Jason Boettger**

Ph.D. Student, Pre-comps

**Advisor: James Kubicki**

Paleoclimate proxies based on isotopic fractionation in biogenic calcium carbonate minerals constrain paleotemperatures and aid in assessments of the current rate of anthropogenic global warming. Corals and some other calcifiers tend to display  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  at isotopic disequilibrium with surrounding waters (so-called “vital effects”), introducing potential errors to paleoproxies. Some research attributes vital effects to slow isotopic exchange during the hydration reaction between CO<sub>2</sub> and H<sub>2</sub>O to form H<sub>2</sub>CO<sub>3</sub> in the semipermeable membrane-bound calcifying space (the “kinetic” vital effect model). Unfortunately, it is difficult to experimentally observe reaction rate as a function of isotopologue, preventing accurate evaluation of the potential magnitude of the kinetic vital effect in calcifiers.

We present atomistic, *ab initio* simulations to elucidate the potential contribution of kinetic vital effects to non-equilibrium C and O isotope fractionation in the skeletons of calcifying organisms. The model utilizes density functional theory and transition state theory to evaluate isotopologue-specific reaction rates for CO<sub>2</sub> hydration. Model accuracy is tested against experimental, non-isotopologue-specific reaction rates and against equilibrium fractionation factors using both forward and reverse reactions. More accurate results are obtained when using more H<sub>2</sub>O molecules in the hydration shell surrounding CO<sub>2</sub>, as the hydration reaction involves proton transfer and H bonding between several water molecules. These *ab initio* models will show whether or not the kinetics of hydration and hydroxylation reactions can account for vital effects in calcifiers, or whether other models are necessary to account for non-equilibrium fractionation.

# **The temporal development of surface roughness and its relationship with evaporite mineralogy and water in a playa dust source**

**Heather Tollerud**

Ph.D. Student, Post comps

**Advisor: Matt Fantle**

To model the role of dust in the Earth system and in geochemical cycles, it is critical to understand fundamental controls on dust emission in dust source areas. Surface properties such as roughness and surface strength affect dust emission by changing the erodibility of the surface. Accordingly, knowledge of temporal controls on surface properties is important. In this study, we investigate the temporal evolution of a playa dust source (the Black Rock Desert, NV, USA) over seven years to elucidate the effects of water on surface roughness. We compare the observations in the natural system to simple lab experiments simulating the development of surface roughness in the playa to improve our understanding of the processes controlling soil erodibility.

The effect of mineralogical composition on soil erodibility in playas is not well understood. To test the hypothesis that the presence of evaporite minerals in playa surface crusts reduces the availability of ablatable particles by smoothing the surface, we performed lab experiments. Semi-quantitative X-ray diffraction analysis of surface sediments from the Black Rock Desert demonstrates that the mineralogical composition by weight of the playa is ~30% quartz, 45% clay, 10% calcite, and 5%; thus we used a mixture of quartz and clay for our experiments, and added a solution with dissolved halite (5 wt%) and calcite (10 wt%) to simulate evaporites. Changes over time in the surface area of the experimental surfaces with and without evaporites were quantified in 2D using an optical profilometer (Zygo NV7300). Over 8 wetting-drying cycles, surface area increased in both evaporite (7% increase) and non-evaporite (16% increase) surfaces, but the evaporite surface had less surface area initially and experienced a slower increase. Additionally, RMS roughness increased over time, suggesting that wetting-drying cycles disrupt the playa surface, increasing surface roughness.

In dynamic playa systems, we hypothesize that inundation by surface water is critical to surface development. To evaluate this hypothesis, we utilize radar backscatter data (ESA Advanced Synthetic Aperture Radar (ASAR) instrument) to characterize centimeter scale surface roughness and its evolution over time. Radar data from 65 images between 2004 and 2010 are compared to inundation maps derived from 472 MODIS images (1640 nm, band 6) from the seasons preceding the ASAR images. Regions of the playa that dry after May exhibit systematically increased backscatter (-13.3 dB to -11.6 dB,  $p < 10^{-5}$ ). One potential explanation is that late drying areas dry more quickly, and thus have the potential to undergo more rewetting, and wetting-drying cycles, increasing surface disruption.

# **Contamination in private water wells related to Marcellus Shale drilling**

**Paul Grieve**  
M.S. Student

**Advisor: Susan Brantley**

Garth Llewellyn, Appalachia Hydrogeologic and Environmental Consulting, Inc.  
Todd Sowers, Penn State University  
Frank Dorman, Penn State University

The rapid pace of Marcellus shale gas development in the northeastern United States has prompted many scientists to seek a better understanding of potential impacts from drilling. In Bradford County, Pa several homes have had their well water contaminated possibly as a result of drilling in the area. Samples were collected from three neighboring houses that all had reported disturbances in their water supply. Samples were analyzed for methane concentrations and their corresponding isotopes values. The samples showed high concentrations of methane and  $\delta^{13}\text{CH}_4$  isotope values similar to those of methane gas from Middle Devonian Shales, such as the Marcellus Shale. The same houses also have had their water disturbed with a foam substance that could possibly be related to air foam that is used during drilling of wells. Samples from two sites were analyzed spectroscopically and a chemical, 2-Butoxythanol (2-BE), was discovered. This compound is also found in air foam. An aquifer test was conducted in the same area to better understand the subsurface and flow of groundwater. Samples of other wells in the area are being collected and analyzed.

# **Geochemistry of the Union Springs Member of the Marcellus Formation**

**Anna K. Wendt**

Ph.D. Student, Pre-comps

**Advisor: Mike Arthur**

High-resolution geochemical data was collected for the Union Springs Member of the Marcellus Formation from a core drilled by the Appalachian Basin Black Shale Group in Southeastern Pennsylvania. Geochemical data provides information regarding the paleodepositional environment, such as paleoredox conditions, clastic flux, and biological activity. Specifically, the trace elements uranium and molybdenum can serve as proxies for the reconstruction of the paleoredox history of the sediment pore waters, and possibly the water column, beginning with the onset of deposition of the Marcellus Formation.

# Oral Session Four: Astrobiology

Saturday, March 16  
3:15-4:30, 114 EES

Time	Presenter	Advisor	Title
3:15	Sonny Herman	James Kasting	The Atmospheric Production of Glycolaldehyde under Hazy Prebiotic Conditions
3:30	Jamie Brainard	Hiroshi Ohmoto	An Estimate of Archean Ocean Sulfate from the 3.2Ga Panorama Hydrothermal Ore Deposits
3:45	Kyle Rybacki	Lee Kump	Evidence for extensive oxidation of terrestrial surfaces across the Kola Peninsula in Fennoscandia, arctic Russia
4:00	Becky McCauley	Jennifer Macalady	Enough Rope to Think On: Rope-Like Microbial Communities in the Frasassi Caves
4:15	Khadouja Harouaka	Matthew Fantle	An evaluation of the morphology of gypsum precipitates from the Frasassi caves: Can crystal morphology serve as an indicator of biologically induced gypsum precipitation?

# The Atmospheric Production of Glycolaldehyde under Hazy Prebiotic Conditions

**Sonny Harman**

M.S. Student

**Advisor: James F. Kasting**

The early Earth's atmosphere, with extremely low levels of molecular oxygen and an appreciable abiotic flux of methane, could have been a source of organic compounds necessary for prebiotic chemistry. Here, we investigate the formation of a key RNA precursor, glycolaldehyde (2-hydroxyacetaldehyde, or GA) using a 1-dimensional photochemical model. Maximum production of GA occurs when the atmospheric  $\text{CH}_4:\text{CO}_2$  ratio is close to 0.02. The total production rate of GA remains small, only  $1 \times 10^7$  mol/yr. Somewhat greater amounts of GA production, up to  $2 \times 10^8$  mol/yr, could have been provided by the formose reaction or by direct delivery from space. Even with these additional production mechanisms, open ocean GA concentrations would have remained at or below  $\sim 1 \mu\text{M}$ , much smaller than the 1-2 M concentrations required for prebiotic synthesis routes like those proposed by Powner et al. [2009]. Additional production or concentration mechanisms for GA, or alternative formation mechanisms for RNA, are needed, if this was indeed how life originated on the early Earth.

# **An Estimate of Archean Ocean Sulfate from the 3.2Ga Panorama Hydrothermal Ore Deposits**

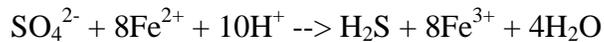
**Jamie Brainard**

Ph.D. Student, Pre-comps

**Advisor: Hiroshi Ohmoto**

There is a widely held belief that prior to 2.4 Ga, the Archean oceans and atmosphere were reducing, and therefore sulfate poor (concentrations <0.1 mmol). However, in this study we demonstrate that in some Archean-aged volcanogenic massive sulfide (VMS) deposits there is evidence for abundant seawater sulfate.

Volcanogenic Massive Sulfide (VMS) deposits are formed by submarine hydrothermal fluids that are derived from seawater circulating through the seafloor. Much of the seawater sulfate is reduced to sulfide at depth through the following reaction:



This reaction creates zones of increased  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios that can be observed in both the modern and the Archean. These distinct oxidized zones have been observed in the 3.2 Ga Panorama district suite of VMS deposits in Western Australia (see below).

By determining the amount of  $\text{Fe}^{3+}$  that has been added in a circulation cell, it is possible to estimate the amount of sulfate that would be required for the oxidation. Using estimations of fluid circulation from the short thermal life of a hydrothermal cell (~5ka), we have found that an ocean concentration of at least 10 mM most likely at 3.2Ga.

# Evidence for extensive oxidation of terrestrial surfaces across the Kola Peninsula in Fennoscandia, arctic Russia

**Kyle S. Rybacki**

Ph.D. Student, Pre-comps

**Advisor: Lee R. Kump**

One of the most important events in Earth history was the establishment of an oxygen-rich atmosphere at ca. 2.45 Ga based upon the suppression of the mass-independent fractionation of sulphur within the geologic record. Our research investigates evidence for deep oxidative weathering of the continental crust at ca. 2.0 Ga resulting from buildup of oxygen in the atmosphere during the preceding positive Lomagundi-Jatuli carbon isotope excursion at ca. 2.2 Ga.

Evidence in support of this buildup is the oxidized subaerial volcanic series observed across the Kola Peninsula of arctic Russia (Fennoscandia). These volcanics are characterized by noticeably elevated ferric-ferrous ratios when compared the adjacent volcanic formations. In particular, the ca. 2.06 Ga Kuetsjärvi Volcanic Formation, comprised of mostly subaerially erupted picrites to trachydacites and intervening fragmental rocks, is anomalously oxidized. In the Kuetsjärvi volcanics, the ratio of oxidized iron to total iron ( $\text{Fe}^{3+}/\Sigma\text{Fe}$ ) has a very large range with most being greater than 0.35, whereas adjacent volcanic formations have  $\text{Fe}^{3+}/\Sigma\text{Fe}$  which commonly fall below 0.35. The difference in the oxidation state of iron may partly be explained by the geotectonic environment during eruption, as the two youngest volcanic formations are submarine while the two older formations are subaerial. The present redox state of the two oldest volcanic formations (Ahmalahti and Kuetsjärvi) is striking in that both represent subaerial volcanism, yet exhibit different  $\text{Fe}^{3+}/\Sigma\text{Fe}$  values.

Based on the petrographic and geochemical data, it is evident that the high  $\text{Fe}^{3+}/\Sigma\text{Fe}$  values are due to post-crystallization hematization. At the top of FAR-DEEP drill core 6A the primary magnetite crystals have been completely replaced with hematite. At intermediate depths within the core the primary magnetite crystals exhibit complex trellis structures comprised of magnetite, hematite, rutile, and sphene. At the bottom of the drill core the primary magnetite crystals have not been replaced. Secondary, very fine grained to massive hematite is observed throughout the drill core filling amygdales and the hairline fractures which connect amygdales. These petrographic observations suggest that oxidation occurred from the top, and progressed downward exploiting the oldest fracture sets.

Petrographic features suggest that this oxidation affected the rocks prior to regional metamorphism, which took place at ca. 1800 Ma during the Svecofennian orogeny. Oxidation is believed to have occurred during, or immediately following, eruption as evidenced by the inclusion of the oxidized Kuetsjärvi volcanic clasts into the overlying conglomerate units which do not exhibit pervasive oxidation.

# **Enough Rope to Think On: Rope-Like Microbial Communities in the Frasassi Caves**

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Microbial communities in the terrestrial subsurface are not well characterized nor are their role in biogeochemical cycling understood. By studying unique biofilms in cave systems, we have an opportunity to discover new metabolisms, novel lineages, and expand our understanding of microbial community function in the subsurface. Three biofilms with rope-like morphology were recovered by divers from the anoxic and sulfidic water of three remote cave lakes (Lago Infinito, Lago Verde, and Lago dell'Orsa) within the Frasassi cave system. The Lago Infinito biofilm has high species richness, and is dominated by bacteria in the phyla Deltaproteobacteria and Chloroflexi. Previous analysis has suggested an energy-limited, sulfate-reducing community capable of carbon fixation through various pathways, and more recent data will link phylogeny with carbon fixation genes using metagenomic-binning methods. The community composition based on 16S rDNA clone libraries for biofilms from Lago Verde and Lago dell'Orsa will be presented and similarities with the Lago Infinito biofilm will be discussed.

# **An evaluation of the morphology of gypsum precipitates from the Frasassi caves: Can crystal morphology serve as an indicator of biologically induced gypsum precipitation?**

**Khadouja Harouaka**

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The determination of mineral biosignatures is of the utmost importance to the field of astrobiology, as these signatures can serve as an indication of the presence of life that is preserved over geologic time scales in the rock record. The process of biomineralization can leave unique fingerprints in the chemical and physical properties of a mineral, such as in the isotopic composition and the overall crystal morphology. In order to establish the biological origin of a mineral, the physical and chemical properties of biominerals must be explored. In the Frasassi caves of northern Italy, gypsum minerals are thought to precipitate as a result of microbial metabolism. Atmospheric  $H_2S$  is oxidized by *Acidithiobacillus thiooxidans*, that colonize the limestone walls and creates a very acidic environment (pH=0-1) due to the generation of sulfuric acid, which results in gypsum precipitation. The cave gypsum occurs in three distinct morphologies: micro-crystalline toothpaste, wall crust and small and large needles. The cause of the variety in gypsum morphology is currently unknown, and it is hypothesized that some crystal types may be produced through direct precipitation on the surface of the biofilm. To determine if the different morphologies contain any hint of a biological origin of the crystals, gypsum samples of all morphology types were collected from the Grotto Bella chamber of the Frasassi caves at known locations using the main  $H_2S$  source as a reference point. The crystals were characterized using the following techniques: XRD for phase identification, SEM for imaging and determination of aspect ratio, and a Malvern mastersizer to determine particle size distribution. SEM images reveal that the wall crust gypsum is comprised of both small needles and aggregates of toothpaste gypsum held together by biofilm. The images and aspect ratios show a spatial correlation in the caves, such that the smaller crystals with smaller aspect ratios tend to be located closer to main  $H_2S$  source, whereas the larger needle like crystals are found in more distant locations. A possible interpretation of these observations is that the smaller toothpaste morphology results from the rapid microbial oxidation of sulfide, and may even use the surface of the biofilm as a template for precipitation. Since preliminary elemental concentration measurements show that the cave drip waters are generally undersaturated in gypsum, the larger needle like morphologies may then have resulted from a slower dissolution and re-precipitation type process.