

22ND GEOSCIENCES STUDENT RESEARCH SYMPOSIUM

FEBRUARY 23 & 24, 2017
KELLY HALL RM. 310 & CAFE X



22nd Annual

Geosciences Student Research Symposium

Thursday February 23rd, 2017 11:00 – 5:15

Friday February 24th, 2017 9:30 – 4:50

Kelly Hall Room 310 and Café X

Virginia Tech

Welcome to the Geosciences Student Research Symposium! GSRS is produced and organized by the graduate students of the Department of Geosciences at Virginia Tech. The symposium is designed to allow students the opportunity to prepare and present talks 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. Constructive feedback on student presentations from faculty, students, and visiting guests is highly encouraged.

On both days of the symposium, morning refreshments, coffee, and 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, Due South BBQ, Next Door Bake Shop, Strange Coffee Co., Sub Station II, The Beast of Blacksburg, and several generous faculty and alumni! We also thank the Department of Geosciences for their generous support. Finally, thanks to the faculty, volunteers, and student participants for donating their time and expertise – without you this event would not take place.

Your 2017 GSRS Coordinating Committee:

Committee Chair: Lowell Moore

Fundraising: Kirkland Broadwell, Eszter Sendula, Rui Serra Maia

Abstract Book/Scheduling: Lisa Whalen, William Whalen

Food/Drink: Kannikha Kolandaivelu, Calvin Mako

Website: Sebastian Mergelsberg, Sheyla Palomino Ore

Faculty Advisor: Jim Spotila

Special thanks to Aly Hoehner for planning the Up-Goer V session and to our invited speakers Besim Dragovic and Sayako Inoue.

Thursday, Feb. 23rd

Time	Name	Title
------	------	-------

10:30 – Coffee (Kelly Hall, Rm. 310)

11:05	Caitlin Colleary	SIMILARLY-AGED MAMMOTH FOSSILS PRESERVE ORGANIC MATERIAL DIFFERENTLY BASED ON DEPOSITIONAL ENVIRONMENT
11:20	Lisa Whalen	AMA DRIME: A WINDOW INTO CORE COMPLEX FORMATION
11:35	Selva Marroquin	INVESTIGATING AN OPEN OCEAN GEOCHEMICAL RECORD FROM THE LATE TRIASSIC THROUGH THE EARLY JURASSIC TOARCIAN OCEANIC ANOXIC EVENT WITHIN PANTHALASSA
11:50	Eszter Sendula	IN SITU MONITORING OF THE OLIVINE TO MAGNESITE REACTION WITH RAMAN SPECTROSCOPY – IMPLICATIONS FOR REACTION RATES

12:05 – Lunch (Kelly Hall, Rm. 310)

1:00 – Up-Goer V Challenge - Academic talks without jargon (Kelly Hall, Rm. 310)

1:40	Besim Dragovic (Invited)	EVIDENCE FOR EXTREMELY RAPID HEATING AT THE SUBDUCTION INTERFACE
2:00	Sayako Inoue (Invited)	NEW PERSPECTIVE ON STABILITY OF FE-RICH CHLORITE AND SERPENTINE GROUP MINERAL
2:20	Sebastian Mergelsberg	THE MG-DEPENDENT SOLUBILITY AND LOCAL STRUCTURE OF AMORPHOUS CALCIUM CARBONATE (ACC): TOWARD AN UNDERSTANDING OF INVERTEBRATE BIOMINERALIZATION
2:35	Qing Tang	EARLY EVOLUTION OF SPONGE ANIMALS: A PERSPECTIVE FROM SPICULOGENESIS AND BIOMINERALIZATION
2:50	Tyler Rasmussen	3-D SUBSURFACE CHARACTERIZATION USING AMBIENT NOISE SEISMIC INTERFEROMETRY IN AN ACTIVE MINE
3:05	Candice Stefanic	FORM AND FUNCTION IN THE FOSSIL RECORD: THE EVOLUTION OF VERTEBRAL MORPHOLOGY IN LIVING AND EXTINCT ARCHOSAURS

3:20 – Coffee

3:30	Sheyla Palomino Ore	EVALUATING THE FORMATION OF ALUMINUM OXY-HYDROXIDE COATINGS IN ANOXIC LIMESTONE DRAINS USED TO TREAT ACID ROCK DRAINAGE
3:45	Tahiry Rajaonarison	THE MALAGASY LITHOSPHERE-ASTHENOSPHERE SYSTEM CONSTRAINED BY INDEPENDENT INITIAL TEMPERATURE CONDITIONS: IMPLICATIONS FOR EXTENSIONAL PROCESSES
4:00	Yury Klyukin	FLUID EVOLUTION IN THE NORTH AMERICAN EMERALD MINE (NAEM), HIDDENITE, NC
4:15	Rui Serra Maia	ROLE AND EVOLUTION OF STRUCTURAL AND PHYSICOCHEMICAL PROPERTIES OF COMMERCIALY-SOURCED PLATINUM NANOCATALYSTS DURING THE CATALYTIC DECOMPOSITION OF H ₂ O ₂ .
4:30	Yong Huang	QUANTITATIVE ANALYSIS OF FINE-GRAINED MIXTURES OF MINERALS BY RAMAN SPECTROSCOPY
4:45	Josh Jones	INVESTIGATING STRESS INTERACTIONS IN A YOUNG RIFT SEGMENT OF THE EAST AFRICAN RIFT SYSTEM
5:00	Hao Wu	A PARAMETIRC ANALYSIS OF CAPILLARY PRESSURE EFFECTS DURING THE CARBON SEQUESTRATION INJECTION PROCESS IN A SANDSTONE RESERVOIR

Friday, Feb. 24th

9:00 – Breakfast (Kelly Hall, Rm. 310)

9:30	Adam Angel	THE ROLE OF THE CONTINENTAL BIOSPHERE IN EARTH'S GEOHYDROLOGIC CYCLE IN DEEP TIME
9:45	John Bartos	EVIDENCE OF PLEISTOCENE GLACIAL RECHARGE IN A CRYSTALLINE FRACTURED BEDROCK IN NEW ENGLAND
10:00	Matthew Wilson	CHARACTERIZING THE FRACTURED CRYSTALLINE BEDROCK AQUIFER AT PLOEMEUR, FRANCE USING MULTIPLE SURFACE DEFORMATION AND WATER-LEVEL SIGNALS
10:15	Karel Kletetschka	SYNTHESIS AND CHARACTERIZATION OF PRECURSORS TO SCHWERTMANNITE, A FERRIC OXYHYDROXIDE SULFATE NANOMINERAL
10:30	Chris Griffin	DOES THE MAXIMUM BODY SIZE OF THEROPOD DINOSAURS INCREASE ACROSS THE TRIASSIC-JURASSIC BOUNDARY? INTEGRATING GROWTH PATTERNS AND ANCESTRAL STATE RECONSTRUCTION

10:45 – Coffee Break

10:55	Kannikha Kolandaivelu	ANALYSIS OF A CONDUCTIVE HEAT FLOW PROFILE IN THE ECUADOR FRACTURE ZONE
11:10	Richard Jayne	CONSTRAINING THE EFFECTS OF PERMEABILITY UNCERTAINTY FOR GEOLOGIC CO ₂ SEQUESTRATION IN A BASALT RESERVOIR
11:25	Zhen Guo	FINITE-FREQUENCY TOMOGRAPHY OF THE 410-KM AND 660-KM DISCONTINUITIES USING SS PRECURSORS
11:40	Lowell Moore	A NUMERICAL METHOD FOR DETERMINING THE VOLATILE CONTENTS OF BUBBLE-BEARING MELT INCLUSIONS IN OLIVINE

11:55 – Lunch (Kelly Hall, Rm. 310)

1:00 – Poster session (Kelly Hall, Café X)

3:15	Aly Hoehner	DETERMINING THE EFFECTS OF pH AND SOLUTION CHEMISTRY ON THE STRUCTURE AND TRANSFORMATION OF AMORPHOUS CALCIUM PHOSPHATE
3:30	Matt Sublett	LIQUID-VAPOR PARTITIONING OF NA AND CA IN THE H ₂ O-NACL-CACL ₂ SYSTEM AT 500-700°C AND 550-750 BARS.
3:45	Matt Leroy	EVALUATING THE USE OF THALLIUM ISOTOPES AS A PALEOREDOX PROXY
4:00	Emma Tulskey	AN INVESTIGATION OF THE EFFECTS OF CONTACT METAMORPHISM BY A DIKE OF THE CENTRAL ATLANTIC MAGMATIC PROVINCE ON ITS HOST ROCK
4:15	Alexandra Nagurny	ANALYSIS OF GARNET-QUARTZ GRAIN BOUNDARIES IN METAMORPHIC ROCKS VIA TRANSMISSION ELECTRON MICROSCOPY
4:30	Calvin Mako	IS SHEAR HEATING IMPORTANT IN METAMORPHIC SYSTEMS?

4:45 – Closing remarks

5:00 – Reception (Museum of Geosciences, Derring 2062)

Abstracts

(in scheduled order)



SIMILARLY-AGED MAMMOTH FOSSILS PRESERVE ORGANIC MATERIAL DIFFERENTLY BASED ON DEPOSITIONAL ENVIRONMENT

COLLEARY, Caitlin, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

A major goal in paleontology is to extract as much information possible from the fossilized remains that contain the history of life on Earth. We use preserved biomolecules (e.g., DNA, proteins and lipids) as indicators of the chemical and physical processes that occurred during the life of an extinct animal and where it falls in an evolutionary and phylogenetic context. However, the degradation of biomolecules with high preservation potential (e.g., proteins, amino acids and lipids) and the mechanisms that enable them to persist in the sedimentary record for 10s of thousands, millions or even hundreds of millions of years are not well understood. To examine biomolecule preservation in the 'shallow' fossil record (up to ~150,000 years), I used mass spectrometric analyses of amino acids (the building blocks of proteins) and analyses of lipids (e.g., fats and sterols) in mammoth fossils from different depositional settings (e.g., permafrost, natural asphalt, a sinkhole, a stream deposit), combined with maturation experiments (that range from 100° C to 250° C to approximate diagenetic changes) on modern elephant bone. This combination of techniques demonstrates the same degree of biomolecule preservation and levels of degradation; the permafrost sample retained the most organic information and has experienced the least degradation (e.g., all 20 whole amino acids were present) whereas the mammoth rib from the hot spring fed sinkhole retains the least biomolecular information (e.g. only 12 whole amino acids were present). The main amino acids that make up collagen (i.e., glycine and proline) are among the most thermally stable, and persist in all fossil samples and through out all of the maturation experiments, indicating the high preservation potential of the constituents of collagen. The use of *in situ* mass spectrometric analyses (e.g., time-of-flight secondary ion mass spectrometry) preserves evidence often lost in fossil biomolecule studies, retaining important molecular information regarding the mechanisms for preservation within the bone. The combination of these techniques used to examine organic preservation and degradation in fossil mammoth ribs all tell the same story: the preservation of organics differ based on depositional environment. The biomolecular changes that take place in fossils based entirely on varying preservational environment can be used to evaluate interpretations about the physiologies and evolutionary histories of extinct animals and how biomolecules preserve in the fossil record.

AMA DRIME: A WINDOW INTO CORE COMPLEX FORMATION

WHALEN, Lisa, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The Himalayan orogen is the primary example of ongoing continental collision on Earth. However, there are regions of the Himalaya undergoing extension perpendicular to the strike of the main orogenic belt. The Ama Drime massif (ADM) is a relatively unstudied core complex formed through extension. The ADM records anomalously high peak P/T conditions (~ 800-900 °C and 14-16 kbar), and erosion rates (1 mm/yr to ~3.8 mm/yr). The ADM lines up spatially with the Munger-Saharsa ridge, a topographic high on the subducting Indian plate. The ridge, imaged with seismic, gravity, and magnetic data is composed of basement rock overlain by a few kilometers of sediment. A recent study used gravity data to show that the ridge and its bounding faults not only extend northward beneath the Tibetan plateau, but the bounding faults may also span from mantle depths to the surface. The surficial expression of the subducting Munger-Saharsa ridge may be the Xainza-Dinggye rift system and may be responsible for the formation of Ama Drime. The connection between the subducting ridge and the ADM will be investigated by determining if an elevated thermal gradient existed prior to the exhumation of the high-grade core. This will be accomplished by examining the deformational fabrics of the core of the ADM using anisotropy of magnetic susceptibility (AMS). This fast, quantified, and nondestructive technique utilizes the magnetic alignment of all the contributing grains in an individual sample to yield strain, kinetic and geometric information. If there was an elevated geothermal gradient sufficient to cause a thermal upwelling that led to the formation of the ADM, the deformational fabrics should be oriented radially and dip down and out from the center of the massif. Such an upwelling may have formed from a tear in the subducting slab that could be due to the presence of the Munger-Saharsa ridge.

Advisor: Dr. M.J. Caddick

INVESTIGATING AN OPEN OCEAN GEOCHEMICAL RECORD FROM THE LATE TRIASSIC THROUGH THE EARLY JURASSIC TOARCIC OCEANIC ANOXIC EVENT WITHIN PANTHALASSA

MARROQUÍN, Selva, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The Early Jurassic (201-174 Ma) was a time of intense disturbance for marine communities. Ecosystems recovering from the end-Triassic mass extinction and the loss of ~80% (Hallam & Wignall, 1997) of known species were again affected by another interval of environmental crisis during the Pliensbachian and Toarcian Stages (190-174 Ma). This later interval contains major carbon cycle perturbations, a protracted interval of elevated marine extinction rates and at least one interval of widespread oxygen deficiency within the oceans (Harries & Little, 1999; Caruthers et al., 2014). The Late Triassic-Early Jurassic interval, with its well-documented biotic crises, is a great case study of the biotic response to drastic changes within the environment. However, our understanding of the Early Jurassic is limited because few studies have been conducted on stratigraphic successions outside of the Tethys Ocean (present day Europe). To expand our understanding of this critical interval, I will investigate the changes in the carbon and sulfur cycles and oceanic redox conditions preserved within two sedimentary successions in Alaska that span the Late Triassic through the entire Early Jurassic. Specifically, I aim to test whether the expansion of anoxia and/or perturbations to the carbon and sulfur cycles correlate to the recorded biological extinctions.

The sedimentary successions that are the target of my study are preserved in the Talkeetna and Wrangell Mountains and were deposited in a tropical, open ocean setting adjacent to island arcs in the Panthalassic Ocean. These successions afford a unique view of open marine conditions during this time. I will examine the environmental history at both sites using several geochemical proxies: carbon ($\delta^{13}\text{C}_{\text{org}}$ and % total organic carbon), and sulfur ($\delta^{34}\text{S}$), as well as pyrite contents and Fe speciation. These proxies make tracking changes in the carbon and sulfur cycles and reconstructing oceanic redox conditions possible and will be integrated with sedimentary facies and fossil occurrences data in order to reconstruct environmental and biological change within the Panthalassic Ocean. Once combined with the existing geochemical records from the Tethys Ocean, my data will provide a more holistic view of the environmental changes from the Triassic-Jurassic and a unique perspective on the changes in global oceanic conditions contributing to these extinctions.

Advisor: Dr. B. C. Gill

IN SITU MONITORING OF THE OLIVINE TO MAGNESITE REACTION WITH RAMAN SPECTROSCOPY – IMPLICATIONS FOR REACTION RATES

SENDULA, Eszter, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Since relationship of climate change and increased CO₂ concentration in the atmosphere became clear, possible tools to help reduce anthropogenic CO₂ emissions to the atmosphere have received increasing attention. Sub-surface storage of CO₂ in various geological settings such as saline aquifers, organic shale formations, ultramafic and mafic rocks, depleted oil and natural gas reservoirs, and deep unmineable coal seams are proposed to be effective for long-term storage of CO₂. Each of these storage scenarios has advantages, disadvantages, and various dominant CO₂ trapping mechanisms. The conversion of CO₂ into carbonate minerals is the most preferred mechanism to ensure the long-term stability of the geologically trapped CO₂. Mineralization of CO₂ requires the reaction of divalent cations (e.g. Ca⁺², Mg⁺², Fe⁺²) with the dissolved CO₂. Ultramafic and mafic rocks contain large quantities of olivine and pyroxene, minerals, which have the largest potential to fix significant amounts of CO₂ due to the high molar proportion of divalent cations in their structures. Therefore, it is important to understand better the effect of various physical and chemical parameters on the reaction rates of olivine and pyroxene carbonation.

In this study, we produced CO₂-bearing synthetic fluid inclusions in natural olivine to study the rate of olivine to magnesite (MgCO₃) conversion, and the effect of temperature and varying pCO₂ on the reaction rates. The fluid inclusions were synthesized at 700 °C and 2 kbar with the nominal CO₂ concentrations of 20 mol% and 11 mol%. The reaction between the olivine host mineral and the fluid inclusions was monitored by measuring the change in the density of the free CO₂ phase within the inclusion. The CO₂ density, in turn, was determined by measuring the splitting of the Fermi diad for CO₂ using Raman spectroscopy. Previous workers have calibrated the Fermi diad splitting as a function of CO₂ pressure. The pressure determined from Raman analysis was converted into CO₂ density at the temperature of the analysis using an equation of state. In order to measure the effect of temperature on the reaction rate, the reaction was followed in situ at temperatures relevant to CO₂ sequestration (100°C and 50°C) using a high temperature stage. Our preliminary data show a measurable decrease of CO₂ density in the fluid inclusions as a result of the reaction of the CO₂-bearing aqueous phase and olivine. Magnesite formation was observed in several hours and most of the reactions occurred within two days.

EVIDENCE FOR EXTREMELY RAPID HEATING AT THE SUBDUCTION INTERFACE

DRAGOVIC, Besim, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Dehydration and densification of subducting oceanic crust and mantle may ultimately drive plate tectonics, control elemental cycling to the deep Earth, and induce arc magmatism and intermediate-depth seismicity. Subduction can persist for many millions of years, but processes related to fluid release and densification are brief and may be associated with inherently stochastic seismicity. By combining thermal models, convergence velocities, and models of mineral changes during subduction, heating rates are shown to possibly be several orders of magnitude higher than typical for most geologic environments and that dehydration and densification can occur in just tens to hundred of thousands of years. By coupling geodynamic models with constraints from phase equilibria, we explore the potential implications of such short metamorphic durations and rapid changes in P-T regime, focusing on the geochemical, rheological, and petrological properties and processes in subduction zones and subduction-related metamorphic rocks. Particularly profound implications of rapid heating would be seen in terms of: a) dehydration, fluid-rock interaction, and elemental mass transfer; b) slab densification, solid and fluid volume changes, deformation; and c) required rates of metamorphism, kinetics of mineral nucleation and growth, the development of metamorphic textures and the likelihood of substantial departures from chemical equilibrium. Finally, observations from the exhumed rock record are entirely consistent with extremely rapid heating, highlighting that brief metamorphic durations and metamorphism-related phenomena should be expected rather than surprising.

NEW PERSPECTIVE ON STABILITY OF FE-RICH CHLORITE AND SERPENTINE GROUP MINERAL

INOUE, Sayako, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Chlorite($(\text{Fe},\text{Mg})_6(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_8$) is everywhere from soils to detrital sediments, to sedimentary and diagenetic systems, to hydrothermal alterations and to low- and medium-grade metamorphic rocks. Chlorite has a wide variety in chemical composition and crystal structure. Changes in chemical composition and crystal structure are functions of temperature and possibly other intensive variables. Hence, chlorite is a key to reconstruct paleo-geochemical conditions. Although the formation mechanism of chlorite is known to be strongly linked to the temperature and chemical composition especially $\text{Fe}/(\text{Fe}+\text{Mg})$, how these factors influence the formation processes of chlorite is still open to discussion. Particularly, the crystallochemical features of Fe-rich chlorite were not fully characterized in the previous studies.

Fe- and Al- rich serpentine group minerals, berthierine and odinite, are strongly related to the formation mechanism of chlorite and often considered as a low temperature precursor of Fe-rich chlorite. It is generally accepted that 7 Å minerals convert to chlorite (14 Å) via a 7 Å – 14 Å interstratified mineral with increasing temperatures in iron rich environment. A range of temperature where each stage of chlorite formation occurs and how $\text{Fe}/(\text{Fe}+\text{Mg})$ values influence the formation processes are still open to discussion. In Inoué and Kogure (2016), the crystallochemical characteristics of Fe-rich chlorite from hydrothermal systems were investigated by high resolution transmission electron microscopy (HRTEM). These chlorites have $\text{Fe}/(\text{Fe}+\text{Mg})$ values in a range of 0.5 to 0.99 and were formed at temperatures higher than 200 °C. Our results suggested that the 7 Å minerals can occur at temperature higher than 200 °C when $\text{Fe}/(\text{Fe}+\text{Mg}) > 0.8$. We also observed the crystal structure of pore-lining Fe-chlorite from diagenetic systems by HRTEM. The diagenetic samples were formed at temperature in a range of 100 to 220 °C, and have a range of $\text{Fe}/(\text{Fe}+\text{Mg})$ values between 0.7 and 0.8 (Hillier, 2004). The samples contain small amount of interstratified 7 Å layers but they are mostly consisting of 14 Å layers. The results imply that the conversion from 7 Å mineral to 14 Å mineral started at temperatures below 100 when $\text{Fe}/(\text{Fe}+\text{Mg}) < 0.8$. Our study strongly suggested that the stability of Fe- and Al-rich serpentine group mineral is not only linked to the temperature condition but also $\text{Fe}/(\text{Fe}+\text{Mg})$ value and a necessity to reconsider the stability of Fe-rich chlorite and Fe- and Al-serpentine group mineral.

THE MG-DEPENDENT SOLUBILITY AND LOCAL STRUCTURE OF AMORPHOUS CALCIUM CARBONATE (ACC): TOWARD AN UNDERSTANDING OF INVERTEBRATE BIOMINERALIZATION

MERGELSBERG, Sebastian, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Calcium carbonate minerals are an essential component in the exoskeletons of crustaceans and mollusks. The onset of exoskeleton mineralization includes the precipitation of amorphous calcium carbonate (ACC) as a reactive intermediate that later transforms to calcite in diverse structures. Despite the importance of ACC as a critical phase during skeleton formation, the chemical and physical properties are not well characterized at conditions that approximate biological environments. Recent advances showing the widespread occurrence of multistep pathways to mineralization in biological and geological settings (De Yoreo et al., 2015) underline the importance of understanding the thermodynamic and kinetic properties of amorphous intermediates. Of particular interest are the solubility of ACC, the short-range structure at the time of formation, and the evolution of ACC structure to final products.

This study quantifies the solubility of ACC in parallel with the physical characterization of the corresponding structure. Using quantitative laboratory techniques developed by our research group (Blue et al., 2013; Blue and Dove, 2015; Blue et al., 2017) ACC was synthesized under controlled chemical conditions and variable Mg activity that approximate biological and environmental systems. We measured ACC solubility at specific time points shortly after precipitation using ICP-OES spectroscopy. In parallel experiments, structural data were collected by *in situ* high-energy x-ray scattering and analyzed by pair distribution function (PDF) to follow the evolution of individual samples from initial precipitation to final product.

Solubility and structure measurements reveal that ACC can form to produce more than one type of medium-range ordering depending on ion activity ratios in solution. The data shows ACC stability depends upon Mg content and the solubility differs by orders of magnitude depending on ratios of cation to anion activity. Measured solubilities are approximately 2 to 3 orders of magnitude higher than that of calcite at similar conditions. Insights from this study hold promise for better understanding the nature of the initial ACC and its influence on the chemical and structural properties of the final products.

EARLY EVOLUTION OF SPONGE ANIMALS: A PERSPECTIVE FROM SPICULOGENESIS AND BIOMINERALIZATION

TANG, Qing, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Most modern sponges have biomineralized skeletons in the form of siliceous or calcareous spicules. Siliceous sponge spicules consist of a thin axial filament surrounded by concentric layers of amorphous silica. The axial filament serves as a template for silica deposition, contains the biosilicification enzyme silicatein, and has either a triangular or tetragonal in cross section. Sponge spicules are unsurprisingly common in the rock record, but fossil axial filaments are rare. Because sponges are some of the earliest animals to have developed biomineralization, it is critical to understand the role of axial filaments in the early evolution of sponge spiculogenesis. Here we report well-preserved axial filaments in taphonomically demineralized spicules from the early Cambrian Hetang Formation in South China. The axial filaments were examined using secondary electron microscopy, backscattered electron microscopy, energy dispersive X-ray spectroscopy, and element mapping techniques. These axial filaments are micrometric in diameter and monaxonal or triaxonal in shape, consistent with the shape of their hosting spicules. Thus, the axial filament must have played an important role in guiding and regulating sponge spiculogenesis and biomineralization. However, unlike their modern counterparts, the Cambrian axial filaments are proportionally large relative to spicule size, suggesting that the earliest sponge spicules were composed of a significant amount of organic material and represent a case of weak mineralization or early ontogenetic development. In addition, these Cambrian axial filaments are neither triangular nor tetragonal in cross section; they are cylindrical instead, suggesting a greater diversity of axial filament morphologies among early sponges. This discovery has implications for the phylogenetic relationship and to evolution of spiculogenesis among the earliest sponges.

3-D SUBSURFACE CHARACTERIZATION USING AMBIENT NOISE SEISMIC INTERFEROMETRY IN AN ACTIVE MINE

RASMUSSEN, Tyler, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Seismic imaging has been used extensively in the oil and gas industry for many years to guide exploration and development. It could be equally beneficial for a 3-D subsurface characterization for mines. Ore deposit geology is more challenging to image than that of oil and gas, but successes have been documented. These methods have not been widely adopted, but provide an opportunity for improved and cost-effective decision making in development. A new direction in mining seismology is to use ambient noise to produce seismic images. The mine environment presents a unique opportunity due to the noise from mining operations and induced seismicity. I will investigate the use of ambient noise sources recorded on an underground passive seismic network to image subsurface geology.

A monitoring network of 62 seismographs was deployed at 1508 to 2302 m depth in the Creighton hard-rock nickel mine in Sudbury, Canada. The network recorded more than 10,000 events during a month, including rock blasts and induced earthquakes. I will use ambient noise from microseismicity as virtual sources for imaging the subsurface. The goal will be to image scatterers and reflectors in the subsurface using virtual sources and interferometry methods. The results will be tested using the known locations of the ground surface and the mine chambers, which act as scatterers and reflectors. Ultimately, the goal is to use virtual sources and interferometry to image geologic structures beyond the boundaries of the mine. If successful, these methods could improve the exploration and development of subsurface mines for the entire mining industry.

Advisor: Dr. J. A. Hole

FORM AND FUNCTION IN THE FOSSIL RECORD: THE EVOLUTION OF VERTEBRAL MORPHOLOGY IN LIVING AND EXTINCT ARCHOSAURS

STEFANIC, Candice, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Understanding the functional implications of skeletal morphologies seen only in extinct animals in the fossil record is a fundamental goal of paleontologists. We can study the skeletons of living relatives to make predictions about how morphologies have evolved over time; for example we look at the bones of crocodiles and birds to make predictions about dinosaurs. To tackle questions about how animals moved (e.g. walking, flying, swimming), it is critical to study the axial skeleton, which includes the vertebral column and ribs, of both extinct and extant animals. The vertebrate clade Archosauria includes two living groups (e.g. crocodylians, birds) that are extremely disparate in skeletal morphology and locomotory strategy, so we need to look at fossils to understand what intermediate morphologies were present over the past 220 million years. Many extinct archosaurs were larger than any other living terrestrial animal (e.g. sauropod dinosaurs, tyrannosaurs), so understanding how skeletal morphology is related to body size is a key component to interpreting form and function in the fossil record. Because the vertebral column is the main axis of support against the forces of gravity, studying the structure of vertebrae and how articulation structures (i.e. zygapophyses) that fit vertebrae together can provide insight into the evolution of novel locomotory strategies or large body sizes. My research focuses on understanding how articulation surface area (e.g. the planes of a vertebra that touch adjacent vertebrae) along archosaur vertebral columns has changed over time and the functional implications of these changes. Many extinct members of Archosauria independently evolved extra articulation structures (i.e. hyposphene-hypantrum), not seen in any living organism, that add an additional surface of articulation at a different angle to the zygapophyses. This leads to the question: why was the hyposphene-hypantrum lost in crocodiles and birds? This could possibly be due to disparate locomotory strategies or miniaturization in extant clades. My hypothesis is that accessory intervertebral articulations increase the relative surface area of articulation between vertebrae. To test this I have taken measurements of articular surface area of extinct and extant archosaur taxa with and without the hyposphene-hypantrum. Preliminary data has shown that birds ($n = 8$) and crocodiles ($n = 1$) have similar ratios of articular surface area to their vertebra height. These data allow us to better understand the evolution of vertebral morphology and to make interpretations about how increased area of articulation is related to body size and locomotion.

Advisor: Dr. S. J. Nesbitt

EVALUATING THE FORMATION OF ALUMINUM OXY-HYDROXIDE COATINGS IN ANOXIC LIMESTONE DRAINS USED TO TREAT ACID ROCK DRAINAGE

PALOMINO ORE, Sheyla, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Anoxic limestone drains are an effective and low-cost method for passive treatment of acid rock drainage (ARD). The goal of the method is to add alkalinity to AMD under anoxic conditions, keeping iron (Fe) in its reduced form to avoid the oxidation and precipitation of ferric hydroxide on the limestone, which can reduce the limestone's neutralization capacity and efficiency. In addition to Fe, ARD often has elevated concentrations of aluminum (Al), which can precipitate to form hydroxide, sulfate, and/or hydroxysulfate minerals on the surface of the limestone. Although Fe mineral coatings have been well-studied, there have been few studies evaluating formation of Al coatings in limestone drains.

My M.S. project will use batch reactor experiments to evaluate the reaction between acidic Al-rich solutions and calcite and the formation of secondary Al-rich minerals. During the experiments, I will measure the concentrations of Al, calcium and pH of the solutions to quantify the rates of Al mineral formation and calcite dissolution. Solids will be characterized using x-ray diffraction (XRD), scanning electron microscopy (SEM), and additional techniques if needed. The experimental results will be used to quantify the effect of the mineral coatings on the dissolution kinetics of the underlying calcite, which will provide insight into fundamental processes of mineral coating formation. This research also has applications to the natural environment and the design of water treatment systems, as the results can be used to estimate the lifetime of a limestone drain used for treating ARD under different pH conditions and Al concentrations.

Advisors: Dr. M. Schreiber, Dr. D. Rimsdit, Dr. J. Chermak

THE MALAGASY LITHOSPHERE-ASTHENOSPHERE SYSTEM CONSTRAINED BY INDEPENDENT INITIAL TEMPERATURE CONDITIONS: IMPLICATIONS FOR EXTENSIONAL PROCESSES

RAJAONARISON, Tahiry, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Lithospheric factors such as pre-existing weaknesses and heat transfer by magmatism are known to promote continental rift initiation, however the balance of forces driving the onset of continental rifting remains elusive. Madagascar is ideal for studying continental rift initiation because a range of geophysical observations indicates the continental island undergoes extensional processes. In this study we seek to understand the dynamic role of upper mantle flow on present-day expressions of extension in Madagascar. We use the 3D finite element numerical code Advanced Solver for Problems in Earth's ConvecTion (ASPECT) to compute asthenospheric flow and lithospheric deformation in Madagascar and surroundings. In a first step we use a realistic 3D ellipsoidal model to calculate and compare lithosphere-asthenosphere velocities driven by two independent initial temperature conditions: (1) conductive-convective thermal structure defined by a lithosphere isotherm, i.e. edge-driven convection, and (2) a temperature perturbation derived from the SAVANI global shear wave velocity model, i.e. whole-mantle convection. In a second step we compare depth-dependent velocities with surface expressions of extension. Preliminary solutions indicate edge-driven upper mantle flow is slower than whole mantle convection, but the patterns are consistent with asthenosphere upwelling in central Madagascar. Whole mantle flow patterns beneath Madagascar align with global kinematic predictions of broad-scale Somalian plate motion in a hot-spot reference frame, yet small-scale, edge-driven convection is consistent with global kinematics only in regions with thickened lithosphere. These results suggest small-scale convection may play a key role in localizing extensional forces in central Madagascar.

Advisor: Dr. D. Sarah Stamps

FLUID EVOLUTION IN THE NORTH AMERICAN EMERALD MINE (NAEM), HIDDENITE, NC

KLYUKIN, Yury, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Emerald is a green gemstone variety of the beryl, in which color is defined by trace amounts of Cr and V. Gem quality emeralds can be formed in very different geological settings, in which only a few conditions have to be fulfilled. According to Zwaan (2006) these conditions are defined as: 1) availability of Be and Cr (V), 2) chemical and physical conditions at which beryl is stable and 3) sufficient free space for emeralds to grow.

NAEM is located near Hiddenite, North Carolina and produced more than 60,000 carats. The emeralds occur in cavities in close association with quartz, muscovite and carbonate. Cavities located in Alpine fissure-type quartz veins hosted by Silurian migmatitic metasedimentary rocks interlayered with calc-silicate rocks that reached upper amphibolite facies (sillimanite grade). Fluid inclusions (FI) are abundant in minerals forming in cavities.

FI in emeralds, carbonates, rutile, tourmaline and quartz were analyzed to characterize fluid composition and its evolution. Based on room temperature phase ratios, the fluid has a composition of ~80-90 mole% CO₂ and 10-20 mole% H₂O. Raman and microthermometry analysis showed that the FIs composition dominated by high density CO₂ (average density ~0.77 g×cm⁻³ for quartz, ~0.74 g×cm⁻³ for carbonates and emerald, ~0.88 g×cm⁻³ in rutile, ~0.64 g×cm⁻³ in tourmaline). Low density CO₂ inclusions appear in quartz only with density ~0.26 g×cm⁻³.

Salinity of the fluid in FI in carbonates and rutile was estimated to be ~ 3 wt. % NaCl eq. based on clathrate melting temperature. In some samples next daughter phases of FIs identified: graphite in emerald and carbonates, nahcolite in quartz. Graphite could indicate that the fluid is characterized by reducing conditions while presence of nahcolite – alcali conditions of the fluid.

Oxygen isotopes were measured for quartz, rutile and muscovite samples from single emerald-bearing cavity and two cavities without emeralds. Assuming that these minerals formed in paragenesis, for these cavities temperature of the fluid and δ¹⁸O were calculated. Temperature evaluated as 450-510 °C, δ¹⁸O ranged between ~11-12 ‰ indicating magmatic or more likely metamorphic source of fluid. Metamorphic fluid hypothesis supported by presence of CO₂-rich fluids, which are characteristic of medium-grade metamorphic environment. At identified temperature, PVTX data for the system H₂O-CO₂ indicate a minimum pressure of formation of ~2 kbar.

ROLE AND EVOLUTION OF STRUCTURAL AND PHYSICOCHEMICAL PROPERTIES OF COMMERCIALY-SOURCED PLATINUM NANOCATALYSTS DURING THE CATALYTIC DECOMPOSITION OF H₂O₂.

SERRA MAIA, Rui Filipe, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Platinum (Pt) based nanocatalysts are important in many industrial and technological processes, ranging from catalytic conversion in modern automobiles to renewable energy production by hydrogen fuel cells. These technological innovations have a tremendous impact on our environment in terms of global climate change and, soil, water and air quality. The majority of research on catalysis has focused on uniform catalytic structures at controlled conditions. However, commercial catalysts in real-world applications are physicochemically and structurally complex, particularly at the surface, and modify with time. Our goal is to understand how the physicochemical and structural attributes of two commercially-sourced Pt nanocatalysts affect the catalytic rate and mechanism of H₂O₂ decomposition at different conditions of reaction. My overarching hypothesis is that the impact of different reaction conditions (pH, temperature, and H₂O₂ concentration) on the catalytic activity of Pt nanocatalysts during the decomposition of H₂O₂ is related to changes in the catalyst (surface) structural and chemical properties.

We have been using high-resolution transmission electron microscopy, x-ray diffraction, and spectroscopic methods to evaluate and quantify physical, structural and chemical properties of nanosized Pt catalysts during the decomposition of H₂O₂. Our results show that crystal size and shape, and the incorporation of different amounts of oxygen at or near the surface have a significant impact in the catalytic activity of Pt nanocatalysts. *Ex situ* electron microscopy and Raman spectroscopy results suggest that surface dynamics play an important role in this reaction. A transient phase of PtO_x forms at the surface of the catalysts during the reaction with H₂O₂, but is absent before H₂O₂ comes in contact with the catalyst as well as after it is all decomposed to water. In addition an adventitious carbon-bearing layer is present at the surface of both catalysts and its chemical composition and morphology change during the reaction.

We will soon perform *in situ* electrochemical TEM studies (Oak Ridge National Laboratory, TN) to elucidate in real-time the evolution of surface PtO_x phases (crystal structure, oxidation state, etc.) formed during the catalytic decomposition of H₂O₂. The information from my characterization and activity studies will form the basis of a general model that describes the mechanisms underlying the enhanced reactivity of Pt nanocatalysts. As Pt is important in many industrial and technological applications, our findings will have the potential to increase process selectivity and improve nanocatalyst design and performance.

Advisor: Dr. F. M. Michel

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

HUANG, Yong, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

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 intensity of each peak can provide important information of molecule structures of minerals. But, the intensity of a given Raman peak is also influenced by the molecular structure as well as the amount of each mineral, grain size and orientation. The change of physical properties of powder samples (such as particle size, packing density) has a significant effect on the Raman spectrum. However, there is little research on how to eliminate the influence of changes in the physical properties to improve the accuracy of Raman spectroscopy quantitative analysis of powder samples. 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 changes in physical properties. However, these spectral preprocessing methods have very demanding requirements on the system under test. For example, MSC, SNV and EISC require that different chemical composition changes between the samples are very small, and the shapes of spectra need to be highly similar. These requirements are very difficult to meet in practice. In addition, these spectral preprocessing methods are all empirical methods which were not proved theoretically. 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. A simple mixture of quartz and feldspar was selected for the first test, and they will be mixed in known proportions and analyzed by Raman spectroscopy. The first tests will be done on samples ground to less than 20 micrometers. The first step of grinding the minerals under 88 micrometers has been done.

Advisor: Dr. Robert J. Bodnar

INVESTIGATING STRESS INTERACTIONS IN A YOUNG RIFT SEGMENT OF THE EAST AFRICAN RIFT SYSTEM

JONES, Joshua, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Tectono-magmatic processes play a crucial role in strain accommodation during continental rifting. Previous studies of 2007 diking events in the incipient continental Natron Rift link associated stress changes to subsequent diking, eruptions at Ol Doinyo Lengai, and slip on intra-rift faults spanning 2007-2008. Small stress changes (0.1 MPa) are considered sufficient to promote ensuing tectono-magmatic events e.g. intrusions, eruptions, and faulting. In this project we seek to understand the influence of stress changes from a local volcanic event to slip on the Natron border fault where the majority of strain is accommodated in the incipient Natron Rift. We test this interaction by (1) developing a new analytical model of the Ol Doinyo Lengai Natron Border Fault system, (2) calculating the evolution of Coulomb stress changes and displacements on the Natron border fault due to the 2007-2008 rifting episode in the Natron rift, and (3) comparing results with existing geodetic observations that measure ~ 2.8 cm on the Natron Fault adjacent to the volcano and ~ 1.5 cm 18 km north on the border fault. Our preliminary results indicate that ~ 2 MPa of Coulomb stress change associated with Ol Doinyo Lengai eruptions in 2008 and $\sim .03$ MPa on the Natron fault 18 km north of the volcano supports slip on a segment of the Natron Fault. However, the geodetic evidence used shows that there is potential missing surface displacement to still be accounted for in slip on more of the Natron Fault.

Advisor: Dr. D. S. Stamps

A PARAMETIRC ANALYSIS OF CAPILLARY PRESSURE EFFECTS DURING THE CARBON SEQUESTRATION INJECTION PROCESS IN A SANDSTONE RESERVOIR

WU, Hao, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24060

Geological Carbon Sequestration (GCS) is considered as a key method for mitigating the adverse effects of steadily increasing atmospheric CO₂ concentrations. Numerical simulation is one technique for better understanding the injection, migration and leakage of supercritical CO₂ (scCO₂) during GCS. At the field scale, capillary pressure (P_{cap}) is an important factor governing the subsurface movement of scCO₂. Constitutive models of P_{cap} as a function of wetting phase saturation (S_w) are essential to field-scale GCS simulations; however, such P_{cap} models are based on core-scale laboratory measurements. As a result, there exists uncertainty in the application of laboratory-measured P_{cap} models to field-scale GCS simulations. In this study, a parametric analysis of commonly used van Genuchten P_{cap} model is undertaken to quantify the effects of variability in the model parameter space. The study focuses on two parameters: the non-wetting phase entry pressure (P_0) and the pore-size distribution index (λ), the latter of which controls curvature of the P_{cap} model. A two-dimensional parameter space is selected that covers a wide range of laboratory-scale P_{cap} measurements in the scCO₂-brine system, and scCO₂ injection processes are modeled within a homogeneous sandstone reservoir over the complete parameter space. Simulation results demonstrate how changes in the P_{cap} model parameters influence scCO₂ migration within the storage reservoir. Maximum injection pressure is largely insensitive to variability of P_{cap} model parameters; however, vertical scCO₂ migration is strongly controlled by P_{cap} model parameter selection. Since vertical scCO₂ migration is the key point to estimate scCO₂ leakage risk through caprock sealing, these results illustrate the importance of P_{cap} model parameter selection in field-scale numerical models of GCS.

Advisor: Dr. R. M. Pollyea

THE ROLE OF THE CONTINENTAL BIOSPHERE IN EARTH'S GEOHYDROLOGIC CYCLE IN DEEP TIME

ANGEL, Adam, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The continental biosphere consists of all life on Earth's land surface and is largely comprised of plant biomass. Although the biosphere is the smallest major reservoir of water on Earth, the hydrologic processes linking the biosphere to other exospheric water reservoirs influence rates of precipitation and surface runoff to the oceans. Furthermore, the presence or absence of plant life on Earth influences the global carbon cycle, which plays a major role in climate change throughout Earth's history. The amount of water in the BIO reservoir, as well as the movement of water into and out of the BIO reservoir, has varied over the past 444 Ma. Before the Silurian, the amount of water in the continental biosphere was essentially nil, whereas the amount of water in the modern biosphere is 2.9×10^{15} kg H₂O. Previous workers have investigated variations in BIO-related hydrologic processes over short time scales (yr-ka), though none have linked these processes to deep-time variations (Ma) in the global water cycle.

As part of an ongoing study of the exospheric hydrologic cycle, we have developed a numerical model to assess variations in the amount of water in the continental biosphere over the past 444 Ma. Input data for the model combines the amount of water in the various geohydrologic cycle reservoirs (Bodnar et al., 2013) (atmosphere, the cryosphere, the biosphere, continental surface water, groundwater, and the oceans) with the fluxes of H₂O between these reservoirs. Starting from modern values, we examine how the amount of water in the biosphere and adjacent reservoirs change in proportion to some observed environmental change (e.g., variations in global temperature) and literature estimates of variations in plant biomass during Earth's history. The fluxes of H₂O between the biosphere and other reservoirs also change in response to changing environmental conditions, e.g., variations in the surface areas of the continents, ice caps, or oceans. We further examine the influence of extinction events on the hydrologic cycle and quantify the sensitivity of hydrologic processes with respect to the removal of land plants from the whole-Earth system.

Our results suggest that total annual precipitation decreases by 0.11% for every 1% decrease in biomass (from modern values). Results also suggest that surface runoff increases by 0.69% for every 1% decrease in biomass (from modern values). As plant life is removed from the Earth's surface, less water is transpired to the atmosphere, and thus less water is precipitated to the surface. Furthermore, a portion of water removed from surface water by the biosphere via transpiration is allocated to surface runoff. These results are consistent with observations of high-flow braided river deposits formed during major extinction events in Earth's history (e.g., Late Permian). Furthermore, these results have implications for temporal variations in seawater chemistry, whereby an increase in surface runoff during extinction events will result in an increase in dissolved chemical species transferred to the oceans.

EVIDENCE OF PLEISTOCENE GLACIAL RECHARGE IN A CRYSTALLINE FRACTURED BEDROCK IN NEW ENGLAND

BARTOS, John, Department of Geosciences, Virginia Tech, Blacksburg, VA 24061

As part of an ongoing Remedial Investigation (RI) at a Superfund facility in New England, a geochemical evaluation of the surface water and groundwater was conducted to identify the different groundwater flow paths in both overburden glacial deposits and fractured crystalline metamorphic bedrock. The geochemical evaluation included the collection of field parameters, major cations and anions, and stable isotopes of oxygen and hydrogen in water in 27 monitoring wells and 3 surface water stations. The evaluation determined that the groundwater had distinct geochemistry based on the presence of anthropogenic chlorinated aliphatic compounds (ACIA). The native groundwater was a lower Total Dissolved Solids (TDS) calcium-bicarbonate type water while the impacted groundwater was a higher-TDS calcium-chloride type water.

Using the stable isotopic portion of the evaluation and supplemental regional data from the USGS, a groundwater mixing between a “shallow flow system” and a “deeper regional flow system.” The presence of the ACIA had very limited isotopic effect on the water molecule itself. The shallow flow system had an oxygen-18 value of -6.5 per mil VSMOW and a deuterium value of -45 per mil VSMOW. The determination of the isotopic values for the regional flow system itself is less ambiguous. Based on the general circulation modeling of the last Wisconsinian-age glaciation event for the area from Ferguson and Jasechko (2015), the postulated regional flow system isotopic values would have an oxygen-18 value of -12 per mil VSMOW if recharged by this glacial event. The isotopic mixing between the two flow systems suggest that the regional flow system was derived from this glacial recharge.

CHARACTERIZING THE FRACTURED CRYSTALLINE BEDROCK AQUIFER AT PLOEMEUR, FRANCE USING MULTIPLE SURFACE DEFORMATION AND WATER-LEVEL SIGNALS

WILSON, Matthew, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Aquifers in fractured crystalline bedrock are located over half of the earth's surface and are vital social and economic resources. As social resources these aquifers provide potable water to a significant percentage of municipal and domestic entities across the globe. Economically important, these aquifers also provide water to industry in areas where surface water is scarce, as well as provide deep, long term storage for contaminated water or nuclear waste. Understanding the characteristics of these aquifers is important for quantifying sustainability and projecting effects of water usage.

When hydraulic head changes in a fractured crystalline system, it is associated with changes in effective stress, which ultimately affect the apertures of fractures that carry the water through these aquifer systems. The widening and narrowing of fractures associated with fluid-pressure changes can be detected and measured by surface-mounted tiltmeters. These measurements provide information about a multitude of aquifer characteristics, including changes in fracture aperture and fluid flow direction, as well as important poromechanical properties of the fracture and host rock.

Investigation of multiple surface tilt signals at different temporal scales at the Ploemeur research site in Brittany France will allow us to investigate fault and contact zone fracture characteristics in this complex hydrogeological setting. There are three main components to the aquifer's hydrologic system: 1) a fault dipping 70° and striking 20° north, 2) a shallow dipping contact zone between granite basement rock and an overlying mica-schist formation, and 3) a 10m to 20m thick layer of connected saprolitic overburden, which moderates recharge to the underlying system. Presently only the impact of the fault has been thoroughly characterized from short term cyclical pumping and subsequent tilt measurements. Moving forward the remaining components of the system will need to be characterized in order to create a comprehensive regional hydrological model that describes the fault-fracture system and recharge characteristics of this locally important aquifer system.

Adviser: Dr. TJ Burbey

SYNTHESIS AND CHARACTERIZATION OF PRECURSORS TO SCHWERTMANNITE, A FERRIC OXYHYDROXIDE SULFATE NANOMINERAL

KLETETSCHKA, Karel, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The iron oxyhydroxide sulfate known as schwertmannite is a poorly-crystalline nanomineral that is ubiquitous in iron-rich, acid sulfate waters, particularly in acid rock drainage (ARD) environments. To advance our understanding of biogeochemical processes in ARD systems, in-depth knowledge of the mineral formation mechanisms involved is crucial; namely, the (potentially) non-classical pathways of nucleation and growth. The aggregation and self-assembly of small clusters via partially or fully oriented attachment has been increasingly observed in numerous natural and synthetic systems and evidence suggests that these mechanisms may be essential in understanding schwertmannite formation. Exploring the nature of these clusters, how they aggregate, and whether or not their physicochemical characteristics are inherited in the final structure of the material is essential in fully comprehending ARD biogeochemical processes. Preliminary *in situ* synchrotron total scattering experiments in our group have shown evidence of 1.5 nm schwertmannite-like clusters in syntheses involving rapid ferrous iron oxidation. However, considering the delicate nature of nucleation/growth events, differences in synthesis parameters have the potential to significantly alter the formation mechanism and must therefore be carefully controlled. For instance, the effect of redox processes on pre-nucleation clusters and final product composition can be explored using trivalent, ferric iron precursors instead of their divalent analog; coordination chemistry will behave differently in the two syntheses along the associated pH range and this may impact product formation and homogeneity. Detection and characterization of pre-nucleation clusters in both schemes necessitates a range of material characterization techniques, each elucidating different aspects of the mineral growth pathway. Previous studies (Weatherill et al. *ES&T* 50:9333-9342, 2016) involving *in situ* small angle x-ray scattering (SAXS) have provided direct evidence of iron pre-nucleation clusters in ferrihydrite syntheses, setting a precedent for using the technique in analogous iron-oxide systems such as schwertmannite. We propose using a suite of *in situ* techniques such as SAXS, synchrotron x-ray total scattering, and high-resolution transmission electron microscopy (HR-TEM) under variable synthetic conditions (stirring rate, ferrous vs. ferric iron reagents, etc.) to detect and characterize these pre-nucleation clusters in real time. Central to these characterizations will be the use of mixed flow reactor systems, which allow for real time monitoring as well as precise tuning of reaction conditions (flow rates, residence times, etc.). By employing these mixed flow reactors, we aim to introduce more precision into iron oxide mineral nucleation/growth studies - improving both reproducibility as well as environmental relevancy in laboratory-based geological research.

Advisor: Dr. F. Marc Michel

DOES THE MAXIMUM BODY SIZE OF THEROPOD DINOSAURS INCREASE ACROSS THE TRIASSIC-JURASSIC BOUNDARY? INTEGRATING GROWTH PATTERNS AND ANCESTRAL STATE RECONSTRUCTION

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

Dinosaurs originated in the Late Triassic ~230 million years ago as small (2–3 m long) carnivores, but by the Early Jurassic they had evolved huge body sizes and a range of diets. A sharp increase in the maximum body size of theropods (carnivorous dinosaurs closely related to birds) has been reported across the Triassic-Jurassic boundary in central Pangaea based on footprint data, but quantifying the maximum body size of Triassic theropod body fossils is necessary to enable comparison with large-bodied theropods of the Early Jurassic (e.g., the theropod *Dilophosaurus*, 6 m long). Because the dinosaurian fossil record is dominated by immature, still growing individuals, ignoring the growth stage of specimens when undertaking an analysis of body size can skew reconstructed body size. Only a few large Triassic theropods are known (although smaller than the largest Jurassic theropods), and I incorporated analyses of skeletal maturity of available specimens to better understand body size evolution across the Triassic-Jurassic boundary. I assessed the maturity of large-bodied Triassic theropods from North America (*Gojirasaurus*; ~79% the size of *Dilophosaurus*), Europe (*Liliensternus*; 70% *Dilophosaurus* size), and Argentina (*Zupaysaurus*; ~69% *Dilophosaurus* size), as well as two large unnamed theropod individuals (a partial skeleton and an isolated fibula) from the Late Triassic of New Mexico, using skeletal features known to be indicative of immaturity in closely related theropods (i.e., unfused bones, lack of muscle scars of bones). The skeletal features present are most consistent with immature individuals still growing rapidly. I also sampled the bone microstructure of the partial isolated fibula, ~68% *Dilophosaurus* size, and a partial skeleton ~56% *Dilophosaurus* size, which strongly suggests that they were still growing rapidly as well. This suggests that these individuals had not yet reached skeletal maturity, although they are of sufficient size to form the largest Triassic tracks in central Pangaea. Furthermore, I placed these individuals into a hypothesis of evolutionary relationships to construct an evolutionary tree of early theropods, and using body size data from these species I reconstructed the ancestral body size for theropod dinosaurs using a Brownian motion model. This reconstruction suggests that the ancestral theropod was small, but that theropods increased in maximum body size before the Triassic-Jurassic extinction. These data suggest that the sharp increase in theropod track size in central Pangaea is a local, not worldwide, trend. The maximum body size of theropods does not expand much or at all across the Triassic-Jurassic boundary.

Advisor: Dr. S. J. Nesbitt

ANALYSIS OF A CONDUCTIVE HEAT FLOW PROFILE IN THE ECUADOR FRACTURE ZONE

KOLANDAIVELU, Kannikha, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

We report 18 new conductive heat flow measurements collected from a sediment pond located in the inactive part of the Ecuador Fracture Zone in the Panama Basin. The data were collected along an east – west transect coincident with a multi-channel seismic reflection profile that extends from the Hole 504B to west of the sediment pond. Conductive models indicate that heat flow should decrease from 416 mWm^{-2} on the 1.5 Ma western plate to 208 mWm^{-2} on the 6 Ma eastern plate; however the observed heat flow increases nearly linearly toward the east from approximately 140 mWm^{-2} to 190 mWm^{-2} . The mean value of 160 mW m^{-2} represents an average deficit of $\sim 49\%$, which we attribute to lateral advective heat transfer between exposed outcrops on the western and eastern margins of the sediment pond. We apply the well-mixed aquifer model to explain this eastwardly flow, and estimate a volumetric flow rate per unit length in the north-south direction of $\sim 438 \pm 268 \text{ m}^2 \text{ yr}^{-1}$ through the basement aquifer. Using a Darcy flow model with the mean flow rate, we estimate permeabilities of $\sim 2 \times 10^{-11}$ and $7 \times 10^{-13} \text{ m}^2$ for aquifer thicknesses of 100 and 1000 m, respectively. The estimated permeability values are similar to other estimates in young oceanic crust and suggest that vigorous convection likely occurs in the basement. These data suggest that lateral heat advection significantly modify the thermal regime of fracture zones, which might then perturb their observed gravitational signals and topographical evolution. Additional heat flow data are needed to determine the importance of advective heat transfer in fracture zones on a global scale.

CONSTRAINING THE EFFECTS OF PERMEABILITY UNCERTAINTY FOR GEOLOGIC CO₂ SEQUESTRATION IN A BASALT RESERVOIR

JAYNE, Richard, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The concentration of atmospheric CO₂ is currently at the highest levels within the last 800,000 years. It is well documented that increasing anthropogenic CO₂ emissions results in increasing global temperatures. Carbon capture and sequestration (CCS) in geologic reservoirs is one strategy for reducing anthropogenic CO₂ emissions from large-scale point-source emitters. Recent developments at the CarbFix CCS pilot in Iceland and the Wallula Pilot Project in Washington have shown that basalt reservoirs are highly effective for permanent mineral trapping on the basis of CO₂-water- rock interactions, which result in the formation of carbonates minerals. In order to advance our understanding of basalt sequestration in large igneous provinces, this research uses numerical simulation to evaluate the feasibility of industrial-scale CO₂ injections in the Columbia River Basalt Group (CRBG). Although bulk reservoir properties are well constrained on the basis of field and laboratory testing from the Wallula Basalt Sequestration Pilot Project, there remains significant uncertainty in the spatial distribution of permeability at the scale of individual basalt flows. Geostatistical analysis (i.e. variogram map and directional semivariograms) of hydrologic data from ~540 wells illustrates that CRBG reservoirs are reasonably modeled as layered heterogeneous systems on the basis of basalt flow morphology; however, the regional dataset is insufficient to constrain permeability variability at the scale of an individual basalt flow. As a result, permeability distribution for this modeling study is established by using the cumulative distribution frequency and a sequential indicator simulation (SISIM) that is conditioned on the Wallula borehole, which results in a spatially-correlated random permeability distribution within the target reservoir. In order to quantify the effects of this permeability uncertainty, constant pressure CO₂ injections are simulated within 50 equally probable synthetic reservoir domains (5km×5km×1.3km). Each model domain comprises three-dimensional geometry with 530,000 grid blocks with dimensions of 50m×50m×25m, and fracture-matrix interaction is simulated as interacting continua for the two low permeability layers (flow interiors) bounding the injection zone. Currently simulations are run utilizing TOUGH3 with the ECO2M module, to evaluate CO₂ phase change during buoyancy driven flow. Preliminary results from this research illustrate that permeability uncertainty at the scale of individual basalt flows may significantly impact both CO₂ accumulation, distribution, and leakage rates into overlying formations.

Advisor: Dr. R. M. Pollyea

FINITE-FREQUENCY TOMOGRAPHY OF THE 410-KM AND 660-KM DISCONTINUITIES USING SS PRECURSORS

GOU, Zhen, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The mantle transition zone is characterized by two discontinuities at depths of about 410 and 660 km. Mineral physics studies suggest that wavespeed and density jumps across the discontinuities are associated with olivine phase transformations and the depths at which the phase transformations occur are strongly dependent on temperature. Imaging lateral variations of the discontinuities depths is important for constraining thermal structure in the mid mantle. S410S and S660S waves are underside reflections of SS waves off the 410-km and 660-km discontinuities. Traveltime measurements of SdS waves at teleseismic distances can be used to constrain the depths of the two discontinuities at global scale.

We measure frequency-dependent SS precursors traveltimes using seismograms recorded at GSN stations for earthquakes occurred between 2004 and 2014. The measurements are made using cosine tapers and reveal significant dispersion. We calculate finite-frequency sensitivity kernels for SdS-SS differential measurements based on traveling-wave mode summation, which account for complete wave interaction within the measurement window. We parametrize the surface of the Earth using a set of spherical triangular grid points and solve the least-square problem of the inverse equation using singular value decomposition method. We compare our measurements with published models and show the effects of 3-D crustal structure and mantle wavespeed structure. We will show our results of the depth perturbations of the MTZ discontinuities as well as the MTZ thickness. We will also discuss the correlation between the topography of the 410- and 660-km discontinuities and comparison with the mantle shear velocity anomalies.

Advisor: Dr. Ying Zhou

A NUMERICAL METHOD FOR DETERMINING THE VOLATILE CONTENTS OF BUBBLE-BEARING MELT INCLUSIONS IN OLIVINE

MOORE, Lowell, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The volatile contents of silicic melts are important for understanding the geochemical evolution of our planet and for assessing volcanic hazards. Melt inclusions, droplets of melt trapped at the surface of growing minerals, are the only part of the geologic record that retains information about melt volatile contents. Because melt inclusions cool and decompress as they are brought to the surface, the silicic melt that is trapped is converted into mixture of fluids and solids. Thus, to determine the bulk composition of the melt, it is necessary to use a combination of analytical, experimental, and numerical methods to homogenize the inclusion. For this reason, many workers prefer to analyze melt inclusions that have quickly quenched so that they only contain glass and a fluid bubble. In this relatively simple case, it is possible to analyze the glass using a combination of microanalytical methods and the bubble using Raman spectroscopy. A mass balance calculation is then used to derive a bulk composition for the inclusion. Because many labs do not have high-resolution Raman spectroscopy available, it would be useful to have a numerical method for calculating the volatile content of the bubble. The goal of this study is to develop and evaluate such a model. In our modeling approach, we use the major element composition of the glass, the bulk composition of the host rock, and the composition of the mineral host to calculate the cooling interval of the inclusion and the extent of postentrapment crystallization. The volume of exsolved fluid is calculated based on the density change of the host and the melt over the temperature interval. The volatile content of the glass is used to calculate the pressure of the exsolving fluid, and an equation of state for a mixed H₂O-CO₂ fluid is used to determine the molar volume of the fluid. Compared to the data from Raman spectroscopy, the model results are accurate. Further refinement of the model is challenging because of a significant analytical uncertainty that is compounded by the mass balance calculations, and uncertainty associated with estimating the volume of melt inclusions is the primary limiting factor. The results indicate that a modeling approach is an adequate substitute for Raman analysis, and further improvement in estimating melt inclusion volumes is necessary.

Advisors: Dr. Esteban Gazel, Dr. Robert J. Bodnar

DETERMINING THE EFFECTS OF pH AND SOLUTION CHEMISTRY ON THE STRUCTURE AND TRANSFORMATION OF AMORPHOUS CALCIUM PHOSPHATE.

HOEHER, Aly, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Minerals are a common natural resource, present in the water we drink, makeup we apply, buildings we reside in, phones we communicate with, and the bones that support our bodies. They are a critical component of our existence and modern lifestyles. The processes and mechanisms behind how a crystal grows and develops are important questions for understanding the origin and potential uses of such critical materials. Classical models of crystal growth involve atom by atom addition to mineral surfaces in terrace, step, or kink positions. Recent studies are demonstrating minerals forming in ways outside of the classically defined models. These ‘non-classical’ processes often include the formation of partially to fully-formed nanoparticle precursors that aggregate or transform into a bulk crystalline end member (De Yoreo et al. 2015).

Hydroxylapatite and brushite form in aqueous solution from an amorphous calcium phosphate (ACP) precursor. It has been proposed that ACP is an aggregation of calcium phosphate clusters that are about 1 nm in diameter (Posner and Betts 1975), although the existence of these clusters, as well as their structural and chemical characteristics remains uncertain. We are using pair distribution function (PDF) analysis to examine the effects of pH and presence of magnesium on the structure of ACP and its crystallization process. Data are collected *in situ* using a mixed flow reactor, at a certain reaction time related to the speed at which the initial solutions are pumped into the reactor. Data has been collected at a reaction time of about 10 minutes. ACP precipitated at a pH of 7 crystallizes into brushite, whereas ACP formed at a pH of 10 results in crystalline hydroxylapatite. The structures of ACP precursors formed at different pH conditions vary, suggesting that initial ACP structure influences the final crystalline product. The presence of Mg in the reaction chemistry inhibits crystallization of ACP, but does not have a significant effect on the short-order structure of the amorphous precursor. Examining dried samples with thermogravimetric analysis (TGA) also has shown that samples with magnesium are more hydrated than their, otherwise identical, magnesium-free counterparts. Future efforts will focus on lengthening the reaction time of data collection, which will provide insights into the calcium phosphate crystallization mechanisms.

Advisor: Dr. F. M. Michel

LIQUID-VAPOR PARTITIONING OF NA AND CA IN THE H₂O-NACL-CACL₂ SYSTEM AT 500-700°C AND 550-750 BARS

SUBLETT, D. Matt, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The partitioning behavior of Na and Ca between two immiscible fluid phases in the H₂O-NaCl-CaCl₂ system at 500-700°C, 550-750 bars, and for Na:Ca molar ratios of 2:1, 1:1, and 1:2 was determined using the synthetic fluid inclusion technique. The partitioning behavior of Na in the H₂O-NaCl binary limb of the ternary H₂O-NaCl-CaCl₂ system has been well described in the literature, however data for the partitioning behavior of Ca in the H₂O-CaCl₂ binary limb at the PT conditions of interest is lacking and as such, fluids with a Na:Ca molar ratio of 0:1 (i.e. on the H₂O-CaCl₂ binary) were also used. For the synthetic fluid inclusion technique, a single-phase fluid of known composition is sealed inside a platinum capsule with an inclusion free quartz core that has been thermally fractured. This platinum capsule is then placed inside a cold-seal pressure vessel and taken to the experimental run conditions. For most of the studied PTX combinations, a single-phase fluid underwent phase separation into a high density, high salinity liquid and a low density, low salinity vapor, each of which was then individually trapped in the form of fluid inclusions (FI) as the fractures in the host quartz healed. At room temperature, the FI that trapped the vapor phase contain a vapor bubble and a small amount of liquid that condensed from the vapor during quenching. At room temperature, the FI that trapped the liquid phase have liquid, vapor and either a halite daughter mineral or both halite and antarcticite (CaCl₂·6H₂O) daughter minerals, depending on the composition of the liquid at the experimental run conditions. The salinities of the liquid rich FI were determined from the dissolution temperatures of the last daughter mineral to dissolve before the halite, either a calcium chloride hydrate or hydrohalite (NaCl·2H₂O) depending on the true composition of the liquid, and the halite during heating of the FI. In many cases, this initially required freezing of the inclusions to precipitate the hydrohalite or calcium chloride hydrate. The salinities of the vapor rich FI were determined by measuring the freezing point depression of the liquid that condensed from the vapor in the FI. Measured compositions of the coexisting liquid and vapor phases were used to calculate the partitioning coefficients of Na and Ca between the coexisting liquid and vapor phases. Preliminary results indicate that Ca preferentially partitions into the liquid and Na preferentially partitions into the vapor.

EVALUATING THE USE OF THALLIUM ISOTOPES AS A PALEOREDOX PROXY

LEROY, Matthew, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Marine anoxia is often invoked as a contributing factor in biological crises throughout Earth history. While recent technical developments have advanced our ability to recognize anoxia, obstacles still remain for reconstructing the extent and timing of these ancient environmental changes. This is especially true for studies focused on events prior to the mid-Jurassic, as much of the volume of relevant sediment record has been lost through subduction. This limits the applicability of traditionally used qualitative measures (e.g., increased occurrence of black shales) for inferring increases in the areal extent of anoxic bottom waters. A number of quantitative approaches using redox-sensitive metals and isotopic systems (e.g., Fe, Ni, V, Cr, Mo, U) as proxies for both local and global changes in oceanic oxygenation have been developed to address this fundamental limitation. However, the proxies used for estimating global changes in marine redox—the type of change most relevant to large extinction events—can often be complicated by local redox changes.

The geochemical behavior of the stable isotopes of thallium (^{203}Tl and ^{205}Tl) has recently emerged as a proxy with potential for resolving some of the ambiguity inherent in estimating global marine redox conditions. The thallium isotope proxy's utility relies upon: (1) isotopic homogeneity of the ocean due a residence time of ~ 23 ka, roughly an order of magnitude greater than oceanic mixing. (2) Authigenic Fe-Mn oxides, which only form in sediments deposited under oxic bottom waters, are isotopically enriched in ^{205}Tl relative to seawater. (3) Pyrite formed under anoxic bottom waters inherits the Tl isotopic composition of coeval seawater ($\epsilon^{205}\text{Tl}_{\text{SW}}$). Therefore $\epsilon^{205}\text{Tl}_{\text{SW}}$ from pyrite deposited in anoxic basins, can be used to track changes in the magnitude of the global Fe-Mn oxide removal flux, which is a reflection of the extent of oxic bottom waters.

To evaluate the thallium isotope proxy, we analyzed the $\epsilon^{205}\text{Tl}$ of samples from the Cambrian Alum Shale, a black shale deposited along the margin of Baltica. The studied interval contains the SPICE event, a putative global anoxic event. The persistently anoxic depositional conditions during the deposition of the Alum make it ideal for tracking potential global changes in $\epsilon^{205}\text{Tl}_{\text{SW}}$ and anoxia over the SPICE.

AN INVESTIGATION OF THE EFFECTS OF CONTACT METAMORPHISM BY A DIKE OF THE CENTRAL ATLANTIC MAGMATIC PROVINCE ON ITS HOST ROCK

TULSKY, Emma, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The rapid emplacement of the Central Atlantic Magmatic Province (CAMP) has been suggested as a driver for the Triassic-Jurassic mass extinction event through the large-scale release of greenhouse gases to the atmosphere. The thermal alteration of sedimentary rocks through contact metamorphism caused by CAMP may have also significantly contributed to this release of gas. This process can alter the carbon and sulfur bearing phases within the host rock leading to the release of volatile species containing these elements. In this study I aim to quantify the carbon and sulfur budgets of one such host rock, the sedimentary rocks of the Newark Supergroup, during the contact metamorphism generated by CAMP within the Culpeper Basin of Virginia. Specifically, I wish to identify the sources of the carbon and sulfur species in these rocks and the mineralogical transformations that occurred due to thermal alteration.

The Culpeper Basin consists of shale and siltstones that have been intruded by CAMP diabase. This diabase intrusion and host sedimentary rock are exposed in the Luck Stone Quarry in Centreville, Virginia presenting an ideal field site for this study. Samples of the sedimentary host rock were taken every half meter along three beds that dip orthogonal to the diabase intrusion. Geochemical analysis reveals an increase in sulfur content in a zone between 7.8 and 9.8m from the intrusion, suggesting sulfur from circulating fluids was precipitated in a reaction zone. Carbon isotopic data show both minimal total organic carbon within the rocks as well as a biological source for this organic carbon. Sulfur isotopic data will be presented to help bring to light the processes that are taking place during this particular dike emplacement of the CAMP. These results, paired with thermodynamic modeling and SEM analysis, will provide potential insight into the processes that occurred during the contact metamorphism of the host rock in this portion of CAMP and more generally, inform models for the alteration of sedimentary host rock through contact metamorphism.

ANALYSIS OF GARNET-QUARTZ GRAIN BOUNDARIES IN METAMORPHIC ROCKS VIA TRANSMISSION ELECTRON MICROSCOPY

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

Grain boundaries can be defined as the 10-20 nm distance from one grain to its neighbor and are important because they represent the most significant pathways for intergranular diffusion in metamorphic rocks. The properties of grain boundaries are important because they probably control equilibration and crystallization processes. However, they are generally not well characterized. The purpose of this study is to analyze garnet-quartz grain boundaries from different metamorphic terranes (subduction zone, regional, and contact) and over increasing temperatures in a contact metamorphic aureole to understand the characteristics of grain boundaries at different metamorphic conditions.

Garnet-quartz grain boundaries are an important grain boundary to analyze. Both minerals are stable over a range of metamorphic conditions, and while the chemistry and structure of quartz remains relatively static over the duration of metamorphism, garnet's chemistry can record tectonic processes. Thus, the quartz provides a baseline to analyze the changes in garnet at increasing pressure and temperature.

First, the samples will be analyzed under Petrographic Microscope and Scanning Electron Microscope to determine the location of garnet-quartz grain boundaries. Chemical element maps will be created on an Electron Microprobe to understand the garnet growth zoning. The samples will then be prepared for Transmission Electron Microscopy (TEM) Analysis. I will use multiple imaging techniques in the TEM to analyze the nanoscale chemistry and structure of the grain boundaries. I plan on specifically looking for the presence or absence of: voids, nanoscale inclusions, and nanoscale elemental zoning. I plan on also quantifying the width of the grain boundaries and the crystallographic lattice orientation between grains using high resolution electron microscopy. This will allow me to map how grain boundaries differ in rocks that have been subjected to varying pressures, temperatures and deformation. Ideally, my results will allow me to connect nanoscale processes that occur at grain boundaries to larger tectonic and metamorphic events.

Advisors: Dr. Mark Caddick, Dr. Marc Michel

IS SHEAR HEATING IMPORTANT IN METAMORPHIC SYSTEMS?

MAKO, Calvin, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

It is widely known that numerical models of crustal deformation and metamorphism have difficulty reproducing temperatures that are commonly observed by metamorphic petrology and other techniques in orogenic belts. An often-neglected component of large-scale numerical models is the contribution of mechanical work to the heat budget of a deforming system. Viscous or frictional deformation is expected to produce heat as a function of strain rate and the differential stress causing the deformation. Many numerical studies have shown that mechanical work, causing shear heating, could be an important factor in strain localization and the thermal evolution of orogenic belts. Very few field based studies have demonstrated that significant shear heating has occurred or that it contributed significantly to the heat budget of a metamorphic system. In this contribution, I review microstructural constraints on differential stresses and strain rates experienced by naturally deformed rocks and calculate the maximum amount of heat that could be produced under these deformation conditions.

Quartz microstructures are particularly useful for understanding mechanical work during deformation. A calibrated paleopiezometer exists that relates recrystallized quartz grain size to differential stress. Stress values can be used to calculate strain rates via flow laws. With these parameters, heat production due to mechanical work can be calculated. I have calculated the change in temperature due to shear heating over a wide range of deformation conditions and durations using a one dimensional implicit finite difference scheme. Paleopiezometry estimates from the Main Central thrust and South Tibetan detachment in the Himalaya (Francis, 2012) suggest heat production rates of $0.1\text{-}300\ \mu\text{W}/\text{m}^3$ with most values at $1\text{-}50\ \mu\text{W}/\text{m}^3$. Depending on the duration of deformation, temperatures may increase on the order of 10's to 100's of degrees (C) with these rates of heat production. These estimates should be regarded as maxima because increasing temperature will tend to weaken rocks, which results in less heat generation. For example, initial calculations show that during deformation at 300°C and $3\ \text{cm}/\text{yr}$ convergence, a differential stress drop of $5\text{-}15\ \text{MPa}$ can occur after 10 Ma of deformation with total temperature increases of $25\text{-}45^\circ\text{C}$. More complex strain geometries will do more mechanical work and increase heat production. These calculations provide a generalized first order estimate of the amount of heat that mechanical work can add to a metamorphic system.

Poster Session Abstracts

(in alphabetical order)



WEATHERING OF IN-SITU STRATA AND SPOILS AS A SOURCE OF DISSOLVED SOLIDS ASSOCIATED WITH COAL MINING IN VA, WV, AND KY

ANDERSON, Hannah, M, Undergraduate Student, Department of Geosciences, Virginia Tech, Blacksburg, VA 24060

A petrographic analysis of weathered in-situ and spoil samples from Appalachian coal mines reveals the effects of weathering on the streaming of mineral ions into surrounding watersheds. Framework grains in the sandstones consist of quartz, feldspar, and muscovite as well as quartz-mica schist. Rare heavy minerals such as zircon and tourmaline are present. Cements in the sandstones are primarily siderite rims, quartz, kaolinite, and rare carbonates. In the in-situ samples, feldspars typically are replaced by kaolinite. In these samples, the partial dissolution of chlorite and muscovite could be seen as well as the presence of ferruginous carbonate as a replacement mineral. In the spoil samples, feldspar also shows signs of kaolinitization as well as local dissolution. These samples also showed evidence of K-feldspar, plagioclase, and muscovite hydrolysis by acidic groundwater. Feldspar dissolution and hydrolysis is likely volumetrically the most significant source of K, Na, and Ca in river waters. Dissolution of carbonate minerals is another possible source of Ca, but these minerals were rare and thus likely a very minimal contributor to Ca in local watersheds. The partial dissolution of chlorite also contributes Mg to stream waters. Much concern exists of the possible source and effect of SO₄, Na, Ca, K, and Mg in rivers downstream from the sampled mines. The study conducted accounts for the source of all ions; however, the source of SO₄ remains inconclusive.

IMPACT OF PHYSICOCHEMICAL PROPERTIES ON THE CATALYTIC ACITIVITY OF TWO COMMERCIALIZED PLATINUM CATALYSTS

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

Platinum (Pt) nanocatalysts are widely used in technological and industrial processes such as fertilizer synthesis, automotive emission controls, petroleum refinement and also for the development of sustainable next-generation power sources such as hydrogen fuel cells. Previous catalysis researches have mainly focused on understanding idealized systems while relatively few studies have considered the properties of industrially-produced and commercialized catalysts that are used in many applications. The surfaces of commercial nanocatalysts can be heterogeneous due to differences in composition and the presence of organics coatings. The particle sizes and shapes can also vary significantly. This project focuses on understanding how different physicochemical properties of two commercial platinum nanocatalysts, Pt-black and Pt-nanopowder, relate to their catalytic performance. Our characterization results show that Pt-nanopowder and Pt-black are similar in terms of their bulk and surface composition, but also show that Pt-nanopowder has a more spherical shape and a larger average crystallite size and. We hypothesize that differences in the physicochemical properties of the two nanocatalysts lead to differences in their catalytic activity.

We have been measuring the catalytic activity of Pt-black and Pt-nanopowder over a range of reaction conditions (temperature, pH, reagent concentration) using the decomposition of hydrogen peroxide (H_2O_2). Our results show that the catalytic activity decomposition for both catalysts in H_2O_2 is a first order reaction, but the effect of pH on the catalytic activity of Pt-nanopowder is stronger than on Pt-black. In addition, we found that temperature impacts the activity of Pt-black but not of Pt-nanopowder. Despite having larger crystallite size, the normalized catalytic activity of Pt -nanopowder is greater than the normalized catalytic activity of Pt-black in the range of tested conditions. This suggests that particle size, shape and surface chemistry all play a critical role in the catalytic activity of Pt nanocatalysts. Preliminary Raman spectroscopy also suggests that PtO_x forms during H_2O_2 decomposition. We are combining *ex situ* characterization techniques with rate models to develop a comprehensive understanding of the mechanisms that will help to understand the differences in the catalytic behavior of these two catalysts in the decomposition of H_2O_2 . With platinum playing an important role in many industrial and technological applications, our findings will have the potential to increase process selectivity as well as to improve the design and performance of new catalysts.

Advisors: Dr. F. Marc Michel, Rui Serra

TESTING FOR THE PRESENCE OF PERIGLACIAL PROCESSES IN BOULDER FIELDS IN THE SOUTHERN APPALACHIANS: DEVIL'S MARBLEYARD, VA

CATON Summer, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The origin of the Devil's Marbleyard boulder field is generally understood to be the result of periglacial processes although neither quantitative nor qualitative data currently exist to support this theory. This research is significant for understanding the extent of periglacial processes as well as erosional regimes of the southern Appalachians, which together provide a baseline for understanding how the landscape will respond to future climate change and anthropogenic modification. The Late Wisconsinan Glaciation, or the Last Glacial Maximum (LGM) of the Laurentide Ice Sheet in North America, significantly modified the glaciated northern Appalachians. It also brought periglacial conditions to the southern Appalachians that notably affected the landscape (Braun, 1989). Throughout Pennsylvania, south of the glacial limits, the origin of features such as blockfields and boulder streams have been attributed to periglacial processes, including freeze-thaw processes and frost shattering (Ciolkosz et al., 1986). Quantitative data that addresses how far south LGM periglacial conditions prevailed is sparse. Devil's Marbleyard is a large boulder field (approximately 28,277 square meters) composed of quartzite boulders of the Cambrian Chilhowee Group (Antietam Quartzite) in the Virginia Blue Ridge province. High resolution topography based on structure-from-motion was obtained to generate 3D models of the field area, from which in-model measurements of over 200 boulders were used to find if size and orientation distribution trends existed. Associated mapping of the boulders and joints in bedrock was performed in order to determine the processes controlling how the boulder field was emplaced. Cosmogenic radionuclide dating, performed at PRIME Lab at Purdue University, was used to find the age control on the boulder field. Preliminary data suggests that the boulder field may exist due to a unique topographic setting combined with mechanical stratigraphy as a block slide, without the requirement, but possible imprint, of periglacial processes.

Advisors: Dr. James Spotila , Michelle Fame

GEOCHEMISTRY AND VOLATILE BUDGETS OF POST-SHIELD VOLCANOES OF THE CANARY ISLAND HOTSPOT

DATKO, Alexandra, Department of Geosciences, Virginia Tech, Blacksburg, VA 24061

The concentration of volatile components of magma is linked to the explosivity of volcanic eruptions and changes in atmospheric chemistry, as well as the formation of economically important ore deposits. However, because of decompression as the melt rises to the surface, important volatiles such as H₂O and CO₂ are rarely preserved. Melt inclusions are the only way that these volatiles can be trapped and preserved in the geologic record, so analysis of melt inclusion samples is an important part of calculating CO₂ fluxes and evaluating volcanic hazards of volcanoes that are not currently active. Our objective is to analyze melt inclusions from tephra samples from the Canary Island volcanoes to measure the volatile content of the parent magma. We sorted tephra samples and olivine phenocrysts to isolate unbroken, glassy melt inclusions 50 micrometers in length or greater. Several of the tephra samples from Tenerife Island contain abundant olivine phenocrysts with glassy, vapor bubble-bearing melt inclusions. The inclusions typically contain a vapor bubble that is about 1-3 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 CO₂, which homogenizes to a liquid just above room temperature. This indicates that the bulk density of the fluid falls between 0.47 and 0.74 g/cc and the concentration of CO₂ in the trapped melt was at least 1582 to 10936 ppm.

Advisor: Dr. Esteban Gazel

VARIATION IN OCEAN OXYGENATION ACROSS THE TRIASSIC-JURASSIC EXTINCTION

GROVE, Hannah, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The Triassic-Jurassic extinction event is one of the “Big Five” mass extinction event where approximately half of the known species on the Earth became extinct. Several mechanisms have been proposed as causes of this event and include climate change, an asteroid impact, massive volcanic eruptions and the development of marine anoxia. The chemical signals that reflect this past marine oxygen depletion can be recorded in rocks that were formed from sediments that were deposited on the bottom of the ocean during that time. Specifically, redox sensitive elements in the rocks, like iron and sulfur, record the availability of free oxygen and the change in the degree and ubiquity of anoxia can then be determined. The objective of my study is to reconstruct the changes in oceanic redox chemistry during the event in order to test the role of anoxia in the Triassic-Jurassic extinction event.

The samples that are used in this study are from the Felixkirk Borehole located in the United Kingdom and was located in the Tethys Ocean during the Triassic-Jurassic extinction. Geochemical data, such as sulfur isotope and iron speciation measurements, are being collected from these rocks. Preliminary pyrite sulfur contents indicate two distinct intervals of increased pyrite abundance that occur at the extinction which may indicate enhanced reducing marine conditions. Pyrite sulfur isotope and iron speciation data will be used further investigate the local redox changes during the event and test the role of anoxia in the Triassic-Jurassic extinction event.

Advisor: Dr. B. C. Gill

EFFECT OF SWINE MANURE ON LIMESONE DISSOLUTION

HELMS, Tara, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Localized wastewater sources on karst terrain that discharge directly into the subsurface can enhance the dissolution of limestone. Previous work suggests that landfill leachate leads to the formation of localized permeable fissures in karst. Based on this previous work, we hypothesized that manure application may also have an enhanced effect on dissolution of limestone. To address this hypothesis, we conducted a batch laboratory experiment where we observed the effect of swine manure on limestone dissolution. Six treatments were constructed using combinations of diluted swine manure, limestone, soils and deionized water. Limestone of the Boone Formation and overlying soils were collected from Newton County, Arkansas, a karst region characterized by extensive agriculture, including a swine Confined Animal Feeding Operation. Liquid manure was collected from the Virginia Tech swine farm. During the six week experiment, we measured pH, Ca and Mg of the experimental solution. Results show an increase in the pH and in the Ca and Mg concentrations in the treatment containing limestone and manure in comparison to the control (no manure), suggesting that the manure accelerated the dissolution of the limestone. Data will be used to calculate rates to allow for quantitative comparison of the effect of manure on limestone dissolution.

Advisor: Dr. Shuhai Xiao

STUDY OF HEMATITE IRON ROSES

KELLY, Erin, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Hematite, Fe_2O_3 , is an important iron-ore mineral that occurs in a number of different varieties, including kidney ore, martite (pseudomorphs after magnetite), specularite (specular hematite) and iron roses. However, little is known about the crystallographic controls on the formation of these different varieties of hematite, especially for the iron roses. Iron roses are commonly found in the Gotthard Pass located in the northernmost tip of the canton Ticino in Switzerland. A “bud-like” sample collected from this area was found in a pegmatite in association with plagioclase feldspar, biotite, iron hydroxides, and oxidized quartz. The “bud” itself was found in a quartz vein possibly altered by fluids. This sample will be compared with iron rose specimen from Minas Gerais, Brazil that show more platy habits. Experiments are underway using Raman spectroscopy and X-ray diffraction to confirm the presence of iron oxides and to determine crystallographic information such as the orientation of the plates that appear to conform to the hexagonal symmetry of hematite. The experimental results will be combined with crystallographic modelling using the program VESTA to build atomic-scale models that reproduce the forms of the iron roses. The insights gained from this project are expected to provide information about crystallographic controls on the formation of iron roses and the environments in which they form.

Advisor: Dr. Nancy Ross

IRON AND MANGANESE OXIDATION CYCLES IN AN OXYGENATED RESERVOIR

KRUEGER, Kathryn, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Iron (Fe) and manganese (Mn) cause water quality issues in drinking water reservoirs, especially during summer months when thermal stratification can lead to low dissolved oxygen (DO) conditions. Under these conditions, Fe and Mn can be released from the sediment into the water column. These metals are costly to treat; thus, efforts have been made to address the issue *in situ* before the water reaches the treatment plant.

One *in situ* method, installed at a local drinking water reservoir in 2013, includes use of a side stream supersaturation (SSS) system to oxygenate the reservoir to prevent low DO. In past years (2013-2015), the SSS has been activated for different periods of time during the summer to evaluate the impact of oxygenation on metals and other water quality parameters. Results have shown that metals are released from sediment, regardless of the extent of oxygenation. However, increased oxygenation promoted Fe oxidation, with lesser impact on Mn oxidation.

In 2016, the SSS was activated continuously over the period of thermal stratification (April 18, 2016 to October 17, 2016). To evaluate the impact of continuous oxygenation on metal release and cycling within the reservoir, I collected water samples with depth over a five-month period from the oxygenated reservoir and also from a nearby reference reservoir that is not oxygenated. Results show that the SSS significantly lowered the concentrations of soluble Fe and Mn in the hypolimnion of the oxygenated reservoir (maximum Fe = 8.6 mg/L, maximum Mn = 1.9 mg/L) in comparison to the reference reservoir, which had much higher soluble concentrations of Fe and Mn in the hypolimnion (maximum Fe = 29.0 mg/L, maximum Mn = 4.0 mg/L). Comparison of these data with previous years shows that continuous oxygenation results in lower soluble metal concentrations in the hypolimnion in the oxygenated reservoir. However, even during continuous oxygenation, concentrations of soluble Mn in the lowest depths of the hypolimnion still exceed the secondary drinking water standard.

THERMOGRAVIMETRIC ANALYSIS OF AMORPHOUS AND CRYSTALLINE HYDRATED CALCIUM PHOSPHATES

McLaren, Mat, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Hydroxylapatite is a naturally occurring calcium phosphate mineral. Natural hydroxylapatite is similar to the majority of bone mineral, comprising up to 50% by volume and 70% by weight (Junqueira 2003). This biocompatibility makes hydroxylapatite useful in the creation and enhancement of bone implants and replacements. Amorphous calcium phosphate (ACP) is a precursor phase in the crystallization process of both hydroxylapatite and brushite, a hydrated calcium phosphate mineral, when they precipitate in solution. We synthesized ACP with and without magnesium at pH 7 and 10. X-ray diffraction (XRD) showed that samples formed at a lower pH (~7) crystallized to brushite, while samples formed at a higher pH (~10) formed hydroxylapatite. The presence of magnesium in the initial ACP samples inhibited ACP crystallization, which may be related to Mg adsorption onto active growth sites (Souza et al. 2013). Our structural analysis suggests that the ACP precursors to hydroxylapatite and brushite are different. It is not known how the compositions of these phases compare, especially in regards to the abundance of water (OH, H₂O) in ACP. We are hypothesizing that differences in the amount (and possibly type) of water in ACP formed at pH 7 and 10 are related to differences in their crystallization behavior.

We used thermogravimetric analysis (TGA) to examine the water content of ACP, hydroxylapatite and brushite. The mass of each sample (done in triplicate) was measured continuously during heating from room temperature to 1000 °C. TGA results show significant weight losses associated with loss of physi- and chemi-sorbed water at temperatures between 400-1200 °C. The samples were held at 90°C for 10 minutes to evaporate most of the physi-sorbed water. Samples with magnesium showed greater weight loss indicating higher water content, possibly due to Mg-OH bonds. Weight losses for ACP were less than for brushite and hydroxylapatite, and the weight loss events for the crystalline samples were also sharper and more distinct. Major weight loss events in our samples aligned with observations seen in previous literature (Geisse et al. 2011; Liao et al. 1999; Krajewski et al. 2005;). Our work will provide additional scientific value in comparing ACP, brushite, and hydroxylapatite altogether instead of looking at them individually. Future work will use thermal XRD to understand how dehydration relates during heating relates to crystallization. Understanding the role of water in calcium phosphates will give us a better understanding of the relationship between the crystalline and amorphous phases.

Advisor: Dr. F. M. Michel

A PRELIMINARY EVALUATION OF SPINEL-STRUCTURED INCLUSIONS IN OLIVINE AS A RAMAN BASED GEOBAROMETER

NEILLY, Mark, Department of Geosciences, Virginia Tech, Blacksburg, VA 24061

Numerous mineral-based geobarometers are available to constrain pressure in igneous systems, but a barometer for mineral inclusions in olivine does not yet exist. Based on recent studies of mineral inclusion barometry, spinel inclusions in olivine may record trapping pressures that can be applied to estimate the pressures at which olivine phenocrysts begin to crystallize from melts of mafic composition. This method assumes that: 1) the volumetric changes during cooling of the host and inclusion are a function of only the elastic properties of each. 2) the host behaves as a rigid container and that volumetric changes are only a result of thermal expansion and the bulk modulus. 3) The thickness of the host surround the inclusion is infinite. Because the thickness of the olivine host is finite, it is necessary to determine “what thickness of surrounding host is required for the inclusion to adequately preserve original trapping pressure?” We attempt to answer this question by analyzing spinel-structured inclusions in olivine that are hosted at different depths beneath the host surface, using Raman spectroscopy. Previous studies have shown that various peaks in the Raman spectra of spinel-structured minerals such as magnetite and chromite show systematic variations as a function of pressure. To determine the minimum amount of surrounding material required for the inclusion to maintain the original trapping pressure, inclusions in several olivine phenocrysts will be analyzed by Raman repeatedly, each time after reducing the thickness of the surrounding host by careful polishing.

To determine the pressure of spinel-structured inclusions, we use a relationship between the Ag1 peak of the spinel Raman spectrum and the pressure reported by Lin et al. (2014). Trapping pressures can then be calculated from the independently-determined trapping temperature and the elastic properties of spinel and olivine. In addition to developing a geobarometer for olivine controlled igneous systems, this study will also provide a method for evaluating other similar mineral inclusion geobarometers.

Advisor: Dr. Robert J. Bodnar

SYNTHESIS AND CHARACTERIZATION OF IMOGOLITE NANOTUBES

PALFEY, William, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Imogolite is an aluminosilicate clay nanomineral commonly associated with weathered soils rich in volcanic ash. It forms hollow nanotubes with an outer diameter of ~ 2.2 nm, a wall thickness of ~ 0.7 nm, and a length that can be up to several microns. In nature, imogolite has been shown to play an important role in various systems through its ability to contain and transport both contaminants and nutrients, including water (Yuan & Wada, 2012). Additionally, recent studies have begun investigating synthetic imogolite's potential application in polymer composites and as an insulating sheath in nanocables (Kuc & Heine, 2009).

The imogolite growth mechanism is not fully understood. Previous work on synthetic samples showed that short (5-10 nm long) imogolite nanotube segments are precursors to the final elongated nanotubes (Levard et al., 2010). We recently used this to hypothesize that imogolite grows by the aggregation and self-assembly of these precursors in a process known as crystallization by particle attachment (CPA). We developed a synthesis procedure that uses germanium (Ge), which can substitute for silicon (Si) in the imogolite structure, as a chemical label. Our preliminary transmission electron microscopy (TEM) characterization results on imogolite grown from a mixture of Ge-free and Ge-doped ($\text{Si}_{90}\text{Ge}_{10}$ imogolite) precursors showed segmentation along the tube length, which suggested growth via CPA. The substitution of Ge for Si in imogolite causes the nanotube diameter to increase. This raises the question of whether higher amounts of Ge will inhibit the self-assembly of Ge-doped and Ge-free precursors due to a mismatch in tube diameters. In order to test this, we are now performing growth experiments with two groups of imogolite precursors, one containing only silicon (Si_{100} imogolite) and one containing only germanium (Ge_{100} imogolite). Atomic force microscopy (AFM) is being used to measure the dimensions of the precursors and final products in order to assess growth. Subsequent TEM characterization will assess the composition along the tube lengths, as we have done previously. Ultimately, the results of this study could aid in our understanding of low-temperature clay formation in the environment as well as in developing new strategies for synthesizing composite and other materials for technological applications.

LASER ABLATION ICP-MS ANALYSIS OF TRACE ELEMENTS IN PYRITES OF GAS SHALES: IMPLICATIONS FOR MOBILITY

PLECHACEK, Amy, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Trace elements contained in pyrite-bearing shale have the potential to be mobilized when the shale is exposed to oxygen. Although this occurs naturally, hydraulic fracturing processes may enhance pyrite oxidation, and trace element release, from the shale to water. First, the introduction of oxygenated fracturing fluid to the shale source rock may oxidize the pyrite *in situ*, allowing trace elements to be released into flowback water. Flowback water is typically stored in retention basins, which can leak, allowing these toxic trace elements to enter water supplies. Second, shale rock cuttings from drilling are also exposed to oxygen at the surface, producing acid drainage and allowing trace element release. Many trace elements are toxic and are regulated by the U.S. EPA; therefore, examining the mineral sources and potential mobilization mechanisms is important for protecting water supplies in areas impacted by hydraulic fracturing.

In this study, pyrites and the shale matrix of gas-producing shales were evaluated for trace element content using laser ablation inductively-coupled mass spectrometry (LA ICP-MS). Four thin sections from four cores in the Marcellus Formation, the most expansive shale-gas play in the U.S., were analyzed by LA ICP-MS. NIST 612 glass was used as the external standard, and the USGS MASS-1 and BIR-1G were used as check standards. Results show elevated concentrations of some trace elements, including As and Cd, in pyrites compared to the shale matrix. In contrast, Ba, Cr, Ga, Mo, Mn, V, Th, and W are more abundant in the shale matrix than in the pyrite. Future research will include analyzing other phases for trace elements.

FABRICATION OF MICROFLUIDIC DEVICES FOR REAL-TIME CRYSTALLIZATION STUDIES

SUBOWO, Andrew, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Recent research has revealed numerous “nonclassical” pathways of growth for nanocrystals. These pathways involve nanosized precursors that form, grow, and attach together. The precursors of nonclassical pathways are often unstable, nanosized, and partially crystalline or amorphous, which makes characterizing their physical and chemical characteristics challenging. New *in situ* methods are required to observe precursors forming and assembling at environmentally relevant solution conditions. In this project, we are designing and developing microfluidic, or “lab-on-a-chip” devices to study nonclassical crystallization processes in real time. Microfluidic devices offer a distinct advantage over conventional reactor systems because they are highly customizable in terms of creating different mix and flow (turbulent vs. laminar) conditions. However, several design and fabrication challenges need to be overcome in order to use microfluidics for *in situ*, real time crystallization studies. First, to use the devices in x-ray scattering and spectroscopic analysis, the overall thickness of the reactor windows on either side of the channels must be minimized in order to reduce background noise and absorption. This requires novel microfluidic reactor designs because current microfluidic protocols use thick, rigid substrates, such as glass, that interfere strongly with x-ray beams. A second issue is unwanted interactions between the as-formed particles and the polydimethylsiloxane (PDMS) channel walls which lead to aggregation and deposition. We have developed several new protocols to fabricate microfluidic devices without glass substrates. The average thickness of the channels and windows on these prototypes are approximately 250 micrometers (total thickness is 750 micrometers), which are extremely thin by previous standards. Due to the flexible nature of PDMS-based microfluidic devices, a custom device holder was manufactured out of carbon fiber in collaboration with the Virginia Tech Modeling and Educational Demonstration Lab (MEDL). We recently tested the new prototypes at the Advanced Photon Source (APS) synchrotron facility at Argonne National Lab, evaluating the scattering signal obtained from flowing solutions containing different sized gold nanoparticles. We also evaluated whether it was feasible to use cellulose acetate or carbon fiber as rigid-like backing substrates. We anticipate that this work on developing specialized microfluidic reactors for real time crystallization studies will lead to an improved understanding of nonclassical growth processes.

Advisor: Dr. Marc Michel

DISTRIBUTION OF MAGNESIUM AND PHOSPHORUS IN THE *H. AMERICANUS* EXOSKELETON: INSIGHTS FOR CHEMICAL SIGNATURES IN BIOMINERALS

ULRICH, Robert, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Crustacean exoskeletons are complex biocomposites of organic macromolecules and calcium carbonate minerals. The highly divergent functions and diverse morphologies of their exoskeleton biominerals across taxa raise the question of whether these differences are systematically reflected in exoskeleton composition and structure. Previous studies that investigated element concentrations in exoskeletons commonly used Raman and Energy-Dispersive X-ray Spectroscopy (EDS). However, the findings were largely inconclusive because of analytical limitations and the scope of each study. Most concluded that magnesium, phosphorus, and other trace elements are primarily contained in the mineral fraction without resolving the distribution across multiple body parts.

This experimental study was designed to quantify the distributions of Ca, P, and Mg in the mineral versus organic fractions of exoskeletons from the American Lobster (*Homarus americanus*). Samples of exoskeleton from 7 body parts were collected in triplicate and dissolved using three procedures specific to extracting the 1) mineral, 2) protein, and 3) polysaccharide phases separately. Chemical analyses of the resulting effluents using ICP-OES show the mineral fraction of the skeleton contains the most total Ca, Mg, and P content with a ratio of approximately 10:1:1. In the protein and polysaccharide fractions, Ca and Mg concentrations are 100x lower than in the mineral and P content is 10x lower. Previous studies (Hild *et al.*, 2008; Boßelmann *et al.*, 2007) assume P to be contained entirely within the mineral fractions and report higher bulk concentrations of the element.

The findings reveal the chemical composition of an exoskeleton cannot be assumed constant across the different body parts of an entire organism. This is particularly significant when comparing the elevated Mg and P content of the claw exoskeleton to the rest of the body. In both environments (claw and other body parts), however, the ratios of elements to each other are constant. The consistent offset of element ratios in the claws suggest a highly controlled biomineralization process to optimize body part functionality. Measurements of these elements across the body of adult lobsters is highly biased by the presence of biominerals and may impact modern sampling studies. This study holds promise for better understanding exoskeletons crustacean life cycles across species and modern/ancient environmental conditions.

VOLATILE BUDGETS OF HAWAIIAN REJUVINATED VOLCANOES: NEW INSIGHTS FROM MELT INCLUSIONS

VANDERGRIFT, Heather, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

The Hawaiian Islands are made up of a chain of shield volcanoes that continuously erupt during a voluminous shield stage and then reach a dormant stage that lasts for 0.5-2 Ma until volcanic activity resumes. There are several competing models for Hawaiian island evolution that can explain the pause, but they are difficult to evaluate because of a lack of data regarding the volatile budgets of these volcanoes. In this study, we collected fresh tephra samples from Haleakala to quantify the concentration of CO₂ in the melt. Minor recrystallization was seen in some of the inclusions, which exhibited a dark brown color. Although several of the tephra samples contain recrystallized melt inclusions, a few of the tephras erupted near the center of the volcanic complex have glassy melt inclusions, and only these fresh glassy inclusions are considered. Melt inclusions typically contained spinel daughter crystals and a fluid bubble, that sometimes contained a mixture of liquid and vapor. The bubble ranged from 1 to 3 volume percent of the inclusion with an outlier of 10 volume percent. We also observed sulfide globules attached to the edge of the inclusion or attached to the bubble. Carbonates can be seen as spots along the surface of the bubble. We calculated a minimum CO₂ content of the melt using Raman spectroscopy and a mass balance calculation. The density of the CO₂ in the bubbles was between 0.21 g/cm³ and 0.56 g/cm³. From the data analyzed the total CO₂ content resulted in a range between 746 ppm to 19,042 ppm (1.9 wt%). This corresponds to a trapping pressure of about 5.6 kilobars that is close to the minimum for trapping pressures or a 19.53 km depth. A pressure of this agrees with the pressure range that is found in the last stages of equilibration in these volcanoes based on previously-observed pyroxene-melt equilibration. It is important to note that these minimum volatile contents ignore the presence of CO₂ partitioned into carbonate daughter crystals, and further work is needed to quantify this additional CO₂.

CHARACTERIZING SURFACE PROPERTIES OF NATURAL IRIDESCENT IRON (HYDR)OXIDE MINERALS

ZIGAH, Sean, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Iridescent minerals are visually spectacular. Naturally occurring hematite, iris quartz, opal, and labradorite are among the more sought after iridescent minerals because of their intense and often broad, rainbow-like spectrum of colors. Iridescence in minerals is caused by two main mechanisms: repetitive structures that act as a diffraction grating which interferes with visible light, and thin-layer interference. A recent study using electron and atomic force microscopic imaging methods and x-ray diffraction (XRD) showed that these phenomena explain iridescence in hematite and several other minerals (Lin, Xiayang, Causes of Iridescence in Natural Gem Materials, MSc Thesis. Penn State, 2015). Hematite iridescence, in this case, was attributed to the interference of light caused by an ordered microstructure of hematite nanorods on a freshly fractured mineral surface.

In this project we are using scanning electron microscopy and powder XRD to evaluate the origin of iridescence in the natural (unaltered) surfaces of two boytroidal turgite samples. Unlike this previous study, which used fractured hematite samples, we are interested in understanding whether there are other types of surface features that cause iridescence. Boytroidal turgite (goethite and hematite) samples reportedly collected from Graves Mountain, Georgia were purchased online. Bulk XRD patterns showed that both samples consist of goethite-hematite mixtures. SEM imaging and chemical analysis by energy-dispersive spectroscopy (EDS) were performed on small pieces broken off of the iridescent surfaces. Interestingly, imaging showed no evidence of ordered microstructures reported previously for fractured hematite. Rather, we observed random aggregates of pseudo-spherical structures with dimensions of a few hundreds of nanometers. EDS chemical analysis of these spherical structures revealed aluminum and a few other trace elements; however, the overall chemical compositions of these structures were consistent with that of goethite/hematite.

We are using these observations to hypothesize that iridescence from boytroidal Fe (hydr)oxide minerals is caused by light interfering with a surface coating consisting of randomly aggregated nanospheres. Future experiments will further characterize the size distributions of the nanospheres. We will also attempt to correlate differences in iridescence color with variations in the size and/or distributions of the nanospheres at the surfaces. If this is indeed a newly identified mechanism of iridescence, it may be of interest for creating artificial materials with iridescent properties.

GSRS 2017

MADE POSSIBLE BY THE
FOLLOWING DONORS:



ALUMNI DONORS:

ADAM HENRY, CHRISTINA BLUE, ZHIYONG WANG & FANG LIN
ERIC RUFÉ, MAX VITYK, HANNAH KING
CHANGYEOL LEE, NICK WIGGINTON

THANKS ALSO TO OUR FACULTY DONORS AND TO EVERYONE WHO DONATED
TO GSRS 2017 THROUGH THE VT FOUNDATION WEBSITE