

# 23<sup>RD</sup> GEOSCIENCES STUDENT RESEARCH SYMPOSIUM

FEBRUARY 22 & 23, 2018  
KELLY HALL RM. 310, CAFE X AND ATRIUM



GSRS



**23<sup>nd</sup> Annual**

# **Geosciences Student Research Symposium**

Thursday February 22<sup>rd</sup>, 9:10 – 5:00

Friday February 23<sup>th</sup>, 9:00 – 5:00

*Kelly Hall Room 310 Café X and Atrium*

*Virginia Tech*

Welcome to the Geosciences Student Research Symposium fondly known as GSRS! GSRS is produced and organized solely by the graduate students of the Department of Geosciences at Virginia Tech. The symposium is designed to allow both graduate and undergraduate students the opportunity to prepare and present talks and posters in their current research areas for both professional growth and public awareness. Each talk is scheduled to be 12 minutes with three minutes for questions. The posters are displayed in the Café X and Atrium throughout the symposium enabling everyone to take their time to walk through them and understanding them. Constructive feedback on student presentations and posters from faculty, students, and visiting guests is highly encouraged.

On both days of the symposium morning refreshments, coffee, as well as lunch will be served in Kelly Hall, room 310. Dinner in the Museum of Geosciences (Derring Hall, room 2062) will conclude this year's symposium, and all are welcome to attend.

We are extremely grateful and wish to extend our appreciation to the corporate, local, and alumni sponsors of this event: Newmont Mining, Next Door Bake Shop, Carol Lee Donuts, Strange Coffee Company, Due South BBQ, Taqueria el Paso, Professional Catering Inc., ConocoPhillips, and the Departmental Picnic Club and everyone who donated through the VT Jump-Crowdfunding campaign! We also thank the Department of Geosciences for their generous support. Finally, to the faculty, volunteers, and student participants, for donating their time and expertise – without you this event would not take place.

The GSRS Committee extends their sincere thanks to Dr. Robin Panneton, Associate Dean for Undergraduate Programs at College of Science, and Dr. JP Morgan, Associate Dean of Strategic Initiatives and Graduate Studies at College of Science for delivering the opening remarks on Thursday the 22<sup>nd</sup> February and Friday the 23<sup>rd</sup> February respectively. We thank the generous support of the College of Science.

## **Your 2018 GSRS Coordinating Committee:**

**Committee Chair:** Kannikha Kolandaivelu

**Committee Mentors and Advisors:** Rui Filipe Serra Maia, Lowell Moore

**Abstract Book/Scheduling:** Lisa Whalen

**Beverages:** Calvin Mako

**Communications & Up-Goer V:** Aly Hoeher

**Food:** Morrison Nolan

**Fundraising:** Eszter Sendula, Kirkland Broadwell, Tyler Rasmussen, Amin Abbasi Baghbadorani

**GSRS Workshop Series:** Devin Hoffman & Matthew Wilson

**Judiciary:** Dana Korneisel

**Moderators:** Alexandra Nagurney

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**Website:** Sheyla Palomino Ore

**Faculty Advisor:** Jim Spotila

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## 23<sup>rd</sup> Annual Geosciences Student Research Symposium

Breakfasts, Lunches, Coffee Breaks & Oral Presentations: Kelly Hall Room 310

Poster Presentations: Café X (Room 210) and Atrium, Kelly Hall

Thursday, February 22	Presenter	Friday, February 23	Presenter
8:30-9:10	Breakfast	8:30-9:00	Breakfast
9:10-9:15	Welcome Address	9:00-9:05	Welcome Address
9:15-9:25	Opening Remarks: Dr. Robin Panneton, Associate Dean for Undergraduate Programs at College of Science	9:05-9:15	Opening Remarks: Dr. JP Morgan, Associate Dean of Strategic Initiatives and Graduate Studies at College of Science
9:25-9:40	Rui Filipe Serra Maia	9:15-9:30	Lowell Moore
9:40-9:55	Calvin Mako	9:30-9:45	Kannikha Kolandaivelu
9:55-10:10	Richard Jayne	9:45-10:00	Chris Griffin
10:10-10:25	Kristin Chilton	10:00-10:15	Dana Korneisel
10:25-10:40	Emmanuel Njinju	10:15-10:30	Shangxin Liu
10:40-10:55	Krista Koeller		
10:55-11:15	Coffee Break	10:30-10:50	Coffee Break
11-1:00	Undergraduate Poster Session	11-1:00	Undergraduate Poster Session
11:15-11:30	Devin Hoffman	10:50-11:05	Brenen Wynd
11:30-11:45	Kira Dickey	11:05-11:20	Codi Wiersma
11:45-12:00	Joshua Robert Jones	11:20-11:35	Eszter Sendula
12:00-12:15	Morrison Nolan	11:35-11:50	Sheyla Palomino Ore
12:15-12:30	Allie Nagurney	11:50-12:05	Amin Abbasi
12:30-13:45	Lunch & Poster Session	12:05-13:15	Lunch & Poster Session
13:45	Announcements	13:15-14:15	Up Goer 5 Session
14:00-14:15	Jessica Schobelock	14:15-14:30	Zhen Guo
14:15-14:30	Andrew Parent	14:30-14:45	Kirkland Broadwell
14:30-14:45	Selva Marroquín	14:45-15:00	William Whalen
14:45-15:00	Kathryn Krueger	15:00-15:15	Matt Sublett
15:00-15:15	Grant Euen	15:15-15:30	Mitchell Riegler
15:15-15:30	Coffee Break	15:30-15:45	Coffee Break
15:30-15:45	Jessica DePaolis	15:45-16:00	Michael Vadman
15:45-16:00	Wu Hao	16:00-16:15	Qing Tang
16:00-16:15	Yong Huang	16:15-16:30	Matt LeRoy
16:15-16:30	Josh Murphy	16:30-16:45	Aly Hoeher
16:30-16:45	McNeill Bauer	16:45-17:00	Stacey Law
16:45-17:00	Karel Kletetschka	17:00	Closing Remarks
		17:30 Onwards	Reception, Museum of Geosciences

### Poster Presenters

Marion Bellier  
Alexander Bradley  
Alexandra Datko  
Megan Junod  
Alex Kovalick  
Sean Malloy

Sarah Morgan  
Ronald Navarro  
Rohan Parmar  
Ryan Roane  
Andrew Smith

## IMAGING VOIDS AND FRACTURES WITHIN AN UNDERGROUND MINE USING GROUND PENETRATING RADAR

ABBASI BAGHBADORANI, Amin, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Two of the most dangerous events in underground mining are encountering unexpected water influx and structural instability due to excavation into undetected voids and fractures hundreds of meters underground. The most common detection method is probe drilling, either from the mine or from the surface. Mine engineers decide on the spacing and the depth of probe drilling based on the planned excavation depth and the nature of previous voids encountered. However, drilling misses or underestimates the size of fractures and voids between holes or beyond the depth of drilled holes.

Lhoist North America as part of the Lhoist Group is currently mining chemical-grade limestone from the Five Oaks Formation (Middle Ordovician) at Kimballton in Giles County, southwestern Virginia. The mining operation is following the Five Oak formation, which varies in thickness from 25-30 meters along a synclinal structure. The current depth of the mine from the entrance is approximately 600 meters. Since starting operation, excavation has often encountered fractures and karst voids. The company is currently using a 5-m drill bit with 8-12 cm diameter and grid spacing of approximately 1-2 m to detect voids and fractures. However, often these structures remain undiscovered until excavation. Occasionally, the tunnel must be abandoned and the operation re-routed due to structural instability. In the case of water influx, high capacity water pumps are used to pump the water out. Both scenarios lead to loss of time, resources, and pose safety hazards. In one incident in 2016, the lower mine levels were flooded overnight, a major setback and financial lost.

Ground penetrating radar can detect fractures and voids within rock. Our goal is to first confirm the effectiveness of GPR in the Kimballton mine by detecting and imaging a known 17 m<sup>3</sup>-karst void, from different directions, within a 10x25x25 m pillar. Subsequent targets will include karst behind a flat mine wall and fractures above the mine roof. Both would be targeted based on known features, imaging void geometry within the rock, and testing the images by drilling. The ultimate goal is to develop a practical method to be used during mine operations that can detect and locate fractures and voids 30 meters ahead of excavation.

## FACTORS REGULATING SYNTHESIS AND FORMATION STAGES OF ALLOPHANE NANOPARTICLES

BAUER, McNeill, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Nanoclays such as allophane, imogolite, and halloysite strongly control the physical and chemical behavior of soil, due to their high specific surface area, unique surface charge characteristics, mechanical stability and structural properties. Allophane ( $\text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_{1.3-2} \cdot (2.5-3)\text{H}_2\text{O}$ ) is a hydrated aluminosilicate with a 3-5 nm diameter hollow spherical shape. Its structure consists of a curved gibbsite-like ( $\text{Al}(\text{OH})_3$ ) outer layer. On the interior of this layer, on the holes created by octahedral 6-member rings, are isolated silica tetrahedrons. It has been suggested that the curvature of the (spherical) particles is related to the presence of silica during formation of allophane, although the mechanism is not well understood. The objective of this study is to observe that stages of allophane formation in a native hydrated state via *in situ* and *ex situ* characterization techniques.

Heterogeneity in the products has been a significant issue in many of the various laboratory synthesis methods that have been reported for allophane. A common impurity is imogolite, a polymorph of allophane, that forms 2-3nm diameter nanotubes up to micrometers in length. Therefore, the first goal of this study is to develop a procedure for synthesizing pure allophane. **We hypothesize that the initial concentrations of starting reagents, the initial Si/Al ratio, and the mixing and heating conditions all influence the formation of pure allophane.** Tetraethyl orthosilicate (TEOS) is mixed into a solution of aluminum chloride hexahydrate ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ). Idealized Al/Si ratios are set between 2 and 0.5, with initial aluminum concentrations  $[\text{Al}] = 0.05\text{M}$  to  $0.2\text{M}$ . The solution is then hydrolyzed by the addition of  $0.1\text{M}$  NaOH to an ideal hydrolysis ratio of  $[\text{OH}]/[\text{Al}] = 1$ . The solution is stirred for 1 hour at 400 rpm and then heated for 7 days at  $95^\circ\text{C}$ . The resulting suspensions are dialyzed for 7 days (10,000 Da) to remove excess alcohol, as well as  $\text{Na}^+$  and  $\text{Cl}^-$  ions.

Preliminary synthesis results of unheated solutions have been characterized using small-angle x-ray scattering (SAXS). At  $[\text{Al}] = 0.1$  and  $[\text{Al}]/[\text{Si}] = 2$ , the product formed had an average diameter of 2.3 nm with the middle 60% of particles ranging from 1.1-3.2nm in diameter. A  $0.05\text{M}$   $[\text{Al}]/[\text{Si}] = 0.5$  solution had an average diameter of 1.4nm, ranging from 0.9-2nm. Finally, a  $0.05\text{M}$   $[\text{Al}]/[\text{Si}] = 2$  solution had an average diameter of 2.2, ranging from 1.2-3nm. These data suggest that the solutions are possibly comprised of an imogolite local structure, composed of curved gibbsite-like fragments. Next steps include synthesis and heating of allophane in anaerobic conditions, and characterization using TEM imaging.

## DEVELOPMENT OF MICROFLUIDIC DEVICES FOR TIME-RESOLVED CRYSTALLIZATION STUDIES OF NANOMINERALS IN LAMINAR FLOW CONDITIONS

BELLIER, Marion, Dept. of Nanoscience, Virginia Tech, Blacksburg, VA 24061

Recent studies of mineral crystallization have revealed a variety of pathways and mechanisms for crystal growth beyond the classical monomer-by-monomer attachment model. Some examples include crystallization of amorphous materials and oriented nanoparticle assembly. These non-classical crystallization mechanisms often proceed by forming metastatic precursors that assemble into larger particles. The hydrodynamic conditions (laminar, turbulent, and static) are of particular importance in this process because of the effect of shear forces on the interaction that is established between the precursor particles. Quantifying the effect of this variable on the growth mechanisms of different minerals is the key for understanding and potentially controlling many environmental and geological processes. Despite the importance of non-classical crystallization pathways, there is a lack of methodologies to investigate these mechanisms, mostly due to the difficulty of quantifying and characterizing the transient species involved. New real-time techniques are needed to analyze how monomers evolve from dissolved species, into metastatic intermediates, and finally nanocrystallites. We aim to investigate the physical and structural properties of precursor clusters that form in the early stages of crystallization and track their properties as they evolve into larger nanoparticles.

We have developed a microfluidic device to study the crystallization of nanoparticles under laminar flow conditions, which mimic the hydrodynamic flow conditions encountered in channels of reduced dimensions, such as porous rocks. Preliminary experiments show that gold (precursor) nanoparticles form when the initial reagents come in contact and age as they are transported through the channels of the device. As gold exhibits strong interaction with X-ray and electron beams, gold clusters and nanoparticles precipitated in these devices can be analyzed relatively easily, which represents a suitable test case to evaluate how different flow rates affect their growth mechanism and kinetics. Our goal is to use these devices for in situ x-ray scattering studies at the synchrotron to obtain real-time structural, chemical and physical data of the solids in their original state (liquid conditions), as they form and grow along the channel in the device. Our long-term goal is to use these devices to study more complex materials such as nanoparticles that are precipitated in real-world geologic environments.

Advisor: Dr. F. M. Michel

A POSSIBLE NEW SPECIMEN OF THE OWENETIID RUHUHUARIA REISZI FROM THE MANDA BEDS OF SOUTHERN TANZANIA (MIDDLE TRIASSIC) AND ITS IMPLICATIONS FOR SMALL REPTILES DURING THE TRIASSIC PERIOD RECOVERY

BRADLEY, ALEX, Dept. of Geosciences, Virginia Tech, Blacksburg, AV 24061

During the recovery from the end-Permian extinctions in the Middle Triassic, small reptiles (<50 cm) are exceptionally rare, and this gap in the fossil record inhibits our understanding of small reptile ecology and evolution during such a critical transition in Earth history. One of the biggest problems in assigning small reptiles to reptile clades is that most forms are only represented by partial or highly fragmented skeletons. Here, we fully describe two fossil fragments of the jaw of a single individual of a small reptile from the Middle Triassic Manda Beds of Tanzania, CAMZM T1162. CAMZM T1162 shares two diagnostic character states (labio-lingually expanded and anteriorly enlarged dentary teeth) with the recently described taxon, *Ruhuhuaria reiszii* (Procolophonoidea: Owenettidae), which was found at the same locality. From this, we tentatively assign CAMZM T1162 to *Ruhuhuaria reiszii*. CT scanning and SEM imaging were employed to fully examine the morphology of the new specimen and illuminate details of the teeth not available in the holotype. Though the new specimen is much less complete overall, the dentition of CAMZM T1162 is better preserved than that of the holotype and shows that 1) the more posterior teeth of the dentary of this animal were chisel-shaped rather than pointed, 2) at least some of the teeth were transversely expanded at the base, and 3) tooth implantation is acrodont in the posterior portion and pleurodont in the more anterior portion of the dentary. This combination of character states in the new specimen referred to *Ruhuhuaria reiszii* appears to be unique. Furthermore, this potential second specimen of *Ruhuhuaria reiszii* provides new information about the ecology of the taxon, such as its diet, and complicates the previous hypothesized relationships of the taxon by introducing still more ambiguous morphological characters with ambiguous or contradictory distributions among Triassic small reptiles. This new addition to the fossil record further illustrates the difficulties in assigning small reptiles to various clades in the Triassic during the recovery period. If CAMZM T1162 does represent another specimen of *Ruhuhuaria reiszii*, it clearly shows that small Triassic reptiles had more variation in their tooth implantation and tooth disparity than previously appreciated.

# QUANTIFYING THE PERIODICITY OF INTERMEDIATE DEPTH SEISMICITY AS PRESERVED IN ECLOGITE BRECCIAS: AN APPLICATION OF GARNET DIFFUSION MODELLING

BROADWELL, KIRKLAND, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Subduction zones provide a unique view of how plate tectonic processes recycle crust in modern and ancient Earth. Metamorphic reactions that take place during subduction result in the densification and dehydration of the subducting slab and the release of fluids, leading to hazards such as explosive volcanism and earthquakes, and the creation of new continental crust and global geochemical cycling. While most subduction zone earthquakes occur at relatively shallow depths at the boundary between the upper and lower plate (so-called megathrust earthquakes), a sizable amount of seismicity occurs at greater depths, referred to as intermediate depth seismicity. The causal mechanisms of intermediate depth seismicity remain uncertain; there are numerous competing hypotheses, several of which are not mutually exclusive. One hypothesis is dehydration embrittlement, which asserts that fluids generated from dehydration reactions decrease the effective confining pressure, allowing for seismic slip to occur at much greater confining pressures than is usually expected. Theory and lab experiments have been able to document such behavior, but until recently the rock record was largely silent in terms of providing clear evidence for the process. However, new field work in the Western Alps has provided several compelling examples of so-called “eclogite breccias” that are interpreted to represent a preserved record of intermediate depth seismicity at eclogite facies conditions caused by dehydration embrittlement. Evidence includes mylonitic clasts of eclogite that are multiply fractured and cemented by a matrix of eclogite facies minerals.

Several of these eclogite breccias preserve evidence for multiple fracturing episodes which are interpreted to record multiple earthquakes caused by fluid generation and associated dehydration embrittlement in the subducting slab.

An important unanswered question is the recurrence interval of such events as preserved in the rock record. Here, we propose to utilize stranded chemical diffusion profiles in brecciated and chemically zoned garnet crystals to quantify the periodicity of seismicity as recorded in the eclogite breccias. In short, given a set of physical conditions (pressure, temperature,  $fO_2$ ), boundary conditions, and initial chemical zoning profile, a maximum duration of time between each fracturing event can be calculated. The results of this project will also test the hypotheses that these structures 1) formed at eclogite facies conditions and 2) are the result of intermediate depth seismicity involving dehydration embrittlement. This will have important implications for both fluid movement in subduction zones and the ability of metamorphic rocks to record catastrophic events in the crust.

# UNRAVELING THE RELATIONSHIPS BETWEEN BEDROCK PROPERTIES, ERODIBILITY, AND BEDROCK CHANNEL MORPHOLOGY THROUGH HIGH-RESOLUTION FIELD SURVEYS OF BEDROCK RIVERS IN VIRGINIA

CHILTON, Kristin, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Bedrock rivers are the principal agents of erosion in non-glaciated landscapes, and therefore set the pace and pattern of landscape evolution across much of Earth's surface. In addition, the erodibility of the underlying bedrock exerts a primary control on landscape evolution by influencing incision rate and channel form. However, our understanding of the interactions between bedrock rivers and the underlying geology is limited. Bedrock material properties such as tensile strength, joint spacing/orientation, and susceptibility to weathering are known to influence erodibility, which in turn impacts channel form and evolution, but the relative importance and roles of each of these factors remains unclear. This lack of understanding limits our ability to accurately model fluvial incision, and presents a hindrance toward further understanding of landscape evolution processes.

There is therefore need to better define how bedrock properties influence erodibility and, in turn, channel form and evolution. This study seeks to deconvolve the relationships between bedrock material properties, erodibility, and bedrock channel morphology by quantifying empirical relationships between substrate characteristics and channel morphology (slope, steepness index, width, form) at a high spatial resolution (5-10 m scale) in continuous and mixed alluvial-bedrock channels. We specifically focus on slowly eroding channels with minimal evidence for landscape transience, such that variations in channel morphology are mainly due to bedrock properties. We also use channels cut into sedimentary rock, which exhibit extreme variation (yet predictability and continuity) in discontinuity spacing.

Here we present preliminary data comparing the morphology and bedrock properties of a second order, predominantly bedrock channel in the tectonically inactive Valley and Ridge province of the Appalachian Mountains, SW Virginia. Field surveys of channel slope, width, substrate, and form were conducted over a 350m long continuous stream reach, which cuts through tilted Paleozoic siliciclastic stratigraphy. We statistically analyze relationships between fluvial morphology and lithologic strength (based on field and laboratory measurements), discontinuity spacing, and orientation. Results suggest 1) the channel responds to resistant lithologies by changing orientation to run strike-parallel, 2) several knickpoints are present that do not appear to correspond to changes in lithology, and 3) spatial averaging of measurements needs to be adjusted in order to statistically capture lithologic control on channel morphology.

## GEOCHEMICAL EVOLUTION OF MAGMAS FROM TENERIFE, CANARY ISLANDS AND MAUI, HAWAII BASED ON MELT INCLUSION ANALYSIS

DATKO, Alexandra, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The explosivity of volcanic eruptions is related to concentrations of volatile components in magmas, and volatiles also play a role in long-term variations in atmospheric chemistry and the formation of ore deposits. However, because volatile solubility depends on pressure, and because melts undergo decompression as they rise to the surface, volatiles such as H<sub>2</sub>O and CO<sub>2</sub> measured in whole rock samples do not reflect the pre-eruptive composition of the melt. Melt inclusions trap and preserve a sample of the pre-eruptive melt, and analysis of melt inclusions provides important information to estimate volatile fluxes and evaluate the eruptive style and intensity of volcanoes that are not currently active.

In this study melt inclusions from tephra samples from Tenerife, Canary Islands and samples of tephtras and lavas from Hawaiian Island volcanoes were analyzed to determine the major, minor and trace element contents and volatile contents of the parent magma using a combination of Raman spectroscopy, secondary ion mass spectrometry (SIMS), and electron probe microanalysis (EPMA). Inclusion-bearing olivine phenocrysts were hand-selected to isolate unbroken, glassy melt inclusions. The inclusions typically contain a vapor bubble that is, on average, about 3 volume percent of the inclusion, and many also contain spinel crystals, sulfide globules, and carbonate daughter crystals coating the bubble. A few of the bubbles contain a mixture of liquid and vapor CO<sub>2</sub>, which homogenizes to a liquid just above room temperature. This allows an initial estimate that the bulk density of the fluid of 0.47 and 0.74 g/cc, with Raman analysis indicating an average fluid density between 0.2 and 0.4 g/cc. Using Raman analysis, the bubbles in the inclusions from Tenerife were found to contain at least 25% of the total CO<sub>2</sub> in the inclusions, with the bubbles in the Hawaiian inclusions containing closer to 35-45%, depending on whether phenocrysts come from a lava or tephtra, respectively. The Hawaii tephtras have, on average, a significantly higher overall CO<sub>2</sub> content than the Tenerife samples and Hawaii lavas, though the ranges overlap significantly. The trapping pressure for the Tenerife inclusions is ~2.3 kbar, and the trapping pressures for the Hawaii inclusions average ~1.7 kbar for the lavas and 2.6 kbar for the tephtras. These results are consistent with the more explosive nature of eruptions that generated tephtras compared to those that produced lavas.

## MBLG 3.9 SEPTEMBER 13, 2017 EARTHQUAKE IN THE GILES COUNTY SEISMIC ZONE

DEPAOLIS, Jessica, Department of Geosciences, Virginia Tech, Blacksburg, VA, 24061

On September 13, 2017 the USGS NEIC reported a duration magnitude MD 3.2 earthquake at 37.473N 80.703W, depth 18 km near Lindside, West Virginia, close to the Virginia-West Virginia border. The earthquake was felt primarily in Monroe, Mercer and Summers counties, West Virginia and in Giles, Montgomery, Pulaski and Bland counties, Virginia. The maximum intensity reported to the USGS Did You Feel It? program was IV MM. The earthquake occurred in an area of moderate seismicity known as the Giles County Seismic Zone (GCSZ). The largest shock in the GCSZ occurred in 1897 near Pearisburg, VA, with mblg magnitude estimated from the felt area at 5.8. The second largest historical shock occurred on November 20, 1969 with instrumentally determined mblg of 4.6. We relocated the hypocenter of the September 2017 earthquake using a locally specific velocity model at 37.4775N, 80.7035W, depth 21 km. This location is approximately 20 km to the east of the estimated epicenter of the 1969 earthquake and within the location uncertainty of the 1969 shock. We estimated the mblg magnitude at 3.90 +/- 0.26 using 26 stations at regional distances, and determined a duration magnitude MD of 3.71 +/- 0.17, using 33 stations. The duration magnitude is based on a linear correlation between the log of short-period signal duration and mblg developed from many previous earthquakes throughout the southeastern U.S. We determined a focal mechanism (program FOCMEC) using 27 P-wave polarities, 12 SH polarities and 16 SH/P amplitude ratios. The nodal planes with least rms amplitude ratio error are: strike N91E, dip 69 deg., rake -22 deg.; auxiliary plane strike N189E, dip 69 deg., rake -158 deg. This event is notable because it is the largest shock in the GCSZ since May, 1974 (mblg 3.7). This recent shock, like many others in the GCSZ, shares characteristics with those in the Eastern Tennessee Seismic Zone (ETSZ), which is also in the Appalachian Valley and Ridge province. The 2017 GCSZ focal mechanism is mostly strike-slip with a small normal component, on steeply dipping nodal planes trending approximately N-S and E-W. This type of mechanism is dominant in the ETSZ. Also, in both areas, focal depths tend to be greater than 12 km, unlike shocks to the east in the Blue Ridge, Piedmont and Coastal Plain provinces which tend to occur at shallower depths.

# PRELIMINARY RESULTS FROM THE FIRST AIRBORNE EM AND AEROMAGNETIC SURVEY IN YELLOWSTONE NATIONAL PARK

DICKEY, Kira, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Yellowstone National Park hosts over 10,000 thermal features (e.g. geysers, fumaroles, mud pots, and hot springs), yet little is known about the circulation depth of meteoric water feeding these features, the pathways that guide deep, hot fluids to the surface, nor the lithological and structural bounds interconnecting features. Previous near-surface geophysical studies have been effective in imaging shallow hydrothermal pathways in some areas of the park, but these methods are difficult to conduct over the large areas needed to characterize entire hydrothermal systems. Transient electromagnetic (TEM) soundings and 2D direct current (DC) resistivity profiles show that hydrothermal fluids at active sites have a higher electrical conductivity than the surrounding hydrothermally inactive areas. For that reason, airborne TEM is an effective method to characterize large areas and identify hydrothermally active and inactive zones using electrical conductivity. Aeromagnetic data have been useful in mapping faults and geologic boundaries that localize hot springs, making the integration of aeromagnetic and EM data effective for structurally characterizing fluid pathways.

Here we present the preliminary results from an airborne transient electromagnetic (TEM) and aeromagnetic survey acquired jointly by the U.S. Geological Survey (USGS) and the University of Wyoming (UW) in November 2016. We integrate the EM and magnetic data for the purpose of locating hydrothermal fluid sources and the pathways that guide the fluids to the surface. We use many magnetic filtering techniques including horizontal and vertical gradients, upward continuation, and bandpass filtering. The integration of EM with magnetics allows us to constrain hydrothermal alteration depths and determine trends for hydrothermal pathways.

## STUDYING 3D SPHERICAL SHELL CONVECTION USING ASPECT

EUEN, Grant, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Modeling convection in spherical geometries is crucial to gain an understanding of planet-scale mantle processes. However, modeling 3D spherical shells is computationally challenging. Few studies have been done using full 3D spherical shells. Here I present test cases for modeling 3D spherical shells using ASPECT. These cases are based on previous work using CitcomS done by Zhong et al., 2008. The cases were run on the NewRiver cluster at ARC at Virginia Tech. Cases were run using varying numbers of processors and 3-5 global mesh refinements. Each added refinement increases the number of cells by a factor of 8. Three global refinements corresponds to 49152 cells, four has 393216, and five has 3145728. To make these results comparable to Zhong et al., 2008 all adaptive mesh refinement was turned off, and the size of cells in the radial direction was held constant. The cases run were A1 through A8, B1, and C1 through C4. Results are in good agreement for the A cases and B1. The C cases show fair agreement overall. Cases with higher viscosity contrast showed better agreement if the cells were allowed to change in the radial direction. I will present results from various cases focusing on their convective flow patterns and general behavior compared to Zhong et al., 2008.

Advisor: Dr. S.D. King

## CONSTRAINT ON THE VERTEBRAL COLUMN OF MAMMALS IS ABSENT IN EXTINCT MAMMALIAN RELATIVES

GRIFFIN, Christopher, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The sacrum—the vertebrae that articulate with the pelvis—is the nexus between the vertebral column and the hindlimb, and therefore plays a central role in movement of land-dwelling vertebrates. Reptilian lineages have increased sacral vertebrae from the ancestral count of two in several ways (e.g., transforming trunk or tail vertebrae into sacral vertebrae, inserting novel vertebrae), and possess extremes in sacral count and anatomy, from the ancestral state of two sacrals to >20 in some birds. However, little is known of the mechanisms of sacral evolution of mammals and their extinct relatives, or how they relate to reptilian trends. Dicynodonts, a diverse group of extinct mammal relatives, had a wide range of sacral counts (3-8), with a general trend of increasing absolute number of sacral vertebrae through evolutionary time. I explored the addition of vertebrae to the dicynodont sacrum and placed these patterns in the broader context of the evolution of the mammalian body plan. I established sacral count and the identity of each sacral vertebra by the location of sacral rib–hip articulation, either by direct observation in articulated specimens, or by the location of articulation scars on the pelvis bones. Photographs, computed tomography scans, and published anatomical descriptions of specimens supplemented these data. The three ancestral sacral vertebrae are located above the hip socket, with additional vertebrae added to the sacrum towards the head and tail. Using a statistical test called phylogenetic logistic regression, which tests for a correlation between continuous and discrete variables in closely related species, I found a statistically significant correlation between increase in sacral count and larger body size ( $p = 0.002$ ). In dicynodont, anterior sacral vertebrae are not added via the transformation of trunk vertebrae, but by the addition of novel elements anterior to the primordial three. Likewise, all mammals but xenarthrans (e.g., armadillos, sloths, anteaters) are restricted to 2 or 3 sacral vertebrae, and sacrals are added exclusively from the tail. This suggests that dicynodonts were able to escape a constraint on body plan that was otherwise common among mammals and their close relatives.

# GLOBAL DISCONTINUITY STRUCTURE OF THE MANTLE TRANSITION ZONE FROM FINITE-FREQUENCY TOMOGRAPHY OF SS PRECURSORS

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We report global structure of the 410-km and 660-km discontinuities from finite-frequency tomography using frequency-dependent traveltimes measurements of SS precursors recorded at the Global Seismological Network (GSN). Finite-frequency sensitivity kernels for discontinuity depth perturbations are calculated in the framework of traveling-wave mode coupling. We parametrize the global discontinuities using a set of spherical triangular grid points and solve the tomographic inverse problem based on singular value decomposition. Our global 410-km and 660-km discontinuity models reveal distinctly different characteristics beneath the oceans and subduction zones. In general, oceanic regions are associated with a thinner mantle transition zone and depth perturbations of the 410-km and 660-km discontinuities are anti-correlated, in agreement with a thermal origin and an overall warm and dry mantle beneath the oceans. The perturbations are not uniform throughout the oceans but show strong small-scale variations, indicating complex processes in the mantle transition zone. In major subduction zones (except for South America where data coverage is sparse), depth perturbations of the 410-km and 660-km discontinuities are correlated, with both the 410-km and the 660-km discontinuities occurring at greater depths. The distributions of the anomalies are consistent with cold stagnant slabs just above the 660-km discontinuity and ascending return flows in a superadiabatic upper mantle.

Advisor: Ying Zhou

# *IN SITU* INVESTIGATIONS OF THE STRUCTURE AND EVOLUTION OF HYDROXYLAPATITE PRECURSOR PHASES USING PAIR DISTRIBUTION FUNCTION ANALYSIS.

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Mineral nucleation and growth is a fundamental mechanism that underlies our conceptual understanding of rock formation and biomineralization. Classical models of crystal growth involve atom by atom addition to mineral surfaces in terrace, step, or kink positions. Recent studies have identified minerals whose growth mechanics fall outside of the classically defined models. These 'non-classical' processes often include the formation of metastable phases along kinetically and thermodynamically driven pathways. These phases can include nanoparticle, amorphous, or crystalline precursors, which then aggregate or transform into a bulk crystalline end member. Crystallization of hydroxylapatite (HA) in aqueous solution is known to proceed through a series of precursor phases, including amorphous calcium phosphate (ACP). Traditionally ACP formation was seen as the first step in HA synthesis, but recent studies suggest that an additional phase of calcium phosphate prenucleation clusters (PNC), precedes ACP development. Theoretical models of PNCs and the short-range structure of ACP have been proposed, but there is a limited amount of measured structural data for comparison. Our goal is to collect *in situ* structural data of ACP and PNC to compare with the theoretical models.

Using a syringe pump to flow calcium and phosphate solutions through a mixed-flow reactor (MFR) and into the path of an x-ray beam for pair distribution function (PDF) analysis, we have captured short-range structural information of these nano and amorphous phases. By altering the pumping speed of the initial solutions, we also collected a time resolved series of data. This approach is an improvement upon previous structural studies because it allows us to analyze samples in their native hydrated states. We collected structural data of ACP using the MFR, which implies a change in the local bonding geometries between calcium and phosphate ions based on synthesis conditions. Monodentate bonding geometries are predominate at lower Ca/P ratios, while bidentate bonding becomes more prevalent as the ratio increases. There is also a clear structural transformation that occurs over time. Samples collected over a range of reaction times ranging from 1 to 20 minutes show periodic structural changes that believe shows the transformation from PNC to ACP. Future work will focus on modeling the end member structures of this data series with published theoretical models of PNC and ACP in an attempt to structurally distinguish the two phases.

Advisor: Dr. F. M. Michel

## IT'S IN THE BONES: USING LIMB BONE HISTOLOGY TO REVEAL THE EVOLUTION OF GROWTH RATES WITHIN AETOSAURIA (REPTILIA)

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Growth is one of the fundamental requirements used when defining all life and growth characteristics of vertebrates help us understand many aspects of evolution and other life traits such as its metabolism or ontogenetic patterns (embryo through adulthood). This is especially true when looking at organisms in the fossil record, as there is little direct evidence of metabolic activity levels, or abundant fossils of different ages to reconstruct ontogeny. Instead, we can use preserved indicators of growth within the bones of extinct animals to reconstruct their growth and make inferences about metabolic levels and growth stage. Beyond individual organisms, we can reconstruct growth rates of the entire species. Then by comparing multiple species within the same group we can discover how the group as a whole was evolving growth strategies through time.

To examine the growth patterns of an extinct aetosaur (armored extinct crocodile relative), I sectioned multiple bones from a single species of from North Carolina, *Coahomasuchus chathamensis*, including limb bones. The addition of limbs was important because only the one other study has included aetosaur limbs. I characterized the bone tissue of the one species and determine the growth stage of the holotype specimen. I uncovered a rapid growth pattern in which individuals seemed to reach skeletal maturity after only five years, faster than living crocodylians grow. Moreover, I found *C. chathamensis* was growing two to three times faster than a similarly sized aetosaur from Argentina, *Aetosauroides scagliai*. So then why were these fairly closely related animals growing so differently? Unfortunately, these are the two best sampled aetosaurs, and little data of aetosaur limb bone growth has been explored. By systematically sampling the radius and fibula (fore- and hindlimbs) of aetosaurs for representatives across the tree of Aetosauria, and sampling throughout the Late Triassic (~237-201 Ma), I can reconstruct the evolution of growth rates within this single clade.

With such a dataset I will be able to describe the evolution of growth rates within a large group of reptiles across the globe for nearly 30 mya. The predicted outcomes for aetosaur growth rate increases or decreases are: 1) following Brownian motion (random walk) or 2) represent directional change. The discovery of patterns is a case study for how groups of animals evolve their rates of growth through time, and form the basis of linking the evolution of growth to extrinsic patterns, like global CO<sub>2</sub> changes.

Advisor: Dr. S. J. Nesbitt

# QUANTITATIVE ANALYSIS OF FINE-GRAINED MINERALS MIXTURES BY RAMAN SPECTROSCOPY

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Many rock samples are composed of very-fine grained mixtures of various minerals. One example is serpentinite, which often contains mixtures of lizardite, chrysotile, magnetite and brucite with grain sizes too small to be identified optically or by electron microprobe. One technique that holds promise for quantitative analysis of fine-grained samples is Raman spectroscopy. Each mineral phase has a characteristic Raman spectrum, and the peak intensities are proportional to the amount of analyte. However, mineral grain size and orientation also has big impact on the intensity, but there is just little research on how to eliminate the influence of changes in the physical properties to improve the accuracy of Raman spectroscopy quantitative analysis. At present, spectral preprocessing methods such as Multiplicative Signal Correction-MSC, Standard Normal Variate-SNV, Extended Inverse Scatter Correction-EISC, and Extended Multiplicative Signal Corrector-EMSC are often used to eliminate the multiplier effect caused by physical properties change. However, these spectral preprocessing methods have very demanding requirements on the system, so it's kinda very hard to meet these requirements in practice. Therefore, in order to achieve accurate quantitative analysis of complex multiphase samples by Raman spectroscopy, it is necessary to develop a multiphase system, which is of great significance. The goal of my current study is to examine the maximum average grain size that results in an accurate estimate of the proportions of each mineral in a fine grained sample.

Simple mixtures of quartz and feldspar powder below 53 micrometers were selected for the first test, and they were mixed in known proportions and analyzed by XRD, and then we used peak areas to get ratios which is a simple way to estimate percentages. The next step is doing Raman analysis to compare the results with XRD. Furthermore, more experiments with samples of different minerals and sizes and also with different references will be done in the future.

# RELATING REGIONAL-SCALE PERMEABILITY CHARACTERISTICS TO FLOOD BASALT EMPLACEMENT MECHANISMS IN LARGE IGNEOUS PROVINCES

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This study reports on a geostatistical analysis of permeability within the Columbia River Basalt Group (CRBG), USA, and results suggest a direct relationship between regional-scale permeability structure and the lithospheric response to flood basalt emplacement. The geostatistical characteristics of CRBG permeability reveal that (1) horizontal permeability is spatially correlated with a 5:1 anisotropy ratio; (2) the direction of maximum horizontal spatial correlation is N40°E, and parallel to the longitudinal axis of the bedrock depression underlying the CRBG; and (3) CRBG permeability tends to decay with depth until ~950 m, below which permeability increases ~2 orders of magnitude. These observations are consistent with the CRBG emplacement model in which flood basalt flows initially fill a topographic depression, while further basalt emplacement substantially increases lithospheric loading. This rapid loading induces crustal subsidence, which is manifest as basal flexure within the CRBG. The presence of basal flexure results in tensile stresses that preferentially maintain open fractures in the direction parallel to the longitudinal axis of the bedrock depression, thus resulting in (1) higher than expected permeability at depth within the CRBG and (2) anisotropic permeability correlation aligned with the underlying bedrock depression. These results provide compelling evidence for structural controls on the regional-scale CRBG permeability distribution, as well as a process-based explanation relating flood basalt emplacement mechanisms to regional-scale permeability characteristics of continental large igneous provinces.

Advisor: Dr. R. M. Pollyea

## IMPLEMENTING REAL-TIME GNSS MONITORING TO INVESTIGATE CONTINENTAL RIFT INITIATION PROCESSES

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Continental rift initiation remains an elusive, yet fundamental, process in the context of plate tectonic theory. Our early work in the Natron Rift, Tanzania, the Earth's archetype continental rift initiation setting, indicates feedback between volcanic deformation and fault slip play a key role in the rift initiation process. We found evidence that fault slip on the Natron border fault during active volcanism at Ol Doniyo Lengai in 2008 required only  $\sim 0.01$  MPa of Coulomb stress change. This previous study was limited by GPS constraints 18 km from the volcano, rather than immediately adjacent on the rift shoulder. We hypothesize that fault slip adjacent to the volcano creeps, and without the need for active eruption. We also hypothesize silent slip events may occur over time-scales less than 1 day.

To test our hypotheses, we designed a GNSS network with 4 sites on the flanks of Ol Doiyo Lengai and 1 site on the adjacent Natron border fault with the capability to calculate 1 second,  $\sim 3$ -5 cm precision positions. Data is transmitted to UNAVCO in real-time with remote satellite internet, which we automatically import to the EarthCube building block CHORDS (Cloud Hosted Real-time Data Services for the Geosciences) using our newly developed method. We use CHORDS to monitor and evaluate the health of our network while visualizing the GNSS data in real-time.

In addition to our import method we have also developed user-friendly capabilities to export GNSS positions (longitude, latitude, height) with CHORDS assuming the data are available at UNAVCO in NMEA standardized format through the Networked Transport of RTCM via Internet Protocol (NTRIP). The ability to access the GNSS data that continuously monitors volcanic deformation, tectonics, and their interactions on and around Ol Doiyo Lengai is a crucial component in our investigation of continental rift initiation in the Natron Rift, Tanzania. Our new user-friendly methods developed to access and post-process real-time GNSS positioning data can also be used by others in the geodesy community that need  $\sim 3$ -5 cm precision positions (longitude, latitude, height).

## DATA COLLECTION, MANAGEMENT, AND PROCESSING OF DRIPWATER RATES AND CHEMISTRY IN JAMES CAVE, VIRGINIA

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Karst aquifers are important sources of drinking water worldwide. Protection of karst water resources requires information on the source of recharge to the underlying aquifer. In karst, recharge can occur via sinking streams, direct infiltration through features such as sinkholes, and diffuse recharge through the bedrock. A team at Virginia Tech instrumented a cave (James Cave) in Pulaski Co in 2007 to study mechanisms of diffuse recharge via dripwater. As a result, there are 10 years of data, including dripwater rates and specific conductance, that have been collected at multiple sites in the cave. Dripwater rates are measured on 10-min intervals using rain gauges instrumented with dataloggers, and the specific conductance is measured on 10-min intervals using conductivity loggers. In addition to collecting these data, the processing and management of data plays important roles in the project. For my research project I downloaded data from the instrumentation in the cave every month or other month. After downloading, I processed the data through Hoboware software and exported datasets with consistent units and formatting. During data processing, I checked the validity and quality of the data. I then merged datasets in a time series software (Aquarius) and performed basic statistical analysis on the data. The main result of my project is a compiled, merged dataset from Fall 2014 to Fall 2017. The dataset will be appended to a previous dataset made available to the public via VTechWorks. The methods and approaches that I used for data processing and management in this project can be utilized by similar projects that have high-frequency hydrologic data.

Advisor: Dr. M. E. Schreiber

# 3D PRINTED FLOW CELLS FOR REAL-TIME GEOCHEMICAL INVESTIGATION OF FERRIC HYDROXYL-SULFATE FORMATION

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Real-time characterization of mineral nucleation and growth phenomena is becoming increasingly necessary for investigating how materials nucleate, grow, transform, and interact with their surrounding environments. For geochemical conditions in particular, real-time methods are vital for observing the often fleeting, metastable stages of formation. For example, the formation pathways of iron oxyhydroxide sulfates such as schwertmannite are poorly understood, and since these materials are known to co-precipitate and adsorb toxic contaminants, the details of their growth have important implications for quantifying biogeochemical transport of toxic species. However, studying these complex formation mechanisms in the laboratory requires intricate, custom experimental setups. To that end, we are fabricating custom reactors and flow cells for geochemical experiments by 3D printing stereolithography (SLA). Coupled with in-line analytical techniques such as small angle x-ray scattering (SAXS), we can employ these 3D printed devices to obtain novel mechanistic information via *in-situ* characterization.

Before we can comfortably deploy our 3D printed devices, it is necessary to know if the material, a methacrylate-based photopolymer, is compatible with the relevant geochemical conditions. Accordingly, we are performing tests at various post-processing stages of our material and assessing if the custom reactors are stable at a range of pH (0-12) conditions. The stability of the material is being evaluated by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) which provide thermal degradation patterns and mechanical properties, respectively. Early *in-situ* SAXS experiments using 3D printed flow cells allowed us to observe the evolution of ferric hydroxide nanoparticles as they advance towards schwertmannite or goethite, depending on pH. Preliminary results indicate that at low pH (1.8-3.5), the primary particle size remains the same as the system proceeds toward schwertmannite; at higher pH (5.6-6.5), however, particles of the same starting size grow linearly as the system evolves towards goethite. These early experiments suggest that initial FeO(OH)-like particles are rapidly coated by the negatively charged sulfate anions at low pH, inhibiting growth. As the pH increases, -OH group can more easily displace the sulfate groups and the system advances towards goethite. In order to obtain further mechanistic insight, we will couple our custom reactors with in-line analytical techniques across a variety of experimental conditions. With these methods we aim to elucidate the often transient phases of crystallization, improve experimental design versatility, and reduce costs associated with laboratory-based geochemical research.

# A LARGE ARCHOSAURIFORM (?ERYTHROSUCHID) MAXILLA FROM THE MIDDLE TRIASSIC MOENKOPI FORMATION SHEDS LIGHT ON THE BIOGEOGRAPHY OF LARGE BODY SIZE EVOLUTION DURING THE POST-PERMIAN ARCHOSAURIFORM RADIATION

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The ancestors of modern birds and crocodylians, the archosauriforms experienced a major period of diversification following the end-Permian mass extinction 251 million years ago. There is an excellent global record of large bodied archosauriforms from the Late Triassic but their representation is sparse from the Early Triassic, closer in time to the extinction event, and primarily limited to locations that were at high latitudes during that time. Here, we describe three partial maxillae from the Anton Chico Member of the Moenkopi Formation of New Mexico that belonged to a large, carnivorous archosauriform.

We identify these fossils as belonging to an archosauriform based on the presence of an antorbital fossa, tooth serrations, and thecodont dentition, but the presence of a large foramen on the anterolateral portion of the lateral surface excludes it from Archosauria, a less inclusive group containing birds, crocodiles and their ancestors. The convex curve of the ventral edge supports placement within Erythrosuchidae, a group of Archosauriformes with large heads relative to body size, but all specimens are missing the dorsal process, a portion of the maxilla important for diagnosing early archosauriform clades. We estimate that the skull of this animal was at least 60 cm in length, comparable to that of nearly contemporaneous archosauriforms from high latitudes (e.g. *Fugusuchus hejiapensis*).

The presence of this animal in New Mexico confirms that carnivorous archosauriforms of this size were present in low latitudes during the Anisian stage of the Middle Triassic and not restricted to higher latitudes. In addition, this suggests that large body sizes in archosauriforms were already globally distributed by the Middle Triassic, and therefore, must have evolved earlier or over a wider ecological and geographical range than was previously thought. It has been suggested that there is a relationship between latitude and speed of recovery from mass extinctions; however, these specimens suggest that pattern may be restricted to marine systems, and evidence to support this hypothesis in terrestrial systems may merely be an artifact of incomplete sampling.

## EVOLUTION OF HEAT FLOW WITH AGE ON THE SOUTHERN FLANK OF THE COSTA RICA RIFT

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We have analyzed 67 new conductive heat flow measurements at five sites ranging between  $\approx 1.6$  and 5.7 Ma on the young southern flank of the Costa Rica Rift (CRR) that were collocated with a high-resolution multi-channel seismic line, extending from the ridge axis to ODP hole 504B. These data were collected as part of a major interdisciplinary NERC and NSF-funded collaboration entitled: Oceanographic and Seismic Characterization of heat dissipation and alteration by hydrothermal fluids at an Axial Ridge (OSCAR), to better understand links between crustal evolution, hydrothermal heat loss and the impact of this heat loss and fluid mass discharge on deep ocean circulation. For the five heat flow sites, the mean observed conductive heat flow,  $q_{obs}$ , is  $\sim 80 \text{ mWm}^{-2}$ . This is  $\approx 30\%$  of the mean lithospheric heat flux,  $q_{th}$ , expected from half-space conductive cooling model, indicating that the  $\approx 70\%$  deficit is manifested as advective heat flux with a mean of  $\sim 230 \text{ mWm}^{-2}$  between  $\approx 1.6$  and 5.7 Ma. The ratio  $q_{obs}/q_{th}$  varies significantly from site to site, indicating that advective heat loss is influenced by “local” processes of hydrothermal heat transfer in young crust such as outcrop to outcrop flow, discharge through faults, topographically driven convection etc.,

The ratio  $q_{obs}/q_{th}$  reaches  $\approx 1$ , commonly called the “sealing age”, by  $\sim 5.7$  Ma, which contrasts plate cooling reference models that predict a significant deficit in conductive heat flow up to ages  $\sim 60$ -70 Ma. Factors influencing the “sealing age” include crustal permeability reduction, buoyancy drive decrease, and cessation of advective heat loss to the ocean as a result of thick sediment blankets. At  $\sim 5.7$  Ma the CRR topography is buried under  $\approx 250$  m of sediment and we show that sealing age of  $\sim 5.7$  Ma at the CRR is largely a function of increasing sediment thickness and burial of basement exposure. Heat is still redistributed by subcritical, topographically driven fluid convection at and greater than  $\sim 5.7$  Ma crust but significant large-scale advective heat loss across the low permeability sediments ceases.

## **100 MILLION YEAR OLD BLOOD CELLS? INVESTIGATING BIOLOGICAL PRESERVATION IN AN EARLY CRETACEOUS DINOSAUR**

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Body fossils represent an extraordinary set of geologic circumstances leading to the preservation of parts of an organism beyond the time when even the last traces of most no-longer-living things have decomposed into the environment. Most of these exceptional remains are the hard parts of the body such as shells, bones, and scales, but some discoveries preserve soft body parts like leaves or even the internal organs of an animal. Knowing that these body parts can be preserved, what other original features may be present in excellently preserved fossils – can we detect traces of the biological molecules synthesized by these organisms or even find in-tact cells which are not part of the bone?

Over the last few decades, researchers have been debating these possibilities. New evidence for biomolecule and cell preservation are regularly discovered, and face critical analysis by other researchers. In 2001, reddish spheres were found throughout fossilized blood vessels from a 125-million-year-old Chinese dinosaur, they looked very much like red blood cells and were claimed as such. This claim came before potential soft tissues and biomolecules were found in younger North American dinosaur fossils, but did not receive the same critical attention since it was published only in Mandarin. Now, I have started to analyze these same specimens to collect chemical evidence of the identity of these purported blood cells. I have sent bone fragments to the Texas Materials Institute for preliminary ToF-SIMS analysis, and made new thin sections for RAMAN spectroscopy to examine the chemical makeup of the spheres.

I will travel to China to collect sediment samples from the collection site and additional bone material from the original specimen, including a sample of the bone-matrix contact, to compare the chemical makeup of the matrix and the bone – allowing me to measure the chemical makeup across the bone-matrix contact using further ToF-SIMS analysis to determine whether chemical signatures in the bone are original to the dinosaur or have been introduced from the environment during fossilization. This will allow me to accurately assess the chemical data I collect from the spheres and any potential evidence of biomolecules. This research will provide a long-overdue chemical study and hopefully support the inclusion of foundational non-western research in scientific discussion of biomolecule and blood cell preservation. By furthering our knowledge of soft element preservation, we can expand our understanding of the incredible process of fossilization, the very foundation of paleontology.

Advisors: Dr. S. Xiao & Dr. S.J. Nesbitt

## MICROFOSSILS OF THE DOUSHANTUO: TRACE METAL ANALYSIS

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In paleontological research, understanding the nature of preservation can provide information that other observations cannot. Since the fossil record is directly related to the environments that organisms are preserved in, it is crucial to understand the preservational processes and environments. Not only does this help the paleontological interpretation of the organisms, but it can also help narrow down where to look for more fossils. Microfossils from the Ediacaran Doushantuo Formation are famous not only for their significance in the diversification of multicellular eukaryotes, but also for their exceptional (Doushantuo-type) preservation through phosphatization. The nanocrystals that preserve these organisms are micro- and nano-crystalline carbonate fluoroapatite (CFA). The nanometer-size of the apatite crystals is critical for the high-resolution preservation of fine anatomical details that would commonly be absent in other types of preservation. Our goal is to develop a model to understand environmental and geochemical factors that control CFA crystal size through chemical analysis of the fossils themselves.

Apatite is a mineral that tends to incorporate many different elements into its crystal structure. We will be analyzing these trace elements using a variety of methods including Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy, X-Ray Diffraction, Secondary Ion Mass Spectrometry, and Laser Ablation Inductively Coupled Plasma-Mass Spectrometry. The Doushantuo Formation has a variety of microfossil taxa, and our analysis will be focused on two taxa: *Megashpeara*, which is interpreted as an early animal embryo, and *Archaeophycus yunnanensis*, which is interpreted as multicellular algae related to red algae. We will be collecting compositional data on the crystals that make up the fossils and comparing the results from the different taxa. We hypothesize that the magnesium concentration of the crystals may be a factor controlling crystal size and may lend insight into the exceptional fossil preservation in the Doushantuo Formation. With other data such as crystal morphology and other geochemical data from the Doushantuo Formation, this trace element analysis may prove to be crucial for a deeper understanding of these fossils and their preservation.

# METAL FLUXES ACROSS THE SEDIMENT WATER INTERFACE IN A DRINKING WATER RESERVOIR

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Elevated concentrations of soluble iron (Fe) and manganese (Mn) in drinking water degrade water quality by affecting taste, odor, and color. Under oxic conditions (dissolved oxygen (DO) >2 mg/L), Fe and Mn occur as insoluble minerals in sediments but the depletion of DO in the hypolimnion (bottom waters) of reservoirs during summer thermal stratification can lead to the reduction of Fe and Mn to their soluble forms, which can then be released into the water column. In response, many water utilities have installed hypolimnetic oxygenation (HOx) systems to control metal concentrations *in situ* in drinking water reservoirs. However, previous research found anoxic (DO < 0.5 mg/L) conditions can still develop within sediments even with operational HOx systems, allowing for the reduction and release of soluble Fe and Mn into the water column.

My research goal is to directly quantify Fe and Mn fluxes at the sediment-water interface in a local drinking water reservoir in response to varying oxygen conditions. Falling Creek Reservoir (FCR) is a small, eutrophic drinking water reservoir located in Vinton, VA that is owned and operated by the Western Virginia Water Authority. FCR typically exhibits thermal stratification May-October. In 2013, a HOx system was installed at FCR to prevent low DO in the hypolimnion. Our research team has been collecting water quality data at FCR since that time.

For this project, I will directly measure metal fluxes at the sediment-water interface by deploying sediment flux chambers at multiple sites in FCR for a week during summer stratification. Water will be pumped from the chamber to a field spectrophotometer coupled with an autosampler and analyzed for metal concentrations on a minute time scale. Metal fluxes will be calculated using concentration changes of Fe and Mn in chamber water during the deployment period. DO concentrations will be measured using *in situ* probes during the deployment. This research will help drinking water plant managers better predict when metal loads will be high, allowing them to preemptively treat the reservoir using the HOx system.

# NUMERICAL ANALYSIS OF THE FRACTURED ROCK AQUIFER SYSTEM IN PLOEMEUR, FRANCE, TO QUANTIFY LOCAL AND REGIONAL RECHARGE

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Distinguishing the character and geometry of fractured rock aquifers holds great value for evaluating sustainable yields, as well as implementing protective measures for managing these systems. Presently, fractured rock systems have been examined using time series hydraulic head data collected under two conditions: seasonal fluctuations and long-term pumping. However, the hydraulic head data alone is not sufficient to characterize the fracture geometry nor provide insight to the structural controls on the system. These factors are more accurately characterized by surface deformation, as fractures can deform under moderate to high head changes and impact the storage properties of the system.

Our proposed research concerns a system of fractured crystalline rocks near the town of Ploemeur in the Brittany province of France. We plan to characterize the groundwater flow within the system using a combination of surface deformation signals and water level data collected at daily, monthly, yearly, and decadal intervals. Between short-term monitoring of two-day aquifer tests and long-term monitoring over the span of years, two apparent spatial deformation signals have been identified for the research site, visibly displaying the correlation of deformation with groundwater withdrawal and recharge source locations. The recharge sites are of particular significance, as the annual withdrawal from the system nears one million cubic meters and minimal drawdown is observed. This has raised questions as to the origins of the large amount of recharge that would be necessary to sustain such a system. Extensive monitoring has also shown a roughly three-month lag between seasonal water-level and the monthly precipitation, posing additional questions about the groundwater movement through the unsaturated zone. Surface deformation data may help to explain these factors, as we believe it may represent various factors such as declining heads and loading of precipitation in the unsaturated zone.

The primary object of this study is to address the hydromechanical properties and fracture orientations that have led to the development of the unique deformation signals from the Ploemeur site. We plan to use a combination of unsaturated and saturated zone modeling of the faulted system using MODFLOW and ModelMuse to attempt to decipher the mechanisms constraining recharge and the lag between hydraulic head and precipitation, as well as the complex deformation signals and thickness of the unsaturated zone.

## A COMPARATIVE ASSESSMENT OF THE ROLE OF ANOXIA DURING THE CAMBRIAN SPICE EVENT

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The Cambrian SPICE (Steptoean Positive Carbon Isotope Excursion) is recognized as a major oceanographic event recorded in globally-distributed stratigraphic sections as positive isotopic shifts in marine carbonates ( $\delta^{13}\text{C}_{\text{carb}}$ ), organic matter ( $\delta^{13}\text{C}_{\text{org}}$ ), sulfate ( $\delta^{34}\text{S}_{\text{CAS}}$ ) and pyrite ( $\delta^{34}\text{S}_{\text{py}}$ ). These trends are thought to result from a transient increase in the areal extent of marine anoxia, a process that enhances the burial efficiency of organic carbon and pyrite in sediments (materials rich in the light isotopes  $^{12}\text{C}$  and  $^{32}\text{S}$  respectively). However, direct sedimentary (e.g., abundant black shale) and geochemical (e.g., redox proxy) evidence for such a change is scant. While the antiquity of this event is likely responsible for the loss of much of this evidence, through destructive tectonic processes, a number of stratigraphic successions suitable for investigating this hypothesis exist.

Here, three such successions from sedimentary basins distributed around the margins of the Iapetus Ocean are compared to explore the relationship between local redox conditions (tracked using iron speciation as a proxy) and the isotopic trends of the SPICE. The units studied are: the Nolichucky Formation of eastern Laurentia (Ohio and Kentucky), the Alum Shale of Baltica (Sweden), and the Outwoods Shale of Avalonia (U.K.). Our iron speciation analyses indicate consistently oxygenated conditions prior to the SPICE along Laurentia, while Avalonia was intermittently anoxic, and Baltica was persistently anoxic. During the onset of the SPICE (positive shift in  $\delta^{13}\text{C}$ ), anoxic conditions developed in Laurentia, and intensified in Avalonia and Baltica, developing into persistent euxinia (anoxia with free  $\text{H}_2\text{S}$  in the water column) at the later location. These redox changes were coupled with an increase in pyrite abundance and  $\delta^{34}\text{S}_{\text{py}}$  at each location. Average total organic carbon (TOC) showed little change in relation to the SPICE at the location in Laurentia (~0.15 wt.%), but increased in conjunction with the excursion in both the Avalonia (~1 to 1.5 wt.%) and Baltica (~8 to 12 wt.%) sections. While large differences in nutrient availability and sedimentation rates are likely responsible for the between-site differences in TOC, the shift to more reducing conditions during the SPICE is the most likely cause of the within-site TOC increases recorded at the Avalonia and Baltica locations. The data presented here provide compelling geochemical evidence for increased anoxia and organic carbon and pyrite burial associated with the SPICE while also illustrating important differences in its localized stratigraphic expression.

# GLOBAL MANTLE FLOW MODELLING CONSTRAINED BY GEOID AND PLATE MOTIONS: MANTLE RHEOLOGY REVISIT AND LARGE-SCALE DRIVING MECHANISM FOR CONTINENTAL PLATES

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Global surface geoid and plate motions provide important constraints on instantaneous mantle circulation models. Simultaneously fitting these two observables will lead to more reliable predictions on mantle flow, and the buoyancy forces driving the convection. This study constructs 3D dynamically consistent mantle flow models jointly constrained by geoid and plate motions. Through our forward modelling tests, we reexamine some previous assumptions/debates regarding the mantle rheology. Our results show that both the weak upper mantle (100 km - 410 km) and weak transition zone (410 km - 670 km) radial viscosity profiles can achieve similar high fitting to the observed geoid and plate motions. The viscosity jump at ~670 km is more crucial to fit geoid than the viscosity jump at ~1000 km mid-mantle depth. We also confirm the strong dependence of surface geoid on the lower mantle viscosity, which is also found to hardly influence the surface plate motion directions but has a significant control over the magnitudes of plate motions. Clearly-resolved global slab buoyancy plus seismic tomography are required to reproduce the continental plate motions, which indicates the potential difference of the driving mechanism between continental and oceanic plate motions. Due to the less decoupling to the global-scale circulation from the thick cratonic roots, the continental plate motions are significantly controlled by the large-scale driving effect from the far-field slabs. This also indicates that regional geodynamic models, specifically those focusing on continental plates must account for the global-scale mantle flow induced by the far-field subduction zones.

Advisor: Dr. S. D. King

## PETROCHRONOLOGIC EVIDENCE FOR OUT-OF-SEQUENCE THRUSTING, NAVER NAPPE, SCOTLAND

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Northern Scotland hosts an orogenic wedge that consists of several mid-crustal thrust nappes including the Moine (most foreland positioned), Ben Hope and Naver nappes. We have used a combination of metamorphic petrology and geochronology to constrain the thermal evolution of the Naver nappe, which comprises the hinterland of this orogenic belt. Monazite and xenotime, two rare earth element, uranium and lead bearing phosphates, can be used to simultaneously constrain metamorphic temperature and timing of crystallization based on a calibrated thermometer and U-Pb geochronology. Samples from across the Naver nappe suggest temperatures were 675-700°C at 420-425 Ma. These temperatures are in agreement with observed microstructures (chessboard extinction in quartz) and thermodynamic modeling of metamorphic phases. Monazite populations in several samples have very distinct compositional zoning that, when linked to thermodynamic modeling, delineate a temperature-time history. Peak temperatures were reached by a heating rate of 15-25°C/Ma and post-peak cooling occurred at a rate of ~10°C/Ma.

These data allow us to draw important conclusions about the structural and tectonic history of Northern Scotland. The Moine thrust is the basal thrust of the orogenic wedge. It is widely regarded that deformation in the Moine thrust zone ceased by 429 Ma (Goodenough et al., 2011). This implies that all deformation ceased by that time and only passive exhumation was ongoing. In contrast, our data suggest that peak temperatures in the hinterland of this orogenic system occurred at 425-420 Ma and prograde metamorphism was ongoing at 430-425 Ma. Our data imply ongoing burial and deformation in the hinterland of the orogen at the same time igneous features cross-cut the Moine thrust in the foreland (Goodenough et al., 2011). Peak metamorphism in the Naver nappe was thus produced by burial during out-of-sequence thrusting. Additionally, exhumation occurred following peak metamorphism, which suggests continued thrusting in the foreland. This was probably accomplished by thrusting at lower structural levels in the broad Moine thrust zone, rather than on the Moine thrust itself.

## IMPLICATIONS OF SEISMICALLY ACTIVE FAULT STRUCTURES IN ANKAY AND ALAOTRA REGIONS OF NORTHERN AND CENTRAL MADAGASCAR

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The purpose of the study is to gain a better understanding of the seismically active fault structures in central and northern Madagascar. We study the Ankay and Lake Alaotra regions of Madagascar, which are segmented by multiple faults that strike ~N-S. In general, normal seismic events occur on faults bounding the Alaotra-Ankay rift basin where Quaternary alluvium is present. Due to this pattern and moderate amounts of low magnitude seismic activity along these faults, it is hypothesized the region currently undergoes E-W extension. In this work we test how variations in fault strength and net slip changes influence expected crustal movement in the region. Using the Coulomb stress failure point as a test of strength we are able to model the Alaotra-Ankay region using MATLAB Coulomb 3.3.01. This program allows us to define realistic Poisson's ratio and Young's modulus of mapped rock compositions in the region, i.e. paragneiss and orthogneiss, create 3D fault geometries, and calculate static stress changes with coinciding surface displacements. We impose slip along multiple faults and calculate seismic moment that we balance by the 3 observed earthquake magnitudes available in the USGS CMT database. Our calculations of surface displacements indicate 1-3 millimeters could be observed across the Alaotra-Ankay rift. These values are within the observable range of precision GNSS observations, therefore our results will guide future research into the area and direct potential GNSS station installation.

Advisor: Dr. D. S. Stamps

# INVESTIGATING A UNIQUE OPEN OCEAN GEOCHEMICAL RECORD OF THE END TRIASSIC MASS EXTINCTION FROM PANTHALASSA

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The end-Triassic mass extinction (~201 Ma) was a time of intense disturbance for marine communities. This event is estimated to have produced as much as a loss of ~80% of known marine species. The protracted interval of elevated extinction rates is also characterized by a major carbon cycle perturbation and potentially widespread oxygen deficiency within the oceans. While the causes of extinction and environmental feedbacks are still debated it is hypothesized to have been triggered by massive volcanism associated with the Central Atlantic Magmatic Province flood basalts. However, our understanding of the Latest Triassic-Earliest Jurassic interval is limited due to the lack of well-preserved stratigraphic successions outside of the Tethys Ocean (present day Europe), with most of the records from epicontinental and marginal marine settings. To expand our understanding of this critical interval, our study seeks to document biological and environmental changes elsewhere. Specifically, I document and reconstruct these changes in the equatorial Panthalassan Ocean.

I will present new data from a sedimentary succession preserved in the Wrangell Mountains of Alaska that spans the Late Triassic through Early Jurassic. The sedimentary succession represents a mixed carbonate-siliciclastic ramp that was deposited at tropical latitudes, adjacent to an island arc in the open Panthalassan Ocean. This succession affords a unique view of open marine conditions, and also holds the potential for excellent temporal control as it contains abundant ash layers throughout, as well as, key ammonite and bivalve fossil occurrences that provide biostratigraphic control. I will present an integrated geochemical and paleontological record from this site using several geochemical proxies (carbon,  $\delta^{13}\text{C}_{\text{carb}}$  and % total organic carbon, sulfur,  $\delta^{34}\text{S}$ , as well as pyrite contents and iron speciation) along with ammonite and bivalve occurrence data to reconstruct the record of environmental and biological change within the open Panthalassan Ocean, and relate these data to existing marine records of the end-Triassic extinction.

Advisor: Dr. B. C. Gill

# THE APPLICABILITY OF ARTIFICIAL NEURAL NETWORKS IN DETERMINING THE PARTITIONING OF VOLATILE ELEMENTS WITHIN VOLCANIC MELT INCLUSIONS

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Artificial neural networks (ANNs) have become widely used as a data analysis tool because of their flexibility in handling diverse data types and applicability across many fields. An ANN behaves in the same way as an equation that calculates dependent variables from independent variables. However, unlike a theoretically- or empirically-derived equation, the behavior of an ANN emerges from a random starting condition by an iterative process of gradient descent to minimize its error against a dataset that includes pre-labeled inputs and outputs. For this reason, an ANN acts as a so-called “function approximator.” Melt inclusion datasets have a high dimensionality inherent to geochemical data as well as many additional qualitative factors like the identity of the host mineral, the host rock type, and additional morphologic and petrographic information. For these reasons, the challenge of using melt inclusions to infer pre-eruptive volatile abundances in volcanic systems is a problem that may be well-suited for the application of ANNs.

To explore the applicability of applying ANNs in the interpretation of melt inclusions, the goal of this study is to train an ANN to predict the volatile element composition of melt inclusion glasses based on their major and trace element concentrations. The precompiled GeoRoc melt inclusion dataset was used for training, and ANNs were generated using the R library, “neuralnet.” The process of selecting topological features ANNs is non-trivial because a neural net may consist of any number of nodes in different configurations, and the training process must be optimized based on the acceptable error threshold of the ANN, the amount of training steps allowed for the network to reach this threshold, and the number of training iterations to obtain a best result. A “Monty Carlo” approach was used to generate ~600 neural nets so that the optimal features could be determined based on the success of the neural nets in calculating known CO<sub>2</sub> concentrations in the inclusion glasses. Under optimal conditions, the ANNs were able to reproduce about 70% of glass CO<sub>2</sub> concentrations, which are log-normally distributed, within  $\pm 0.4$  log units, which is comparable to the level of precision exhibited by existing models of post-entrapment processes within melt inclusions. This result suggests 1) that both the trapped volatile contents of melt inclusions and the partitioning behavior of volatile elements within them may be estimated using the major and trace element chemistry of the melt, and 2) that the implementation of ANNs in the field of high-temperature geochemistry is likely a useful intermediary step between data collection and the development of theoretically-qualified models.

Advisor: Dr. Yury Klyukin

## INFLUENCE OF TECTONIC DEFORMATION ON ACTIVE VOLCANISM IN CENTRAL AMERICA

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This study involves testing the influence of tectonic deformation on active volcanism and seismic potential in Central America with a particular focus on the Middle America Trench. The approach is to evaluate a tectonic strain rate model to assess (1) the style of deformation and (2) calculate the seismic potential in areas with active volcanoes. The influence of the tectonic deformation can be studied by comparing predicted velocities derived from the strain rate model with existing velocity data. Also, we will quantify seismic potential using the strain rate field for comparison with areas of active volcanism.

Advisor: Dr. D. S. Stamps

# GEODYNAMIC MODELING OF MARTIAN VOLCANISM: FORMATION OF THE THARSIS RISE DUE TO SMALL-SCALE CONVECTION AT THE DICHOTOMY BOUNDARY

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Mars has two major centers of volcanic activity: Tharsis and Elysium. The largest is the Tharsis Rise, a dome ~8000 km in diameter and ~10 km high centered near the equator (Janle and Erkul, 1990). Tharsis has been volcanically active for most of the planet's history, including the past 50-100 Ma (Phillips et al., 2001; Neukum et al., 2004; Richardson et al., 2017). The volcanism is generally attributed to one or more long-lived mantle plumes (Carr, 1973; Kiefer, 2003; Sramek and Zhong, 2012). Tharsis straddles the boundary between the thick crust of the southern highlands and the thinner crust of the northern lowlands, a contrast referred to as the Martian dichotomy (Neumann et al., 2004). Given their positions and correspondingly ancient ages, the dichotomy may be related to the Tharsis Rise (King and Redmond, 2005; Sramek and Zhong, 2010; Sramek and Zhong, 2012; Zhong, 2009). Tharsis could be the result of small-scale edge-driven convection at the boundary, which would explain the volcanism's longevity and the larger size of Tharsis compared to Elysium (King and Redmond, 2005). Edge-driven convection occurs at boundaries between thick, stable lithosphere and thinner lithosphere, for example where cratons meet oceanic lithosphere on Earth (King and Anderson 1998; King and Ritsema, 2000).

I am investigating the origin and evolution of Martian volcanism to evaluate the potential for small-scale convection at the dichotomy boundary to produce the Tharsis Rise. I will use estimates of crustal density to constrain the crustal root thickness required to generate small-scale convection. This study consists of analyzing 3D spherical shell models of solid-state convection in the Martian mantle (e.g. Harder and Christensen, 1996; Roberts and Zhong, 2006). I have implemented several modifications to the finite element code CitcomS to improve modeling of melt production: (1) Internal heating from radioactive decay decreases according to the calculations of Turcotte and Schubert (2002). The code also incorporates (2) the cooling of the core based on Stevenson et al. (1983) and (3) variations in crustal thickness required to support the dichotomy and resulting small-scale convection. The fourth modification, in progress, is the addition of melting calculations. Melting in the mantle is addressed following the method outlined in Kiefer (2003), itself based on the earlier work of Watson and McKenzie (1991). Kiefer et al. (2016) updated this method with the more accurate parameterization of melt fraction developed by Katz et al. (2003).

Advisor: Dr. S. D. King

# INTEGRATING MICRON AND NANOSCALE CHARACTERIZATION OF GRAIN BOUNDARIES IN METAMORPHIC ROCKS

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It is necessary to study metamorphic rocks on multiple scales to understand the processes that drive the transport of heat and recycling of material in the crust. Traditional metamorphic petrology methods involve analyzing rocks from the outcrop scale to the micron scale, but better understanding of recrystallization processes can come through the use of techniques that have not been widely used in metamorphic petrology, by probing nano-scale characteristics of mineral grains and their boundaries.

I develop methods to integrate micron scale petrology with nanoscale structure and chemistry analysis using Transmission Electron Microscopy (TEM). My objective is to characterize garnet-quartz grain boundaries of pelitic schists from the Nelson Contact Aureole, British Columbia, to understand how their properties change as a result of temperature and metamorphic assemblage. Samples from the andalusite, sillimanite, and K-feldspar isograds are the focus of this study.

The rocks were first studied using traditional petrology methods. Mineral textures and grain interfaces were identified using an Optical Microscope, and the chemical zoning of major elements in garnet was determined with an Electron Microprobe. This information can be used to determine whether garnet was growing or breaking down at each metamorphic grade. Garnet was found to be undergoing growth in the sillimanite zone and breakdown in the andalusite and k-feldspar zones.

These classic petrology analyses were used to guide the selection of specific areas of the sample for nanoscale analysis. Samples were prepared for TEM work using the Focus Ion Beam (FIB) liftout technique and Argon Ion Milling. Using a JEOL 2100 TEM, samples were imaged, phases identified by electron diffraction, and chemically characterized spectroscopically. In some grain boundaries, there are voids of up to 400 nm between the phases: these could be due a volume decrease along crystallographic axes during exhumation. The quartz grains contain subgrain boundaries, and the subgrains closer to the garnet crystal have fewer dislocations, which suggests recrystallization of the subgrains at peak temperature. Based on chemical zoning maps collected on the microprobe, the garnet composition is homogeneous near the grain boundary, but finer-scale maps collected on the TEM show nm– $\mu$ m scale compositional changes near the grain boundaries. These observations clearly indicate the importance studying metamorphic rocks using TEM to understand near atomic scale processes in the crust.

Advisors: Drs. M. J. Caddick & F. M. Michel

## CORRELATION OF SULFUR AND STRONTIUM ISOTOPES ACROSS THE BUSHVELD IGNEOUS COMPLEX AND RELATED MAGMATIC FEATURES

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The 2.06 Ga Bushveld Igneous Complex of South Africa is of incredible economic importance, hosting a majority of the world's platinum reserves as well as many other economically important minerals. Because of this, it is critical that the association of separate limbs of the complex at the surface is understood, as there may be vast reserves of resources located underground and unseen between the limbs. Strontium and sulfur isotopes can be used to trace the amount of Archaean sediments assimilated into magma, and may also point towards shared magmatic sources for other Bushveld-aged intrusions nearby. For this research project,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were measured in ten mafic igneous rocks in different zones of the Bushveld igneous complex. When compared to the  $\Delta^{33}\text{S}$  values previously measured from the same rocks, correlations could be drawn between the sulfur and strontium isotope ratio signatures, which allowed us to draw conclusions about the emplacement of the Bushveld complex. For instance, the Northern limb assimilated more sedimentary material than the Eastern and Western limbs. Likewise, it was also found that the nearby Molopo Farms complex reflected  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\Delta^{33}\text{S}$  values of a mantle derived source, with less sedimentary melt contribution. Although the connection of these limbs underground remains unclearly understood, it is known that these intrusions of the same age have incorporated differing quantities of Archaean sedimentary material prior to or upon emplacement.

Advisor: Dr. M. Feineman, Dept. of Geosciences, Pennsylvania State University

## LITHOSPHERIC STRUCTURE OF THE MALAWI RIFT: IMPLICATIONS FOR RIFTING PROCESSES IN MAGMA POOR RIFT SYSTEMS

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Our understanding of how magma poor rifts accommodate strain remains limited largely due to sparse geophysical data from these rift systems. In order to understand the rifting process of magma poor rifts, we investigate the lithospheric structure of the Malawi Rift in the East African Rift System. We analyzed satellite gravity data using the two-dimensional (2D) power-density spectrum technique and 2D forward modeling to estimate the crustal and lithospheric thickness beneath the Malawi Rift. We find (1) thinner crust (~37-39 km) beneath the northern Malawi Rift, and thicker crust (~41-45 km) beneath the central and southern Malawi Rift, (2) along-axis thinning of the lithosphere beneath the entire Malawi Rift with the thinnest lithosphere (115-125 km) occurring beneath the northern Malawi Rift, (3) a relatively east-west belt of thicker lithosphere (~180-210 km) beneath the central Malawi Rift. We infer magma assisted rifting in the northern Malawi Rift where preexisting weaknesses had been observed. Three-dimensional edge-driven convection modeling shows relatively rapid (~30 mm/yr) mantle upwelling beneath the northern Malawi Rift that is coupled to crustal deformation, producing dynamic topography. In contrast, the amagmatic central and southern Malawi Rift segments show slower (~10 mm/yr) mantle upwelling and use preexisting structures to accommodate strain and are characterized by decoupling of the thick crust from the lithospheric mantle. We conclude that continental rift initiation in amagmatic rifts require strain accommodation by preexisting lithospheric structures with further contribution of magmatism as rifting progress.

Advisor: Dr. D. S. Stamps

## RECONSIDERING *BROOKSELLA ALTERNATA*, ENIGMATIC FOSSIL OF THE CONASAUGA FORMATION, SOUTHEASTERN US

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*Brooksella alternata* was first described in 1896 by Charles Doolittle Walcott based on material from the Conasauga Formation in the Southeastern US. The initial report described them as medusoid jelly fish. Since the initial description, *B. alternata* has been variously described as algae, the product of gas bubbles, and multiple feeding traces. The current explanation, based on sectioned samples, is that *B. alternata* is a hexactinellid sponge. In this study, I analyzed samples for the physical criteria (spongocoel, radial canals, oscula, ostia, and hexactinellid spicules) used to support the sponge ascription. I took external measurements and made sections to evaluate these features. I found the bulk composition of *Brooksella* and siliceous and carbonate concretions also from the Conasauga using XRD. I also conducted electron microprobe analysis on thin sections made from both *Brooksella* and concretions to evaluate the composition of specific internal features. I collected in situ samples (most studies rely on surface collected material) to evaluate orientation. I used computed tomography to visualize the internal features of *Brooksella* and co-occurring concretions. I have digitized these internal features and used this data to compare to the expected internal structures of hexactinellid sponges.

My evaluation found *Brooksella* shows large morphological variation, and many of the reported features consistent with a sponge identity are either absent or inconsistent with sponge characteristics. Some features, like reported ostia, I ascribe to taphonomic effects (namely modern weathering by rootlets and lichen). Given the broad morphological diversity of *Brooksella*, similar variation among co-occurring concretions, similar compositions and internal features inconsistent with hexactinellid sponges, the hexactinellid description seems insufficiently supported, and a concretionary origin for *Brooksella* is more likely.

## EFFECT OF ALUMINUM OXYHYDROXIDE COATINGS ON THE PERFORMANCE OF ANOXIC LIMESTONE DRAINS

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Neutralization by limestone is a commonly used treatment for acid mine drainage. The effectiveness of Anoxic Limestone Drains (ALDs) can be reduced by aluminum (Al) oxyhydroxide coatings that form on the limestone, as the coatings can inhibit the transport, and thus neutralization, of hydrogen ions ( $H^+$ ) derived from acid mine drainage. For my M.S. thesis project, I have conducted laboratory mixed flow reactor experiments to determine the effect of Al coatings on the diffusion of  $H^+$  to the surface of limestone and quantify how these Al coatings affect the limestone dissolution rate.

In the experiments, I prepared acidic Al sulfate solutions with Al concentrations ranging from 0.002M to 0.01M and pH ranging from 3.6 to 3.8, typical of conditions found at acid mine drainage sites. I used cleaved surfaces of Iceland Spar as a proxy for limestone. The reactor experiments were conducted at a flow rate of  $2.02 \times 10^{-2}$  ml/sec over a period of 0.20 days. I measured pH in the effluent to determine the rate of  $H^+$  consumption during the reaction of the solutions with calcite. I also analyzed effluent solutions for Al, Ca and S using ICP. Examination of the produced coatings with x-ray diffraction suggests amorphous poorly crystalline gibbsite as the primary Al coating but scanning electron microscope analysis also suggests the presence of poorly crystalline hydrobasaluminite.

Using the experimental data, I calculated the diffusion coefficient of  $H^+$  through the Al coating. Results of the experiments showed that the diffusion coefficient for  $H^+$ , assuming a gibbsite layer, was  $2.4 \times 10^{-13}$  m<sup>2</sup>/sec; assuming a hydrobasaluminite layer, the diffusion coefficient is calculated to be  $3.9 \times 10^{-13}$  m<sup>2</sup>/sec. In either case, the diffusion coefficient is four orders of magnitude smaller than in pure water ( $9.3 \times 10^{-9}$  m<sup>2</sup>/sec). The experimental results will be used to model the decline in the limestone neutralization rate as the coatings grow thicker over time. Results of these experiments will be used to estimate the dissolution of limestone in ALDs under different pH conditions and Al concentrations similar to those found in discharge from pyrite-bearing materials.

## APPLICATION AND VALIDITY OF THE SORTABLE SILT PROXY AS AN INDICATOR OF DEEP-SEA CIRCULATION INTENSITY

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Sortable silt (SS), defined as the 10-63  $\mu\text{m}$  grain-size fraction, is a common paleoceanographic tool in assessing depositional energy and current velocity through time, such as changes in ocean circulation intensity. Ocean circulation is a major forcing on heat and nutrient transfer within and between ocean basins. Global-scale climatic perturbations often affect, to some degree, water mass efficiency and pathways. Understanding changes in ocean circulation, therefore, is a major part of paleoclimatic reconstructions. Here, we use the SS fraction of deep-sea sediments as a physical proxy for deep-ocean currents across the Eocene-Oligocene Transition (EOT;  $\sim 33.7$  Ma). Samples were collected from the Newfoundland Ridge sediment drifts (offshore eastern Canada) during IODP Exp. 342 at Site U1406 and span the middle Eocene to late Oligocene ( $\sim 48$ -26 Ma).

The EOT marks one of the most dramatic climatic changes of the past 100 Ma. A sudden greenhouse to icehouse shift may have resulted in a major reorganization of ocean circulation pathways, ultimately assembling Atlantic Meridional Overturning Circulation (AMOC), which operates today. It is hypothesized that enhanced deep-water formation, carried south along the western edge of the North Atlantic basin, invigorated the Deep Western Boundary Current (DWBC). Grain-size analyses test this hypothesis. Broadly, we hypothesize that grain-size will increase across the EOT, consistent with trends observed  $\sim 250$  km northeast in shallower water ( $\sim 450$  m, both modern and paleodepth) at Site U1411 (Chilton, 2016) and an enhanced DWBC.

Despite the popularity of SS in velocity reconstructions, the method remains untested experimentally. Confirming the validity of SS is paramount to its continued use as a physical paleoceanographic proxy. Under controlled conditions, we aim to test the proxy as a whole, the value of comparing the proportion of SS to proportion of clay in a deposit, and the effects on entrainment and deposition of silts in the presence of varying amounts of clay. Experimental sediment transport work will be done in collaboration with faculty and students in Civil and Environmental Engineering at Virginia Tech. Coupling analyses of natural and experimental sediment will highlight both the value and limitations of SS.

# INVESTIGATING THE EFFECT OF ALUMINUM SUBSTITUTION ON THE PHYSICAL AND CHEMICAL PROPERTIES OF SCHWERTMANNITE, A FERRIC HYDROXYL-SULFATE NANOMINERAL

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The properties and behavior of nanoparticles (NPs) formed in environmental conditions are altered by incorporation of elemental impurities. In ferrihydrite, for example, aluminum (Al) can replace iron (Fe) up to 30 mol% and results in significant differences in stability and (surface) reactivity (Cismasu et al., 2012). Schwertmannite, a ferric hydroxyl-sulfate nanomineral, is also expected to incorporate significant Al, although the amount and type of incorporation and effects on properties are still unknown. Developing a deeper understanding of how schwertmannite incorporates Al is important to understanding the role it plays in contaminated systems such as acid mine drainage (AMD) that affect water quality. This project investigates how the physical and chemical properties of schwertmannite change as a function of initial Al to Fe ratio and pH.

Two series of samples were synthesized by rapid addition of sodium bicarbonate solution to sulfate-bearing solutions with different initial Al/Fe ratios (0, 0.25, 0.5, 0.75, 1.0) and pH (3 and 4.3). The structural and chemical characteristics of the solids were evaluated by powder x-ray diffraction (XRD) and inductively coupled plasma mass spectrometry (ICP-MS). Overall, XRD showed no sharp peaks for most of the samples formed at either pH, indicating that these solids are poorly crystalline to amorphous. XRD profiles for samples up to 90 mol% Al at pH 3 were similar to pure schwertmannite. Samples formed at pH 4.3 were also similar to schwertmannite at up to 50% Al. The profiles of the samples formed at higher Al content were distinctly different, suggesting differences in structures for these samples. Linear combination fitting (LCF) analysis of the XRD for pH 4.3 showed that different proportions of the endmember spectra (i.e., Al/Fe=0 and 1) could describe the intermediate samples. Analysis by ICP-MS also showed differences in the uptake of Al and Fe in the solids for the two series. In general, sulfate uptake was correlated with Al content. These results suggest that Al uptake in the intermediate ratio samples formed at either pH is not occurring only by substitution of Al for Fe in schwertmannite. Instead, we hypothesize that an Al-hydroxide/sulfate phase is co-precipitating along with Fe-rich schwertmannite. Furthermore, these findings suggest that the behavior of Al-bearing schwertmannite will be controlled by a complex mixture of two distinct commingled phases. Further structural and physical characterization by small-angle x-ray scattering (SAXS) analysis and synchrotron x-ray scattering is in progress.

## INFERRING REPTILIAN RESPONSE TO GLOBAL WARMING: STABLE ISOTOPE RATIOS AS A PROXY FOR ECOLOGY

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The Paleocene-Eocene Thermal Maximum (PETM) was a global warming event induced by the release of greenhouse gases about 55 mya, which resulted in a 5°C increase in global temperatures. While the impacts of this event have been studied in mammals, what impact this event had on tropical species, including lizards, is still largely unclear. Lizards today are the largest group of terrestrial vertebrates on Earth, occupying a diverse number of niches and are found in almost all biomes, including tropical forests. With the current human induced global warming event, the health and longevity of both lizards and the tropics have again been put at risk. While modeling animal response to such an event is difficult, understanding lizard response to past events like the PETM can serve as a proxy for modern response. Geochemical analysis of stable isotope ratios ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ) in the enamel of large mammals has been used as a proxy for mammalian paleoecology for decades. We modified this method and applied it to much smaller lizard teeth, providing new paleoecological data for lizards and the tropical environments they occupy.

Because geochemical analyses are in general destructive, we established a working procedure and correction values using readily available extant lizards prior to applying the method to fossil specimens. In addition, isotopic ratios can be altered depending on the diet of the organism. We established these ‘trophic corrections’ in extant taxa with known diets using a carnivore, an omnivore, an insectivore, and two herbivores. Our data indicates a trophic separation in  $\delta^{13}\text{C}$ , with carnivores plotting opposite of herbivores, and omnivores plotting variably in between. Also,  $\delta^{18}\text{O}$  values, which are constant (<1 per mil) in endothermic mammals, are variable (~ 2 per mil) in these ectothermic lizards. Our results support that variation  $\delta^{18}\text{O}$  values can serve as a proxy for types of thermoregulation.

In order to examine trophic structure among lizards from the aftermath of the PETM, we analyzed fossil lizards from the Early Eocene Wasatch Basin in Wyoming. To be as minimally destructive as possible, we conducted isotopic analysis using time of flight mass spectrometry (TOF-SIMS). Such analytical techniques are crucial to this work, as each tooth only has a few microns of enamel, and traditional mass spectrometry requires milligrams of enamel. This work was successful in analyzing exclusively enamel and in collecting geochemical data in ~55mya lizard teeth, and will serve as the groundwork for future lizard paleoecological studies.

## THE EFFECTS OF RHEOLOGICAL PROPERTIES ON EARTH'S MOTIONS

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In this project we investigate how rheological properties affect the deformation of Earth's outer rigid shell and asthenospheric flow. We test how various lithospheric conditions, such as grain size and the water content of olivine, affect deformation that occurs on the Earth's surface, within the Earth's crust, throughout the mantle lithosphere, and within the asthenosphere. This work involves the use of ASPECT (Advanced Solver for Problems in Earth's ConvecTion). ASPECT is an extensible code written in C++ to support research in simulating convection in the Earth mantle and Earth's deformation of the lithosphere. Preliminary results indicate smaller grain sizes induce more vigorous mantle convection and mantle lithosphere deformation, but not crustal motions.

# THE ROLE OF LONG-TERM TECTONIC DEFORMATION ON THE DISTRIBUTION OF PRESENT-DAY SEISMIC ACTIVITY IN THE CARIBBEAN AND CENTRAL AMERICA

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The Caribbean and Central America region (CCAR) undergoes the entire spectrum of earthquake types due to its complex tectonic setting comprised of transform zones, young oceanic spreading ridges, and subductions along its eastern and western boundaries. CCAR is, therefore, an ideal setting in which to study the impacts of long-term tectonic deformation on the distribution of present-day seismic activity. In this work, we develop a continuous tectonic strain rate model based on inter-seismic geodetic data and compare it with known active faults and earthquake focal mechanism data. We first create a  $0.25^\circ \times 0.25^\circ$  finite element mesh that is comprised of block geometries defined in previously studies. Second, we isolate and remove transient signals from the latest open access community velocity solution from UNAVCO, which includes 339 velocities from COCONet and TLALOCNet GNSS data for the Caribbean and Central America, respectively. In a third step we define zones of deformation and rigidity by creating a buffer around the boundary of each block that varies depending on the size of the block and the expected deformation zone based on locations of GNSS data that are consistent with rigid block motion. We then assign each node within the buffer a 0 for the deforming areas and a plate index outside the buffer for the rigid. Finally, we calculate a tectonic strain rate model for CCAR using the Haines and Holt finite element approach to fit bi-cubic Bessel splines to the GNSS/GPS data assuming block rotation for zones of rigidity. Our model of the CCAR is consistent with compression along subduction zones, extension across the mid-Pacific Rise, and a combination of compression and extension across the North America - Caribbean plate boundary. The majority of CCAR strain rate magnitudes range from -60 to 60 nanostrains/yr. Modeling results are then used to calculate expected faulting behaviors that we compare with mapped geologic faults and seismic activity.

Advisor: Dr. D.S. Stamps

## REDOX-SENSITIVE TRACE ELEMENTS IN FLUID INCLUSIONS IN HALITE AS PROXIES FOR PALEOSEAWATER REDOX CONDITIONS

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Oceanic Anoxic Events (OAE) are thought to be partly responsible for mass extinction events and subsequent slow recovery of marine ecosystems during Earth's history. The largest biocrisis occurred at the Permian-Triassic boundary 250 million years ago when ~90% of skeletonized marine species disappeared, and anoxia extended into shallow water well above the storm wave base (e.g. Wignall & Twitchett, 1996, Słowakiewicz et al., 2016). To observe these environmental changes, minor and trace elements that show variations of valence state, isotope fractionation and solubility as a function of redox conditions are extensively used in sedimentary rocks as paleoredox proxies for marine environments. For example, uranium is more soluble under oxidizing conditions than under reducing conditions, thus it precipitates in oxygen-depleted sedimentary facies, while iron and manganese behave in the opposite manner. The concentrations of these elements in the sedimentary record are indirect indicators of the redox state of seawater at the time of deposition. Fluid inclusions (FI) are the only available feature in the geologic record that can provide direct information about the chemical composition of the fluid that was present during rock formation. For example, evaporite minerals (e.g. gypsum and halite) precipitating from evaporating seawater preserve tiny droplets of seawater during their growth. Analysis of primary fluid inclusions in these minerals can provide direct information about the chemical composition of evaporating seawater from which the minerals crystallized.

The goal of this study is to develop a methodology to quantify ratios of minor and trace elements (Rb, Sr, Mo, Ba, Li, B, V, U, Fe, Mn, Se, Cr, Cu) in seawater based on LA-ICP-MS analysis of fluid inclusions in primary marine halites. The samples used to develop and test the methodology are from the Late Permian Zechstein Evaporite Formation in Poland. Previously studied fluid inclusion samples from this formation suggest that the seawater chemistry changed from sulfate-rich brines, similar in composition to modern evaporated seawater, to sulfate-depleted (calcium-rich) brines during the latest Permian. This change was interpreted to be the result of overturn of anoxic sulfidic deep-waters from the Panthalassa stratified superocean coinciding in time with the Permian–Triassic mass extinction event. Our preliminary data show higher iron and manganese concentrations in fluid inclusions in the samples with sulfate-depleted (calcium-rich) brines compared to samples with sulfate-rich brines, which supports this interpretation.

## DEVELOPMENT OF MICROFLUIDIC DEVICES FOR REAL-TIME CRYSTALLIZATION STUDIES OF NANOMINERALS

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Our ability to study crystallization - the transformation of dissolved species into solids – is crucial to understand and control several geologic, biogenic and industrial synthetic processes. Recent studies showed that certain types of crystals, particularly nanocrystals, form and grow through “nonclassical pathways” that involve attachment of transient precursor particles with variable degrees of crystallinity. Despite numerous studies of crystallization by particle attachment, significant gaps remain in our understanding of how solution chemistry and hydrodynamic conditions affect the properties of the precursor particles and how those grow into larger nanoparticles. Current knowledge gaps exist for two main reasons: 1) transient species evolve extremely fast from initial monomers to intermediate complex structures to final nanocrystals; 2) most techniques are not capable of analyzing species in solution, which is the true representation of their structural and chemical properties.

To address these challenges we have developed a novel microfluidic reactor to perform real-time synchrotron X-ray scattering studies. Preliminary tests at the Advanced Photon Source (Argonne National Laboratory) showed that the background signal from the device is relatively weak and amorphous, which allows us to analyze the size, structure and chemical composition of the transient species while they form and evolve with time in aqueous conditions inside the reactor. Benchtop crystallization studies showed that gold nanoparticles form upon mixing of the initial reagents and move along the main reactor channel. These basic characteristics make them a suitable test-case to evaluate the potential of microfluidic reactors for *in situ* crystallization studies. Our current goals are divided in two parts: 1) understand how the time-scale of formation and evolution (growth) of gold nanoparticles is affected by the hydrodynamic (turbulent, laminar, static) conditions and 2) study the size, crystallinity (long and short range order) and chemical composition of the precursors formed in the early stages of nucleation that subsequently grow and assembly into nanoparticles. The results of these two studies will provide time-resolved information (particle size, crystal properties and chemical composition) about the mechanism and kinetics of formation of gold nanoparticles in solution. Our long term goal is to apply this microfluidic reactor to more complex materials nanoparticles that are relevant to geological and environmental processes.

Advisor: Dr. F. M. Michel

## THE INFLUENCE OF MANURE APPLICATION ON LIMESTONE DISSOLUTION RATES

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Animal manure is often spread on agricultural lands to help supply nutrients to the soil. As agriculture is a common land use on karst terrains, which are often characterized by rapid infiltration of waters and any associated pollutants from the surface to the subsurface and limited attenuation capacity, there is concern that manure application can cause pollution of karst aquifers. In addition, recent work suggests that manure application may also enhance limestone dissolution. For my project, I conducted a laboratory experiment using treatments of diluted swine manure, limestone tablets, soil and water, to examine the effects of manure on limestone dissolution rates. Limestone of the Boone Formation and soil samples were collected from a karst region in Newton County, Arkansas. The region is characterized by agricultural use including a swine confined animal feeding operation. During the experiment, the pH, alkalinity, and concentrations of Ca and Mg in solution were measured. Results show an overall decrease in pH and alkalinity in all experiments, with a greater pH decrease in flasks containing manure. The highest Ca and Mg concentrations were measured in the treatments containing manure, suggesting that the manure accelerated the dissolution of the limestone tablet. Further work includes scanning electron microprobe analysis of the limestone tablets to evaluate the surface texture and chemical composition.

Advisor: Dr. M. E. Schreiber

## FUGACITY OF N<sub>2</sub>, CO<sub>2</sub>, AND CH<sub>4</sub> IN N<sub>2</sub>-CO<sub>2</sub>-CH<sub>4</sub> GAS MIXTURES FROM 10-500 BARS DETERMINED USING RAMAN SPECTROSCOPY

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The fugacity represents the “thermodynamic” pressure that takes into account the non-ideality of a component. If a gas behaves ideally, the fugacity is equal to the partial pressure – this value deviates from the partial pressure in nonideal mixtures by a dimensionless factor known as the fugacity coefficient. Determining the fugacity of a gas requires derivation of an equation of state describing the volume (density) of the gas as a function of pressure, temperature, and composition. This is accomplished experimentally by measuring the volume of the gas at a variety of PTX conditions, however this can prove to be an arduous task as a single measurement of the volume at a given PTX condition is not sufficient. Recently, a new method to determine fugacity of gas mixtures was developed that is based on the shift in the Raman peaks of individual gas components with changing pressure. This study extends the method to other compositions to determine fugacities of N<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> in two different gas mixtures; 25% N<sub>2</sub>, 25% CO<sub>2</sub>, and 50% CH<sub>4</sub> and 15% N<sub>2</sub>, 60% CO<sub>2</sub>, and 25% CH<sub>4</sub> (all in mole percent).

Raman spectra have been collected from a gas mixture containing 25% N<sub>2</sub>, 25% CO<sub>2</sub>, and 50% CH<sub>4</sub> at pressures from 10-500 bars at 25°C. The peak positions for each of the individual gases were determined and were calibrated using well-established positions of Ne lines. The partial pressures of the individual components calculated from the peak positions do not correspond to the partial pressures of the individual components calculated from the total pressure assuming ideal mixing, indicating that the gases do not mix ideally. The calculated partial pressure of CH<sub>4</sub> most closely matches the ideal partial pressure while the calculated partial pressure of N<sub>2</sub> is greater than the ideal partial pressure by an order of magnitude. The calculated partial pressure of CO<sub>2</sub> is greater than the ideal partial pressure in the range of 10-180 bars. At pressures greater than 180 bars this relationship is reversed, possibly due to immiscibility. The difference between the ideal partial pressure and the calculated partial pressure has been used to determine the fugacity.

## A PROTEROZOIC OCEAN OF SEAWEEDS: PHOTOSYNTHETIC GREEN ALGAE IN EARLY TONIAN

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The rise of algae in bacterium-dominated oceans marks one of the most fascinating ecological transitions in Earth's history, as it reshaped food webs with more efficient energy transfer that significantly changed the carbon and nutrient recycling. However, little is known about this transition regarding to the causes and timing. This is largely because the early evolution of eukaryotes remains elusive due to the dearth of reliable crown group algal fossils in the Proterozoic Eon. Molecular clocks suggest that the divergence between green algae (Viridiplantae) and red algae (Rhodophyta) occurred ~1.25 Ga, and this is supported by the occurrence of the red algal fossil *Bangiomorpha* at the Meso- and Neoproterozoic transition. However, few green algal fossils have been documented until the Ediacaran. Although the putative coenocytic green alga *Proterocladus* has been reported in the late Tonian (<800 Ma), its biological interpretation is compromised by the incomplete preservation of available specimens, and this fossil taxon has been largely ignored in recent molecular clock analyses. To better understand this taxon, which has great potential to unveil the early evolution of green algae and to calibrate molecular clocks, we carried a paleobiological investigation that revealed abundant well-preserved specimens of *Proterocladus* from the early Tonian (1,000 to 900 Ma) Nanfen Formation in North China. Transmitted light microscopic observations of HF-acid-macerated specimens revealed diagnostic cellular characters of *Proterocladus*, including intercellular septa, large cells with variable length, lateral branching, and segregative cell division. More importantly, reflected light microscopy of well-preserved specimens on bedding surface of mudstone demonstrated that the overall morphology of *Proterocladus* is characterized by complex lateral or dichotomous branching with multiple successive branches to form a tuft thallus with a mm-scale height and distally curved lateral branches, suggesting an erect benthic habit. In combination with the cellular characters, the overall morphology of *Proterocladus* suggests its close relationship with the extant Chlorophyta, in particular to the branching septate siphonocladalean algae *Cladophoropsis* and *Cladophora*. In addition, the large population of *Proterocladus* on bedding surface of the Nanfen mudstone indicates that crown group green algae may have colonized and flourished in early Tonian oceans. Given the many other occurrences of Tonian benthic algae, including *Bangiomorpha*, *Longfengshanian*, and *Protoarenicola*, photosynthetic eukaryotes may have established a strong basis for their ultimate ecological dominance and the subsequent rising of atmospheric oxygen level and the origin of animals in the late Neoproterozoic.

# RECONNAISSANCE NEOTECTONICS OF THE LA PINE GRABEN, OREGON CASCADES, USA

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The Mount Bachelor volcanic chain (MBVC) occurs within an extensional tectonic system along the Cascade volcanic arc in central Oregon (Scott and Gardner, 1992). This array of late Quaternary cinder cone and shield volcanoes is parallel to and a few kilometers east of the volcanic arc, extending southward from Mount Bachelor for ~25 km. South of, and aligned with, the volcanic chain is a <10 km wide zone of active normal faults which cut latest Pleistocene and Holocene deposits. The orientation of young fault scarps with young, aligned volcanic centers suggests a genetic relationship between earthquakes and volcanic activity.

Our goal is to understand this relationship between regional tectonism and volcanism. The majority of these young fault scarps were unknown before the expansion of airborne lidar coverage in this heavily forested region. To document the distribution of faulting across the graben we mapped fault surface traces from airborne lidar data and low water-level satellite imagery, characterizing fault spacing, lengths, and dips. We determined the total surface offset across discrete geomorphic surfaces in the graben. We also conducted paleoseismic investigations on two of the identified fault scarps. One trench exposed deformed Mazama ash (~7.6 ka, Zdanowicz et al., 1999) and therefore records at least one Holocene earthquake.

Future work will involve conducting further paleoseismic investigations across this graben system on each individual fault scarp to determine the timing of surface displacements. With these trenches and subsequent dating of MBVC features I will explore whether the surface displacements on these faults result from dike emplacement-related extension or tectonic mechanisms of deformation.

# GEOCHEMISTRY OF TRIASSIC DIKES OF THE COASTAL NEW ENGLAND MAGMATIC PROVINCE IN MAINE, USA INDICATES AN UPPER MANTLE SOURCE FOR MELTS

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The Coastal New England magmatic province (CNE) is an understudied suite of Triassic alkalic dikes and plutons found along the modern coasts of Massachusetts, New Hampshire, and Maine in the United States, and southwestern Nova Scotia in Canada. The CNE event coincides with the initiation of the rifting of Pangea and precedes one of the largest recognized eruptions of flood basalts in Earth's history – the Central Atlantic Magmatic large igneous Province (CAMP) at ~200 Ma. CNE magmas were originally interpreted to be melts from a mantle plume rising beneath Pangea between 250-200 Ma. Presenting new geochemical analyses of 42 dikes from the CNE in Maine and Nova Scotia, our study indicates that the source of CNE magma melting was not a mantle plume. Instead, melting of the subcontinental upper mantle is suggested by major and trace element compositions and radiogenic isotope (Sr-Nd-Pb-Hf) ratios of CNE dikes. This alternative interpretation for the source of the CNE magmas may elucidate the relationship between the CNE and CAMP magmatic events and their association with the rifting of Pangea.

Advisor: Dr. Robert Tracy

## THE AUTOMATION OF NUMERICAL MODELING OF SEISMOGENIC TSUNAMIS

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Large earthquakes, typically above a magnitude of 7.0, that occur in a subduction zone located along the edges of ocean basins, generate tsunamis. The effects of such tsunamis are generally widespread, and are a significant coastal hazard. As such, a program will be created that will automate models of tsunami propagation caused by seismic sources. These models will allow a study to be conducted to determine the sensitivity in coastal areas to small changes in a given source earthquake. In the early phase of tsunami generation, as they propagate away from the source area, there is a significant amount of uncertainty regarding the earthquake parameters, such as depth and magnitude. A detailed slip distribution on the fault is also difficult to estimate with a level of confidence. Even long after the event, slip distribution on the fault can vary depending on the data that is employed for inversion. As such, different scenarios will be created, each accounting for a different slip configuration. Preliminary results include the creation of multiple slip configurations, with a single and dual faults that run parallel to the subduction zone, a single and dual series of subfaults that run perpendicular to the subduction zone, and an unconstrained geometry of the closest number of fault sources that correspond to the area required to generate an earthquake of sufficient size. Future work will include the automation of tsunami models that occur from these variations of slip distribution and configuration.

Advisor: Dr. R. Weiss

# INFLUENCE OF CAPILLARY FORCE AND BUOYANCY ON CO<sub>2</sub> MIGRATION DURING CO<sub>2</sub> INJECTION IN A SANDSTONE RESERVOIR

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Carbon capture and sequestration (CCS) is one component of a broad carbon management portfolio designed to mitigate adverse effects of anthropogenic CO<sub>2</sub> emissions. During CCS, capillary trapping is an important mechanism for CO<sub>2</sub> isolation in the disposal reservoir, and, as a result, the distribution of capillary force is an important factor affecting CO<sub>2</sub> migration. Moreover, the movement of CO<sub>2</sub> being injected to the reservoir is also affected by buoyancy, which results from the density difference between CO<sub>2</sub> and brine. In order to understand interactions between capillary force and buoyancy, we implement a parametric modeling experiment of CO<sub>2</sub> injections in a sandstone reservoir for combinations of the van Genuchten capillary pressure model that bound the range of capillary pressure-saturation curves measured in laboratory experiments. We simulate ten years supercritical CO<sub>2</sub> (scCO<sub>2</sub>) injections within a 2-D radially symmetric sandstone reservoir for five combinations of the van Genuchten model parameters  $\lambda$  and entry pressure ( $P_0$ ). Results are analyzed on the basis of a modified dimensionless ratio,  $\omega$ , which is similar to the Bond number and defines the relationship between buoyancy pressure and capillary pressure. We show how parametric variability affects the relationship between buoyancy and capillary force, and thus controls CO<sub>2</sub> plume geometry. These results indicate that when  $\omega > 1$ , then buoyancy governs the system and CO<sub>2</sub> plume geometry is governed by upward flow. In contrast, when  $\omega < 1$ , then buoyancy is smaller than capillary force and lateral flow governs CO<sub>2</sub> plume geometry. As a result, we show that the  $\omega$  ratio is an easily implemented screening tool for qualitative assessment of reservoir performance.

Advisor: Ryan Pollyea

# DIVERSITY OF CHONDRICHTHYES THROUGH THE UPPERMOST CRETACEOUS HELL CREEK FORMATION OF GARFIELD COUNTY, MONTANA: IMPLICATIONS FOR THE CRETACEOUS-PALEOGENE MASS EXTINCTION

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The Cretaceous-Paleogene (K-Pg) mass extinction is a well-studied mass extinction event, but there remain two main competing hypotheses that explain the diversity changes observed in the fossil record: (1) a sudden and rapid loss of many species at the K-Pg boundary (ca. 66 Ma) caused by a Bolide impact (Chicxulub); and (2) vertebrate biodiversity declines prior to and at the K-Pg boundary due to multiple factors (e.g., changing sea levels, volcanism, bolide impact). To examine these two hypotheses, we examined the diversity changes of Chondrichthyes (sharks and relatives) from freshwater deposits of the Hell Creek Formation (HC), leading up to the end of the Cretaceous. We analyzed diversity dynamics using 1065 fossil teeth stored at the University of Washington, Burke Museum of Natural History and Culture and the University of California Museum of Paleontology from eight vertebrate microfossil localities stratigraphically distributed throughout the HC.

Our samples include the occurrences of three new shark species based on morphologically distinct teeth, as well as a novel batoid (i.e., rays). We also report on the first sand tiger shark from the HC, as well as a tentative carchariniform tooth, indicating a freshwater incursion by these, otherwise, marine taxa. Using raw taxonomic, standing, subsampled analytic rarefied, and shareholder quorum subsampling (SQS) richnesses, our study shows richness increases to seven species between 30.5 and 35 m above the Hell Creek/Fox Hills contact (HFC). Heterogeneity indices surrounding this interval indicate a faunal restructuring in which relative abundance of the guitarfish *Myledaphus pustulosus* starkly declines throughout the remainder of the HC section resulting in more species-even localities. Species diversity decreases between 35 and 83.2 m above the HFC and rise to a peak of nine species at 84.3 m above the HFC (4.2 m below the Hell Creek/Tullock contact). Nine of the ten HC chondrichthyans extend into the last 10 m of the HC, showing a very rapid, abrupt extinction in HC chondrichthyans. These changes in diversity resemble the abrupt extinction patterns shown for mammals (terrestrial) rather than the stepwise extinction patterns shown for amphibians (aquatic) although the latter shared the same environments. Changes in chondrichthyan community structure and diversity in relation to other HC taxa indicate a unique and complex pattern of extinction, one suggesting that HC chondrichthyans were acted upon by a variety of selection pressures, supporting a multi-cause extinction hypothesis.

# QUANTITATIVE ANALYSIS OF FINE-GRAINED MINERALS MIXTURES BY RAMAN SPECTROSCOPY

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Many rock samples are composed of very-fine grained mixtures of various minerals. One example is serpentinite, which often contains mixtures of lizardite, chrysotile, magnetite and brucite with grain sizes too small to be identified optically or by electron microprobe. One technique that holds promise for quantitative analysis of fine-grained samples is Raman spectroscopy. Each mineral phase has a characteristic Raman spectrum, and the peak intensities are proportional to the amount of analyte. However, mineral grain size and orientation also has big impact on the intensity, but there is just little research on how to eliminate the influence of changes in the physical properties to improve the accuracy of Raman spectroscopy quantitative analysis. At present, spectral preprocessing methods such as Multiplicative Signal Correction-MSC, Standard Normal Variate-SNV, Extended Inverse Scatter Correction-EISC, and Extended Multiplicative Signal Corrector-EMSC are often used to eliminate the multiplier effect caused by physical properties change. However, these spectral preprocessing methods have very demanding requirements on the system, so it's kinda very hard to meet these requirements in practice. Therefore, in order to achieve accurate quantitative analysis of complex multiphase samples by Raman spectroscopy, it is necessary to develop a multiphase system, which is of great significance. The goal of my current study is to examine the maximum average grain size that results in an accurate estimate of the proportions of each mineral in a fine grained sample.

Simple mixtures of quartz and feldspar powder below 53 micrometers were selected for the first test, and they were mixed in known proportions and analyzed by XRD, and then we used peak areas to get ratios which is a simple way to estimate percentages. The next step is doing Raman analysis to compare the results with XRD. Furthermore, more experiments with samples of different minerals and sizes and also with different references will be done in the future.

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