

Geosciences Student Research Symposium



2016

21st Annual Geosciences Student Research Symposium

Thursday, February 25, 2016 - 9:15am – 4:45pm

Friday, February 26, 2016 - 9:15am – 5:00pm

4069 Derring Hall

Department of Geosciences

Virginia Tech

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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.

Faculty, students, and visiting guests are highly encouraged to offer constructive feedback on the presentations using evaluation forms available at the symposium. Completed evaluation forms should be returned to the boxes provided in the presentation room. Each talk is scheduled to last 12 minutes, with three minutes for questions (15 minutes total).

Breakfast and light snacks will be served in the 4th floor West Lobby of Derring Hall. Lunch will be provided in the Geosciences Museum (2062). On Friday, a catered dinner in the Geosciences Museum will conclude the symposium. 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. We also thank the Department of Geosciences for their generous support. Finally, we want to thank the faculty, volunteers, and student participants, for donating their time and expertise – without you this event would not take place.

Graduate Student Coordinating Committee for 2016 GSRS

Rui Serra-Maia, Caitlin Colleary, Emma Tulsy, Lowell Moore, Calvin Mako, Jarek Trela, Sebastian Mergelsberg, Sarah Ulrich, Brady Ziegler

PDF version of the abstract book: <http://www.geos.vt.edu/events/gsr2016/abstracts.html>

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A GEOCHEMICAL AND SEDIMENTOLOGICAL INVESTIGATION OF A TRIASSIC LAGERSTÄTTE IN THE COW BRANCH FORMATION OF THE DANVILLE-DAN RIVER BASIN

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The North American Atlantic passive margin contains a number of early Mesozoic lacustrine basins. The sedimentary record within these basins, now preserved as the Newark Supergroup, is comprised of cycles attributed to Milankovitch climate forcing. Of these basins, the Triassic Danville-Dan River basin is of specific interest as it hosts beds of exceptionally preserved, soft-bodied fossil insects, known as the Triassic Lagerstätte. Our research aims to investigate one sedimentary cycle within the Danville-Dan River Basin, integrating both the chemical and physical features preserved in the stratigraphy to develop a comprehensive model of the depositional environments of the lake through time. More specifically, we are interested in determining whether distinct environmental conditions led to the formation of the Lagerstätte.

Approximately 11 meters of core material was logged and sampled from the Cow Branch Formation of the Danville-Dan River Basin, taken from the Virginia Solite Quarry. Importantly, this core captures a full sedimentary cycle and contains the Lagerstätte layer. Total organic carbon (TOC) and pyrite sulfur contents are highest (up to 3.52 wt% and 0.35 wt% respectively) near the middle of the section, where the facies are laminated and appear darkest. The higher TOC is associated with isotopically lighter (more negative) $\delta^{13}\text{C}_{\text{org}}$ values suggesting a greater portion of the organic carbon is sourced from primary production within the lake. Preliminary iron speciation analyses show that most of the reactive iron is bound in iron carbonates and pyrite. Further iron analyses will be used to determine oxic vs. anoxic conditions in the water column and any changes in oxygenation state during deposition. Moreover, an absence of silica and existence of minerals such as analcime throughout the cycle signal at least intermittent alkaline water chemistry. Together, these initial data suggest the presence of reducing and alkaline conditions within the lake and its sediments over the course of deposition. Continued analysis will determine whether these conditions may have contributed to the Lagerstätte preservation.

Advisor: Dr. B. C. Gill

METHODS FOR EVALUATING AQUIFER PARAMETERS FROM A CUMULATIVE COMPACTION RECORD

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Although there have been many efforts to reduce anthropogenic impacts on aquifer systems in many locations around the world subsidence is still a serious issue. Necessary for sustainable water management, but extremely difficult and expensive, is aquifer characterization. Over a decade of compaction and water-level data collected from an extensometer and multi-level piezometer at the Lorenzi site in Las Vegas Valley was reexamined to explore new techniques to help eliminate uncertainties regarding the aquifer system properties.

Hourly water-level data were measured within three vertically separate confined aquifers, while total compaction was measured on an hourly basis to a total depth of 600 ft, which includes the three aquifers. When the data are graphed yearly, seasonal, and daily signals are observed, as well as a hydrodynamic lag between changing water levels and subsidence within the seasonal signal. Each temporal signal reflects different characteristics of the aquifer system, including the distinction between aquifer and aquitard parameters, since the three temporal stresses influence the compaction record uniquely.

Statistical analyses of the temporal signals are used to determine what significant factors cause the signals and the degree of each factor's influence on the behavior of the signals. The relationship between the fluctuating head levels and subsidence within the seasonal signal can also be determined. Principal Component Analysis, the statistical technique used to observe variation and highlight patterns within data, is one statistical method that is utilized.

Advisor: Dr. T. Burbey

EFFECT OF SALINITY ON MASS TRANSPORT PROPERTIES OF HYDROTHERMAL FLUIDS AT ELEVATED TEMPERATURES AND PRESSURES

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Fluids play a dominant role in mass and energy transport in the Earth's crust. A common assumption in fluid flow models for various geological environments is that the properties of the fluid can be approximated by pure H₂O. While the H₂O system provides a reasonable approximation of the composition of some low-salinity aqueous hydrothermal fluids, the single-component nature of the pure H₂O system results in a phase topology that differs significantly from that of natural, multi-component fluids.

According to conservation of mass equation, the temperature and pressure dependence of fluid mass varies with fluid density. Thus, the ability of hydrothermal fluids to transport mass varies in proportion to changes in fluid density associated with changing temperature and/or pressure. Levelt Sengers et al. (1983) and Johnson and Norton (1991) identified a critical PT region for pure H₂O in which various properties of H₂O exhibit anomalous behavior, such that the magnitude of the property changes by a large amount with a small change in temperature or pressure. Here, we adopt the definition of Anisimov et al. (2004) for the critical region that is defined as the isothermal rate of change of density with respect to chemical potential. The thermodynamic properties that describe the variation in density as a function of temperature and pressure, such as the coefficient of isothermal compressibility (β) and the coefficient of isobaric expansion (α), are used to illustrate how addition of NaCl in H₂O affects the ability of the fluid to transport mass. We have employed the model of Driesner (2007) to estimate properties of H₂O-NaCl fluids at PT conditions for given fluid compositions.

As NaCl is added to H₂O, the critical region migrates to higher temperatures and pressures. For pure H₂O, the largest variations in density occur in the vicinity of the critical point, where α and β approach infinity. The maximum values of α and β decrease significantly with increasing salinity, indicating that fluid density becomes less sensitive to changing temperature or pressure as salinity increases. For example, values for both α and β decrease by about two orders of magnitude as the salinity increases from ~0.1 to ~5 wt. % NaCl. As salinity increases, the PT region in which α and β reach their maximum values also migrates to higher temperature and pressure. Another notable observation is that the critical region expands in PT space with increasing salinity.

AUTHIGENIC AND DIAGENETIC MINERALS AS INDICATORS OF GEOMICROBIOLOGICAL PROCESSES IN SHELL PRESERVATION AND THEIR SIGNIFICANCE FOR EVOLUTION OF NEAR-SURFACE ENVIRONMENTS

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The fossil record is predominantly comprised of biomineralized skeletal elements, specifically shells. For this reason, processes that affect shell preservation significantly influence our understanding of changes in biotic diversity through time. Such processes have been extensively investigated through actualistic studies of shells in modern environments. The vast majority of work in the sedimentary record, however, has been focused on the physical phenomena rather than the microbiological processes that affect shells. Consequently, little is known about how environmental changes that affected microbiological processes in deep time may have impacted shell preservation. To address this issue, we studied authigenic and early diagenetic minerals associated with phosphatic shelly fossils of linguliformean brachiopods from the lower Cambrian of South China and North America. These minerals—which include pyrite, barite, and silica—most likely formed within anoxic sediments in response to focused degradation of the shells' organic matrixes via microbial sulfate reduction. When considered in the context of the late Neoproterozoic-early Paleozoic critical transformative interval in Earth history, which witnessed progressive oxygenation of the ocean and atmosphere, these minerals suggest oxygenation of near-surface environments may have profoundly impacted shell preservation by deepening the aerobic zone of microbial activity in which shells' organic matrixes are most aggressively degraded, and thereby, promoting environments favoring complete organic matrix destruction. As a result, the frequency of organic matrix preservation within shells likely declined, and shells' biominerals may have become more susceptible to dissolution (as organics counterbalance the effects of undersaturated water and high biomineral surface areas). Regardless, our results show that authigenic and early diagenetic minerals provide many opportunities for studying the microbiological processes involved in shelly fossil preservation.

Advisor: Dr. S. Xiao

EVIDENCE FOR A MOHO-PENETRATING STEEP ACCRETIONARY MARGIN FROM THE EARTHSCOPE IDAHO-OREGON CONTROLLED-SOURCE SEISMIC SURVEY

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Seismic refraction and wide-angle reflection travel times from the EarthScope IDOR controlled-source seismic survey were inverted to derive crustal velocity structure in the U.S. Cordillera of Idaho and Oregon. The P-wave velocity model and preliminary analysis of the shear waves reveal a near-vertical boundary that juxtaposes accreted island-arc terranes against Precambrian North America and the Idaho batholith. Post-accretion transpression across the western Idaho shear zone (WISZ) steepened and narrowed the original suture zone to ~5 km at the surface. The seismic data indicate that the WISZ penetrates the entire crust and offsets the Moho by ~7-8 km. The lithosphere of this region has been significantly modified since activity on the WISZ by emplacement of the Idaho batholith, Challis volcanism, the Columbia River Basalts, and Basin and Range-style extension. The crust west of the WISZ is characterized by faster P-wave velocities consistent with oceanic-arc crust and an average Moho depth of ~32 km. A very strong wide-angle reflector and higher seismic velocity are observed in the lower crust beneath the feeder dike system for the Columbia River Basalts; these features are interpreted to represent mafic magmatic underplating. In contrast, the crust east of the WISZ has a much slower P-wave velocity indicating a felsic-to-intermediate composition, and the Moho depth is close to 40 km. There are no major differences in intra-crustal reflectivity or seismic velocity between the Idaho batholith and the adjacent cratonic crust, and there is no evidence of a mafic magmatic residual beneath the Idaho batholith. The strong lateral contrasts across the WISZ provide evidence of inheritance and structural influence by this steepened boundary on the subsequent tectonic events.

Advisor: Dr. J. A. Hole

HEAT FLOW ALONG THE COSTA RICA RIFT, SOUTHERN FLANK: REPORT FROM OSCAR EXPEDITION JC113

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We report detailed heat flow measurements acquired during the operational and scientific expedition JC113, which is one of the component in the four expedition experiment "Oceanographic and seismic characterization of heat dissipation and alteration by hydrothermal fluids at an axial ridge" also known as OSCAR. The overall goal of this experiment is to understand how hydrothermal circulation couples the ocean and lithosphere and how the circulation affects the crustal evolution and the basin-scale ocean circulation. To achieve this, heat flow measurements were collected along the southern flank of the Costa Rica Ridge between Costa Rica Rift and IODP Hole 504B. Heat flow was measured extensively at stations consisting of 85 heat flow measurements using the multi-penetration heat flow probe. Preliminary analysis shows the heat flow to be well below the predicted heat flow based on half space cooling with very low heat flow values near the ridge crust. This shows the effect of a well-ventilated hydrothermal circulation. As the sediment thickness increases to the south of the ridge flank, heat flow values transition to values close to the theoretical curve as hydrothermal circulation transitions from an open ventilated state to a more isolated state.

Advisor: Dr. R. P. Lowell

PACIFIC LARGE IGNEOUS PROVINCES: RECORD OF THE CRETACEOUS UPWELLINGS FROM THE LARGE LOW SHEAR-VELOCITY PROVINCE

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Large Igneous Provinces (LIPs) and their mechanisms of formation have shown to play a key role in the tectonic and life cycles of the planet. As the surface expression of deep mantle dynamics, LIPs are associated to the edges of large low shear-velocity provinces (LLSVP) rooted at the mantle-core boundary. Instabilities in the LLSVP can cause periodical upwellings of materials in the form of mantle plumes which impact the lithosphere forming the LIPs, nevertheless, the time frames of these massive lava outpourings are still uncertain. While continental LIPs are more readily accessible, oceanic LIPs have only been studied through drilling surveys and fragments accreted to continental margins or island arcs, hence, they are relatively less understood. The impact of oceanic LIPs in the oceanic biota is conspicuously recorded in global occurrences of black shale deposits that evidence episodes of anoxia and mass extinctions shortly after the formation of LIPs that ultimately can affect life in the whole planet. Our new geochemical and isotopic data of the accreted Pacific LIPs found in the coasts of Nicoya Peninsula in Costa Rica record three well-defined LLSVP upwelling pulses at 140, 120 and 90 Ma. We created a complete reconstruction of the Pacific Plate configuration from the Mid-Jurassic to Upper-Cretaceous to show the existing correlation between upwelling pulses at the edges of the Pacific LLSVP, oceanic anoxic events and the radiogenic ages from in situ and accreted Pacific LIPs. We propose that since the onset of the Pacific plate at circa 175-180 Ma, a series of upwellings separated by 10 to 20 Ma have affected the planet periodically forming oceanic LIPs that still today can be found at the Pacific seafloor and accreted along the plate margins.

Advisor: Dr. E. Gazel

TESTING THE ROLE OF UPPER MANTLE FLOW ON LITHOSPHERIC DEFORMATION IN MADAGASCAR

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Understanding the role of mantle convection in driving continental deformations remain an unresolved problem in geodynamics. The degree to which viscous mantle flow interacts with the lithosphere can be different from one place to another depending on the vigor of convection beneath a given area, which can be tested using fluid-dynamic models. Previous studies have shown the influence of lithospheric structure can play a major role in driving mantle convection patterns, particularly in areas where evidence of plumes is absent. In this work we use the Advanced Solver for Problems in Earth's ConvecTion (ASPECT), a numerical code based on the finite element method, to solve for lithospheric deformation induced by mantle driven convection in the continental island, Madagascar. Our numerical model incorporates the three-dimensional ellipsoidal shape of the Earth and new methods that allow for an isothermally constrained temperature field by lithospheric structure using the global model LITHO model and material behavior governed by diffusion and dislocation creep flow law. We assume a thermal lithosphere with an isothermal boundary for the onset of an adiabatic temperature gradient for the sub-lithospheric mantle to depth of 500 km. Results from our model show downwelling upper mantle flow occurs mostly beneath the thick lithosphere in the central-western region of the island. Upward flow of upper mantle material is modeled where the lithosphere is thinned in central Madagascar and towards the south. In our comparisons show the calculated surface motions are 20-40% of the magnitude of velocities predicted from the HS3-NUVEL1A model in the hotspot reference. This preliminary work indicates modeled velocity patterns are consistent with rigid plate motions in the region where the lithosphere is thick. This implies that lithospheric structure has an important role in the dynamics of plate tectonic motion.

Advisor: Dr. D. S. Stamps

VERTICAL MOTIONS OF THE SOUTHERN SAN ANDREAS FAULT SYSTEM, COACHELLA VALLEY, CALIFORNIA

MASON, Cody, Department of Geosciences, Virginia Tech, Blacksburg, VA 24061

The southern San Andreas fault (SAF) system is a complex array of dextral and sinistral strike-slip and oblique faults in southern California and northern Mexico. The evolution of the southern SAF system is intricate, with regional tectonic reorganizations linked to both local structural complexities, and to changes in plate boundary dynamics. For instance, the inception of the San Jacinto fault zone (SJFZ) at ca. 1.2 Ma was likely a response to a structural knot in the San Geronio Pass restraining bend (Morton and Matti, 1993). However, major rift-bounding low-angle normal faults potentially initiated in conjunction with changes in plate boundary velocities and inception of the Gulf of Mexico rifting (Shirvell et al., 2009; Axen and Fletcher, 1998). The southern SAF system may have become the main plate boundary at ca. 6 – 5 Ma when plate deformation was focused in the Gulf of Mexico and the Pacific Plate captured the Baja peninsula. This increase or focusing of deformation within the Salton Trough may have been recorded in the cooling histories of crustal blocks surrounding the region.

The Coachella Valley is surrounded by uplifted crustal blocks associated with deformation along the southern SAF system. The Santa Rosa Mountains (SRM), western Coachella Valley, are bound by the late Miocene – Pleistocene west Salton detachment fault (WSDF) (Shirvell et al., 2009). The Little San Bernardino Mountains (LSBM) along the eastern Coachella Valley, are associated with near-field transpression and or transtension (?) along the SAF Coachella strand and subordinate faults. New low-temperature thermochronometry (apatite U-Th/He) from the SRM and LSBM document late Miocene exhumation associated with the southern SAF system in the Coachella Valley.

Preliminary results show the WSDF initiated at ca. 9.2 Ma. This timing leads us to associate slip on the WSDF with early Gulf of Mexico rifting, likely pre-dating inception of the plate boundary in Coachella Valley. A kinematic interpretation of isochron surfaces in the SRM shows northeast crustal-scale tilting on the order of 10° northeast for the central Salton Block since ca. 1.2 Ma. Exhumation in the LSBM initiated at ca. 6 – 5 Ma, possibly associated with an increase in oblique deformation during inception of the SAF in Coachella Valley.

Project P.I. and co-advisor: J. A. Spotila
Advisor: B. W. Romans

CENOZOIC TOPOGRAPHIC EVOLUTION OF PASSIVE MARGINS FROM QTQT MODELING OF APATITE (U-TH)/HE AGES AND $^4\text{He}/^3\text{He}$ THERMOCHRONOMETRY, NW SCOTLAND

FAME, Michelle L., Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Passive margin's characteristic slow background exhumation rates can result in low temperature thermochronometry ages that, individually, may be too old to be useful in investigating Cenozoic topographic evolution. However, where Plio-Pleistocene glaciation and far-field tectonic forces in the Cenozoic have affected passive margins their modern topography is likely to have been at least partially shaped during the Cenozoic. One such region, the highlands Northwest Scotland, maintains kilometer-scale relief in the absence of a classically active tectonic margin and has been extensively glaciated since the Plio-Pleistocene. Most previous thermochronological investigations of Scotland's exhumation have used apatite fission track analysis, however the lower closure temperature of apatite (U-Th)/He and apatite $^4\text{He}/^3\text{He}$ are better suited to investigate late Cenozoic cooling and topographic evolution of the Scottish Highlands. In this study we have thirteen *in situ* apatite (U-Th)/He ages from two age elevation profiles in the central highlands of Northwest Scotland, which range from 14.6 Ma to 350.2 Ma, and apatite $^4\text{He}/^3\text{He}$ diffusion profiles from two low elevation samples. We modeled possible t-T histories for the apatite (U-Th)/He profiles using QTQt and modeled the apatite $^4\text{He}/^3\text{He}$ using Berkeley Geochronology Center's search code. The results of the modeling indicate the peaks have experienced slow cooling rates, from stagnant to $0.1^\circ\text{C}/\text{Ma}$, since the late Paleozoic. However, Scotland's deep valleys experienced an acceleration in cooling rates in the mid to late Cenozoic, to rates between $1^\circ\text{C}/\text{Ma}$ and $6^\circ\text{C}/\text{Ma}$. If all cooling is due to exhumation this indicates that Scotland's modern topographic relief did not emerge until the mid to late Cenozoic.

Advisor: Dr. J. A. Spotila

MORPHOLOGICAL DEPENDENCE OF ELEMENT DISTRIBUTION IN THE *H. AMERICANUS* EXOSKELETON

ULRICH, Robert, Department of Geosciences, Virginia Tech, Blacksburg, VA 24061

The crustacean exoskeleton is a complex biocomposite of inorganic mineral and organic macromolecules that express diverse morphologies across different taxa. Previous studies have measured the elemental concentrations in the exoskeleton through spectroscopic methods such as Raman spectroscopy, Energy-Dispersive X-ray spectroscopy (EDS), and XRD. Due to analytical limitations, most studies have assumed that magnesium, phosphorus, and other trace elements are largely contained in the mineral fraction because concentrations in the organic framework could not be resolved.

The purpose of this study is to quantify the elemental distributions of Ca, P, Mg, and Sr in the mineral and organic fractions of exoskeleton from ten body parts using the American Lobster (*H. americanus*) as a model organism. The composites were dissolved using three procedures specific to extracting the 1) mineral, 2) protein, and 3) polysaccharide phases separately. The resulting effluents were analyzed by ICP-OES; the findings suggest that the cuticle contains significant amounts of mineralized Mg and P and that the protein fraction contains more Mg and P than expected. Element distributions vary depending on the location of the sample on the body, but in thicker samples of cuticle such as the claw, the mineral component controls the overall composition.

Advisor: Dr. P. M. Dove

BIOMOLECULE DEGRADATION IN TERRESTRIAL VERTEBRATES IN DEEP TIME

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The molecular degradation of bone and its expected alteration products are poorly understood, presenting a gap in our knowledge of the fossilization process. Original organic material has been reported in terrestrial vertebrates from the Cretaceous (~66 Ma), yet biomolecules have been detected in arthropods as far back as the Silurian (~417 Ma). In order to detect bone biomolecules and test the predictability of amino acid degradation across the Mesozoic, I will analyze dinosaur and other archosaur material from the Cretaceous (~66 Ma) to the Triassic (~210 Ma) from a variety of terrestrial depositional environments. Using time-of-flight secondary ion mass spectrometry (TOF-SIMS), I will compare the fossil material to modern alligator and ostrich bones because they are close living relatives. TOF-SIMS records an entire chemical spectrum and preserves the spatial distribution of molecules on a sample surface, making it an ideal tool for studying the internal structure of fossil bone. I will also conduct pyrolysis experiments, which approximate diagenesis, in order to make predictions regarding the behavior of biomolecules when they are subjected to various temperatures and pressures. Preliminary data from the Triassic dinosaur, *Tawa hallae*, demonstrate the presence of similar amino acid signatures reported in a Middle Pleistocene horse found exceptionally preserved in permafrost (560-780,000 years ago). The analysis of this specimen will allow for the development of a standard of examination for fossil bones, using surface sampling mass spectrometry (TOF-SIMS) to characterize biomolecules from different internal structures of the bone. This standard will be applied to my future analyses, enabling the identification of original biomolecules as old as the Triassic and will make it possible to trace degradation through the Mesozoic.

Advisor: Dr. S. J. Nesbitt

TIMING CONSTRAINTS ON THE TECTONIC EVOLUTION OF THE SCANDIAN OROGENIC WEDGE, NW SCOTLAND

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The Middle to Late Silurian (c. 435-415 Ma) orogenic wedge preserved in the northwest Scottish Highlands consists of a stack of thrust nappes composed of Neoproterozoic metasedimentary rocks. There is a continuous inverted metamorphic field gradient across the wedge, ranging from anchizone in the most foreland thrust sheets to upper amphibolite facies (migmatite grade) in the most hinterland positions. This area provides an excellent opportunity to study the formation of inverted metamorphic gradients and the effect of heat transfer from higher level thrusts to lower. In order to realistically model these effects, metamorphic constraints must be placed in a robust temporal framework and the association of mineral assemblages and structural features with Scandian orogenesis must be verified. Monazite geochronology and geochemistry can begin to provide the necessary constraints to better understand inverted metamorphic sequences and thermal processes during orogenesis.

Monazite grains were analyzed by electron probe microanalysis and LA-ICPMS. A sample from the footwall of the foreland-positioned Ben Hope thrust yields 420-400 Ma monazite grains that appear to record part of a retrograde path. A sample of upper amphibolite facies schist from the immediate hanging-wall of the overlying Naver thrust (intermediate foreland-hinterland position) hosts a large population of monazite grains that indicate a distinct correlation between Yttrium (Y) concentration and time. In monazite 445-440 Ma domains, Y concentrations are generally low, and one monazite (443 ± 2 Ma) is included in garnet. 440-435 Ma monazite domains record a sharp increase in Y concentration. These trends in monazite may record the breakdown of garnet during exhumation on the underlying Naver thrust. Alternative, a reaction between monazite and xenotime (YPO_4) may be controlling Y availability. Pressure and temperature constraints on reactions between monazite and other REE and phosphate accessory phases will be important in future work.

In contrast to the Scandian ages recorded in more foreland positions thrusts, a sample from the immediate hanging-wall of the hinterland-positioned Sgurr-Beag thrust sheet yields only Precambrian monazite (580-780 Ma) ages, highlighting the polyphase metamorphism of the Moine Supergroup and raising questions about both the age of preserved metamorphic assemblages, and the possibility that high grade metamorphism in the hinterland may be of Grampian (mid-Ordovician) or even Precambrian age - rather than of Scandian age. The continuous inverted metamorphic sequence may actually be a composite effect of multiple phases of metamorphism varying from Scandian age in the foreland to Grampian or even Precambrian age in the hinterland.

Advisors: Dr. R. D. Law and Dr. M. J. Caddick

THE ROLE OF SEDIMENTS IN ARSENIC CYCLING IN HYDROCARBON PLUMES

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Arsenic (As) is present in groundwater at elevated concentrations in a petroleum hydrocarbon plume near Bemidji, MN. Previous work documents that As is naturally occurring in aquifer sediments and is associated with iron (Fe) minerals. Biodegradation of petroleum hydrocarbons is coupled mainly with reduction of Fe(III) minerals, releasing dissolved Fe(II) and associated As to groundwater.

The goal of this study is to assess how Fe and As are redistributed in aquifer sediments resulting from changing redox conditions induced by petroleum biodegradation. Results from acid extractions show that As is associated with Fe(III) in background sediments. Arsenic is below detection in methanogenic sediment. In the Fe-reducing zone, Fe and As are spatially heterogeneous. Close to the methanogenic zone, long-term Fe reduction has resulted in depleted As in sediment. Further downgradient in the Fe-reducing zone, where Fe-reduction is more recent, Fe(II) comprises >50% of total Fe in some areas; these sediments contain As concentrations greater than background sediment. At the leading edge of the plume where groundwater is sub-oxic, sediments are slightly elevated in As, and Fe(III) is the dominant Fe oxidation state. Combined, these data suggest that areas of the Fe-reducing zone that have been exposed to hydrocarbons for a greater period of time have undergone significant Fe-reduction and As mobilization into groundwater. In contrast, more recent Fe-reducing areas of the plume accumulate As and limit its transport in groundwater. Saturation index calculations suggest that Fe minerals, including Fe-carbonates and Fe-hydroxides, are distributed heterogeneously in sediments of the hydrocarbon plume due to the influence of biodegradation on groundwater geochemistry. Arsenic may be sequestered by both of these mineral types. If associated with a carbonate, As will remain immobile under anoxic conditions as the hydrocarbons continue to biodegrade. Arsenic associated with hydroxides is subject to re-mobilization from aquifer sediments as the anoxic zone of the plume evolves over time. Overall, results suggest that petroleum biodegradation occurring over several decades at the site has resulted in dynamic redox conditions that allow different sections of the aquifer to act as sources, sinks, or both sources and sinks for As. Results from this study will be used to assess aquifer vulnerability for As mobilization under current and future geochemical conditions.

Advisor: Dr. M. E. Schreiber

SULFUR AND CARBON TRANSFORMATIONS IN ORGANIC-RICH SEDIMENTARY ROCKS UPON VARYING DEGREES OF CONTACT METAMORPHIC HEATING

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The rapid thermal maturation of organic-rich sedimentary rocks caused by contact metamorphism can significantly alter their carbon and sulfur compositions. This process has been suggested to produce and release of large quantities of carbon and sulfur volatile phases, perturbing global climate on both short and long-term time scales. Previous studies have indicated the importance of the mineralogy of the lithologies that are intruded when examining the potential amount of greenhouse gases released during metamorphism. My study aims to quantify the carbon and sulfur budgets of organic sedimentary rocks during contact metamorphism. Specifically, I seek to quantify carbon and sulfur species, identify their sources (sedimentary or magmatic) and identify their fate during the contact metamorphic process.

Sedimentary rocks in the Triassic basins of eastern North America are host to carbon and sulfur rich compounds which may have been volatilized during the emplacement of the Central Atlantic Magmatic Province (CAMP). The Culpeper basin of the Newark Supergroup contains Triassic organic-rich facies that have been intruded by a diabase of the CAMP, making this basin an ideal field location. Sedimentary and metasedimentary rocks were sampled along individual beds that run approximately perpendicular to contacts with the diabase, with sampling frequency roughly every half meter. Preliminary geochemical analysis indicates an increase in sulfur species with distance from the intrusion, suggesting sulfur was mobilized proximal to the heat source. Sulfur and carbon isotopic data will help to increase our understanding of how reactions within these environments proceed. These results, paired with thermodynamic modeling and petrographic analysis, will illustrate how major and accessory mineral assemblages evolved during contact metamorphism, controlling the release and fractionation of sulfur and potentially modifying global climate.

Advisors: Dr. B. Gill and Dr. M. Caddick

ROCK UPLIFT AT THE TRANSITION FROM FLAT-SLAB TO NORMAL SUBDUCTION: THE KENAI MOUNTAINS, SOUTHEAST ALASKA

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The process of flat-slab subduction results in complex deformation of overlying forearcs, yet how this deformation decays with distance away from the zone of underthrusting is not well understood. In south central Alaska, flat-slab subduction of the Yakutat microplate drives shortening and rock uplift in a broad coastal orogenic belt. Defined limits of the zone of underthrusting allow testing how orogenesis responds to the transition from flat-slab to normal subduction. To better understand forearc deformation across this transition, apatite (U-Th)/He low temperature thermochronometry is used to quantify the exhumation history of the Kenai Mountains that are within this transition zone. Measured ages in the northern Kenai Mountains vary from 10-20 Ma and merge with the exhumation pattern in the Chugach Mountains to the northeast, where high exhumation occurs due to flat-slab-related deformation. In the southern Kenai Mountains, however, ages increase to 30-50 Ma across a transition near Seward, Alaska, above the zone from flat-slab to normal subduction. These ages are relatively old in comparison to ages determined in other studies in southern Alaska and suggest minimal exhumation. Furthermore, transitions in topographic expression of the coastal orogen also occur at the margin of Yakutat underthrusting. These observations suggest that either deformation associated with flat-slab subduction requires tens of kilometers to decay with distance away from the zone of underthrusting, or that orogenesis in the Kenai Mountains is driven by a distinct tectonic cause. A potential driver of deformation is underplating of thick sediments, specifically the Surveyor Submarine Fan, along the Aleutian Megathrust, analogous to the tectonic mechanism responsible for the emergence of the Kodiak Island forearc. If correct, this may represent a recent tectonic transition in the region, given the minimal exhumation of the rugged Kenai Mountains despite the presence of an erosion-conducive glacial climate.

Advisor: Dr. J. A. Spotila

THE INFLUENCE OF TEMPERATURE DEPENDENT PHYSICAL PROPERTIES ON OUR UNDERSTANDING OF METAMORPHIC TIMESCALES AND LENGTH SCALES

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Numerical modeling is an important tool that allows geologists to constrain heat flow mechanisms and timescales in a number of geologic settings, and in turn to better understand the processes that contribute to extreme temperatures in Earth's crust. However, these models sometimes fail to accurately recreate the temperatures that are recorded in metamorphic rocks, implying that additional heat sources are required or that fundamental properties have been overlooked (England & Thompson, 1984; Clarke et al., 2011). Conduction models rely upon the heat equation, in which a thermal diffusivity term is key and is typically set as a constant at all depth-temperature conditions. Thermal diffusivity is itself a function of thermal conductivity, density, and heat capacity of the material. Recent data suggests that these properties vary considerably as a function of pressure, temperature (Whittington et al., 2009; Nabelek et al., 2011; Caddick, 2013), and rock type, most notably during melting or crystallization (i.e. as latent heat), but also during devolatilization. Here, we have calculated heat capacity and density data for typical crustal lithologies using thermodynamic models for a range of pressures (500-15000 bars) and temperatures (373-1273 K). Preliminary results quantify how density generally decreases, while heat capacity increases upon heating, and how these trends are clearly not smooth, linear functions. Overall, this leads to a decrease in thermal diffusivity as temperature increases. These data have been implemented into a numerical model that explicitly calculates the P-T dependence of thermal diffusivity and is currently designed to simulate the cooling of a mafic magma emplaced into crustal sediments. Preliminary findings indicate that a P-T dependent thermal diffusivity decreases the length scale of heat transfer, while increasing the timescale of peak temperature conditions for rocks that are adjacent to a magmatic intrusion. This would have substantial petrologic implications, both around intrusions and at a larger scale for inherently layered crust.

Advisor: Dr. M. J. Caddick

MULTICELLULAR MACROFOSSILS FROM THE TONIAN LIULAIBEI FORMATION, NORTH CHINA

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Multicellularity arose independently multiple times in the evolutionary history of eukaryotes and simple multicellularity may have a deep history tracing back to Paleoproterozoic. However, complex multicellular organisms with cellular and tissue differentiation did not appear in the fossil record until the Mesoproterozoic, and it is not until the Ediacaran Period when diverse assemblages of complex multicellular eukaryotes evolved. In the intervening Tonian Period, the fossil record of multicellular organisms is poorly documented. To address this knowledge gap, we investigated carbonaceous macrofossils from the Tonian Liulaobei Formation in North China, using a combination of optical and electron microscopy. Our study revealed direct evidence of multicellularity in carbonaceous compression fossils that are in gross morphology similar to, but microstructurally distinct from *Chuarina* and *Tawuia*. These multicellular structures were revealed by backscattered electron microscopy (BSEM), indicating that the application of backscattered electron microscopy (BSEM) has the potential to open a floodgate of new microstructural information about seemingly simple Precambrian carbonaceous compressions and to unveil the hidden diversity of multicellular organisms in the Tonian Period.

Advisor: Dr. S. Xiao

EXAMINING THE STRUCTURE OF AMORPHOUS CALCIUM PHOSPHATE: A PRECURSOR IN THE FORMATION OF HYDROXYLAPATITE AND BRUSHITE

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Hydroxylapatite is often used in studies of bones and teeth of humans and animals as a proxy for actual bone mineral because it is easy to synthesize or obtain natural samples. It is commonly being studied for use in the development of advanced prostheses, with the eventual goal of binding the prostheses to bone (Oyane et al. 2003). To obtain these goals, understanding of the growth and formation of hydroxylapatite is critical. The process of crystallization from solution for many minerals, including hydroxylapatite and brushite, is not yet fully understood. Crystallization pathways may include the formation of nanoparticle or amorphous precursors that undergo an aggregation or transformation into a crystalline end member (De Yoreo et al. 2015). Amorphous calcium phosphate (ACP) is a precursor phase in the crystallization process of both brushite and hydroxylapatite. It has been proposed that ACP is an aggregation of calcium phosphate nanoclusters (Posner and Betts 1975) that have been named Posner's Clusters..

Extended x-ray absorption fine structure (EXAFS) spectroscopy and pair distribution function (PDF) analysis were used to examine synthetic and natural samples of ACP, hydroxylapatite, and brushite. These techniques were used to place preliminary constraints on the size and structure of Posner's Clusters. Calcium and phosphorus EXAFS spectroscopy has a limited resolution for examining the structure of nanoparticles, but we were able to extract some structural limits on the first shell of atoms surrounding the calcium and phosphorus sites. The phosphorus atoms in ACP are tetrahedrally coordinated with oxygen. A shell of oxygen atoms surrounds calcium, but the coordination number and geometry is still undefined. PDF analysis shows that the clusters range between 0.9 and 1.5 nm in diameter. While the primary differential factor between the end member formation of brushite or hydroxylapatite is the pH of the solution that ACP forms in, PDF also suggested that the presence of magnesium ions might have a structural effect. Magnesium was added primarily as a stabilization agent to block the transformation of ACP into one of its crystalline end members. PDF results suggest that adding magnesium may also give ACP a greater structural similarity to brushite than to hydroxylapatite. Further PDF analysis is being planned to gain a more total understanding of the structural influences of magnesium on ACP.

Advisor: Dr. F. M. Michel

SODIUM AND POTASSIUM PARTITIONING BEHAVIOR IN THE H₂O-NACL-KCL SYSTEM DURING BOILING AT TEMPERATURES 600-800°C AND PRESSURES 500-1000 BARS

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The magmatic-hydrothermal fluids associated with porphyry copper deposits (PCD) play a vital role in transporting ore forming metals and facilitating the alteration patterns observed. The major constituents of these fluids have been shown to be sodium, potassium, and chlorine, thus the three component H₂O-NaCl-KCl system serves as an appropriate approximation. The single phase fluid will often go through a boiling stage and separate into two immiscible fluid phases, a low density vapor phase and a high density liquid phase. The compositions of these two fluid phases will control the depositional and alteration capabilities of the fluids. As a result, understanding how the major elements partition between the two fluid phases in the system H₂O-NaCl-KCl at the formation conditions associated with PCD will further our understanding of this crucial ore deposit type.

In this study, the partitioning of Na and K between two immiscible fluid phases in the H₂O-NaCl-KCl system at 600-800°C, 500-1000 bars, and for Na:K molar ratios of 3:1, 2:1, 1:1, 1:2, and 1:3 were determined using the synthetic fluid inclusion technique. A solution of known composition was sealed with a thermally fractured quartz core in a platinum capsule and taken to the experimental temperature and pressure conditions. At these PT conditions, the single phase fluid undergoes boiling and the fractures heal, which trap each of the two immiscible fluid phases separately as individual fluid inclusions. At room temperature, the inclusions that trap the vapor phase will have a vapor bubble and a small amount of liquid produced by the condensing vapor. The inclusions that trapped the liquid phase become supersaturated in NaCl and KCl as the sample cools and precipitate daughter minerals of halite and sylvite. The salinities of the vapor rich inclusions were determined by freezing the inclusions and measuring the dissolution temperature of sylvite and melting temperature of ice as the sample was heated. The salinities of the liquid rich inclusions were determined by heating the sample and measuring the dissolution temperatures of the two daughter minerals. Using the microthermometric data, the molar ratios of the inclusions were calculated using the FORTRAN program "SALTY" (Bodnar et al., 1989) and used to calculate the partitioning of Na and K between the liquid and the vapor. Preliminary results show a trend of increasing Na partitioning into the vapor phase as initial potassium molar ratios increase, as well as a trend towards unity as temperature and pressure increase.

Advisor: Dr. R. J. Bodnar

MANTLE FLOW FIELD, DYNAMIC TOPOGRAPHY, AND GEOID ANOMALY PREDICTED BY GLOBAL TOMOGRAPHY MODELS

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Understanding the flow pattern associated with mantle convection is essential to constrain plate driving forces, geoid undulations, lithospheric stresses, and Earth interior thermal structure. With a global seismic tomography model, one can predict the buoyancy-driven mantle flow along with its surface expression such as dynamic topography and geoid as seismic velocity anomalies are interpreted in terms of density perturbations. The scaling factors between seismic velocity anomalies and density perturbations can be calculated from thermodynamic properties of mantle mineral phases, which have various depth-dependent relations. In this study, we build a new geodynamic model based on ASPECT (Advanced Solver for Problems in Earth ConvecTion) that uses buoyancy derived from seismic tomography. We use S4ORTS and SAVANI global tomography models as the initial conditions together with the various depth-dependent viscosity models to compute the mantle flow, dynamic topography, and geoid anomaly. An assembly of the comparison among different tomography models, scaling factors, viscosity structures, and lithosphere/sub-lithosphere density structures will be displayed. We also compare the modeled geoid anomaly with EGM 2008 geoid and the modeled mantle flow with plate motion velocity, where we find the modeled and observed geoid and flow are consistent for oceanic plates. As we focus on the eastern US, where the local shear-wave splitting is primarily parallel to the trend of the Appalachian belt, the modeled mantle flow is not consistent with plate motion velocity and the shear wave splitting observations. The dynamic topography and geoid anomaly both exhibit a coast-to-inland magnitude differentiation along the MAGIC (Mid-Atlantic Geophysical Integrative Collaboration) linear seismic array. The numerical tests also show that the dynamic topography is quite sensitive to the density perturbation of lithosphere/sub-lithosphere in the seismic model used while the geoid anomaly is less sensitive.

Advisor: Dr. S. D. King

EVIDENCE FOR THE DEVELOPMENT OF MARINE ANOXIA DURING THE CAMBRIAN SPICE EVENT IN THE CONASAUGA BASIN OF EASTERN LAURENTIA

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The second half of the Cambrian Period was a dynamic interval in Earth history, characterized by high rates of faunal turnover and large perturbations of the global carbon cycle. Understanding the nature and timing of the events responsible for these patterns may provide important information about the evolution of Earth's surface environments and Biosphere. Here we investigate the end-Marjuman extinction (~499 Ma), a major trilobite extinction which coincides with the initiation of the global SPICE (Steptoean Positive Carbon Isotope Excursion) event. Since these events serve as the best example (largest, most well-documented) of the larger pattern of extinction coincident with changes in the carbon cycle seen in much of the Cambrian record, they provide an excellent opportunity to explore the environmental and evolutionary dynamics of this period.

For this study, we specifically explore the role of anoxia in these events, using material from well cores drilled through the Nolichucky and Eau Claire Formations of the Conasauga Group from Ohio and Kentucky. These units comprise sediments from a mixed carbonate-siliciclastic system deposited in and around the Rome Trough, a structural low (rift graben) within the Cambrian Conasauga Basin of the Laurentian passive margin. Through the chemical analysis of these sediments from five different locations within the basin, we track changes in water chemistry that occurred within the basin across a time interval prior to and during the extinction and SPICE events. Our data records the onset of the SPICE event in both $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$. This onset is coupled with the first appearance of anoxic conditions recorded by our iron speciation data at all study locations; specifically these data record the development of anoxic and ferruginous (iron replete) conditions within the water column in the Conasauga Basin. Pyrite sulfur contents also increase following the SPICE initiation, yet are still considerably below the ratio characteristic of euxinic environments (free H_2S in the water column). This is likely linked to low local organic productivity, as suggested by the low TOC (total organic carbon) contents (0.03 to 0.25 wt %) of the shales. However, the highest TOC values at each location are associated with the SPICE interval and anoxia, suggesting a role for enhanced preservation in the accumulation of organic matter. Taken together, these features suggest that the Conasauga Basin experienced a distinct shift from an oxic to an anoxic basin during the course of the SPICE event; a change capable of causing or influencing the observed faunal turnover.

Advisor: Dr. B. C. Gill

THE HOTTEST LAVAS OF THE PHANEROZOIC: A WINDOW INTO THE CORE OF MANTLE PLUMES

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Komatiite is an exceptional, ultramafic volcanic rock type that represents the hottest lava flows on Earth. Most genuine komatiites (such as the classic Barberton Al-depleted-type) are Archean in age (>2.5 Ga) and signify remnants of a younger Earth, when the temperature of Earth's mantle was substantially hotter. Although Earth's mantle appreciably cooled over the last 4.5 Ga, unusually Mg-rich basalts formed by high degrees of partial melting of the mantle are recorded in the recent geologic past, though less frequently. The lava flows on Gorgona Island, Colombia stand as an exception and represent the only true Phanerozoic komatiite occurrence that formed by melting the Galápagos mantle plume head at ~90 Ma. In this study, we show that another Galápagos-related terrane, the Tortugal Suite, Costa Rica, is petrologically and geochemically similar to Archean komatiites. We performed Al-in-olivine thermometry from olivine-spinel pairs and found that Tortugal samples record crystallization temperatures comparable to or exceeding Archean komatiite values (>1600 °C). We performed petrologic modeling and estimated initial melting pressures (>8 Gpa) and mantle potential temperatures (>1700°C) similar to the classic Barberton, Munro, and Kambalda as well as the Phanerozoic Gorgona komatiite localities. Our results suggest that geologic processes producing anomalously Mg-rich komatiite-like basalts still operate today. The simplest explanation for generating such hot, deep melts is via mantle plume head melting. However, if mantle plumes are chemically and thermally stratified, i.e., being hotter in the center and cooler at the periphery, then melting different sections of a plume will produce melts at different P-T conditions. We suggest deep melting of the hot Galápagos plume axis produced the Tortugal melts and thus, provide a window into the core of mantle plumes.

Advisor: Dr. E. Gazel

GEOCHEMICAL WINDOW ONTO THE TAPHONOMY AND PALEOECOLOGY OF EDIACARAN MACROORGANISMS FROM THE KHATYSPYT FORMATION, OLENEK UPLIFT, SIBERIA

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The Ediacaran Period represents a critical transition in the history of the Earth and life. During this interval our planet experienced major carbon cycle perturbations, progressive oxygenation of deep oceans, and transformative biological innovations. One of these key innovations is the radiation of macroscopic and complex eukaryotic life, which is evidenced by appearance of soft-bodied Ediacara-like fossils. These fossils have been enigmatic since they were first discovered and scientists still strive to find the answers to many questions concerning these fossils: What were the redox conditions of the environments where they lived? Did they have symbionts? How were they fossilized? Here we present preliminary geochemical data from our study of on *Aspidella*-type discoidal holdfasts preserved as casts within carbonate rocks in the Ediacaran Khatyspyt Formation of northern Siberia in order to address these questions.

We performed geochemical analyses on microsamples taken from *Aspidella* fossils and surrounding carbonate matrix. Iron speciation data show that the water column was not anoxic based on the low Fe and organic carbon contents ($Fe_{total} < 0.5$ wt.%, C_{org} 0.1–1 wt.%), although the Fe speciation proxy is not very well calibrated at such low Fe_{total} levels (Clarkson et al 2014). Organic carbon isotopic compositions range from -36.95‰ to -31.55‰ , and there are no significant differences among different parts of the holdfast or between holdfasts and the matrix. Together, these data do not support the hypothesis that *Aspidella* holdfasts hosted symbionts in an anoxic water column, although microbes may have played a role in the preservation of *Aspidella*.

Pyrite sulfur isotopic values are generally very high ($+32.0$ – $+41.9\text{‰}$) and holdfasts have pyrite that is slight enriched in ^{32}S than the matrix ($+35.2$ – $+40.0\text{‰}$ for holdfasts; $+37.4$ – $+41.9\text{‰}$ for matrix; $p \sim 0.01$, one-tailed Student's t-test). Due to isotopic fractionation associated with microbial sulfate reduction, pore-water sulfate typically becomes increasingly enriched in ^{34}S below the water-sediment interface. Our data indicate that the holdfasts were lithified through early authigenic processes facilitated by MSR under closed system conditions, and fossil mineralization predated matrix cementation. However, carbonate carbon isotope values show no significant differences between different parts of the holdfast or between the holdfasts and matrix. Although fossil mineralization predated matrix cementation, both seem to have occurred during early diagenesis and largely derived from seawater alkalinity.

Advisor: Dr. S. Xiao

DIFFRACTIONAL IMAGING OF MANTLE TRANSITION ZONE DISCONTINUITIES USING SDS-SS TRAVELTIMES

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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 2010 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 will discuss preliminary results from finite-frequency imaging using SdS-SS dispersion measurements and the effects of 3-D crustal structure and mantle wavespeed structure.

Advisor: Dr. Y. Zhou

THE ROLE OF THE CRYOSPHERE IN EARTH'S GEOHYDROLOGIC CYCLE IN DEEP TIME

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Water plays a major role in virtually all critical zone processes, including climate change, continental weathering, and the evolution of life. The cryosphere is the second-largest reservoir of water on Earth, and the waxing and waning of polar ice influences regional ocean chemistry and marine biological primary production. The amount of water in the cryosphere, as well as the movement of water into and out of the cryosphere, has varied over the past 700 Ma. For example, during Cryogenian low-temperature "snowball-Earth" conditions, the cryosphere enveloped Earth in a shell of ice, whereas during high-temperature greenhouse conditions, the amount of water in the cryosphere was zero. Previous workers have investigated variations in cryosphere-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 cryosphere over the past 700 Ma. Input data for the model combines the amount of water in the various geohydrologic cycle reservoirs [1] (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 cryosphere and adjacent reservoirs change in proportion to some observed environmental change, e.g., variations in global temperature. The fluxes of H₂O between the cryosphere 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.

Our results suggest that changes in cryosphere-related fluxes are most sensitive to variations in global temperature compared to other environmental parameters. Results also suggest that during snowball-Earth conditions the amount of water in the oceans decreased by ~32%, (from the modern value), assuming a 1 km-thick global ice sheet and that all water contained in the ice was removed from the oceans. The planetary coverage of ice would have completely removed the surface water reservoir from the hydrologic cycle and limited atmosphere-ocean interactions. Conversely, results suggest that during greenhouse conditions the amount of water in the oceans increased by ~2% (from the modern value), assuming all water in the cryosphere returned to the oceans. The total melting of the cryosphere would expose more continental and ocean surface area and increase atmosphere-surface water and atmosphere-ocean interactions.

[1] Bodnar et al. (2013), Geol. Soc. Am. Sp. Paper 500.

Advisor: R.J. Bodnar

CONTINUOUS BACK-PROJECTION IMAGING OF AFTERSHOCKS RECORDED BY THE DENSE AIDA ARRAY AFTER THE 2011 VIRGINIA EARTHQUAKE

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Aftershocks provide valuable information about the complex geometry of the main shock's rupture plane and the spatiotemporal distribution of the released tectonic stress. Regardless of their weak energies, aftershocks can sometimes be more damaging than the mainshock since they shake already weakened structures. Studying aftershock sequences is important to assess future hazards as well as to increase the understanding of earthquake mechanics and triggering mechanisms.

The Aftershock Imaging with Dense Arrays (AIDA) project recorded 12 days of the aftershock sequence following the 23 August 2011 magnitude 5.8 earthquake in central Virginia. AIDA utilized short-period, vertical-component seismographs at 201 locations at 200-400 m spacing to drastically reduce spatial aliasing as compared to traditional aftershock networks.

Reverse time migration (RTM) is traditionally used as an imaging algorithm in exploration seismology to refine structural boundaries. The back-projection method (BPM) is a simplified version of RTM that does not require extensive wavefield computations. The BPM is being applied to AIDA aftershocks to project recorded seismic energy back to the source in time and space. Based on our feasibility analysis, events as tiny as magnitude -2 and with signal smaller than noise are successfully imaged as point sources with ~200 m resolution. This detection and location threshold is 1-2 orders of magnitude smaller than traditional methods applied to traditional aftershock arrays.

The BPM algorithm has been modified to enable automated imaging from a large volume of continuous seismic data. Noise bursts on single stations result in false triggers during earthquake detection, and are canceled out by a diversity stack. Automatic event detection is performed by Short Term Average/Long Term Average (STA/LTA) algorithm applied after back-projection and stacking, detecting events at their hypocenter. Final tests and modifications for parallel processing are underway. The BPM will soon be applied to automatically to 12 days of AIDA data to locate the aftershocks that followed the 2011 Virginia earthquake. The earthquake catalog will map the evolution of stress in the aftershock zone, including much smaller events. This will enable a better understanding of the behaviors of small earthquakes and their triggering mechanisms. The continuous BPM code can be applied to future aftershock sequences as well as to human-induced microseismic events which may be generated by hydraulic fracturing, wastewater injection, fluid injection for enhanced oil recovery, or CO₂ sequestration.

Advisor: Dr. J. A. Hole

INTRASPECIFIC VARIATION AND THE EVOLUTION OF THE ANCESTRAL DINOSAURIAN GROWTH STRATEGY

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

Understanding growth patterns of extinct groups has been a persistent problem in vertebrate paleontology, especially for dinosaurs and other archosaurs, which possess the widest range of body sizes and growth rates of any group of terrestrial vertebrates. Determining the level of skeletal maturity an individual has attained is important for interpreting species synonymy, body size, paleoecology, and growth rates; however, few non-destructive methods for determining skeletal maturity exist, and none have been placed into a broader evolutionary context. Understanding the ancestral dinosaurian growth condition, and how that condition changed through time, is vital to properly interpreting the evolution of this group.

For this study, I analyzed 32 anatomical features that vary based on maturity in *Coelophysis bauri* and its close relative *Megapnosaurus rhodesiensis*. These animals were chosen because 1) they are early-diverging dinosaurs and therefore closer to the ancestral dinosaurian condition, 2) they are temporally close to the origin of dinosaurs in the Late Triassic, 3) they are known from growth series with large sample sizes from a single population, and 4) they possess many anatomical characters that vary with maturity. I used ontogenetic sequence analysis to reconstruct the developmental pathway(s) of these features and quantify the amount of intraspecific variation in pathways, then used non-metric multidimensional scaling (NMDS) to test whether these characters vary bimodally and are indicative of sexual difference, or vary continuously, suggestive of growth characters. My NMDS analysis found no evidence of bimodal variation, but rather a single cluster of individuals with the least and most mature individuals on the extremities, suggestive that these characters are developmentally variable. My data suggest a high level of intraspecific variation, with >50 equally parsimonious developmental sequences found for these animals. Size is poorly correlated with skeletal maturity in both species.

Variation in growth patterns is widespread among early-diverging dinosaurs and their closest relatives, suggesting that this high level of variation in development is the ancestral dinosaurian condition. Given that strong variation in developmental sequence and size during growth is absent in extant birds and more derived dinosaurs, this intraspecific variation was lost during the evolution to living birds. Such variable characters should be used with care in the reconstruction of evolutionary relationships. High variation should be assumed in early dinosaur taxa and are not necessarily indicative of taxonomic diversity or sexual difference; evaluation of the anatomical characters in this study can help determine maturity of individuals in these groups.

Advisor: Dr. S. J. Nesbitt

HIGH-FIDELITY NUMERICAL SIMULATION OF LONG WAVES' INTERACTION WITH ARRAYS OF EMERGED CYLINDERS

ZAINALI, Amir, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Flow around a fixed groups' of localized bodies are often encountered in the context of environmental fluid mechanics. Common examples include surface wave propagation through vegetation and flow around the offshore and coastal structures. Furthermore, with advances in technology, it is expected to have more man-made offshore and coastal structures in addition to natural ones such as small islands in the future. High energy water waves, namely tsunamis, and storms have occurred more frequently during the past two decades. Thus, it is crucial to understand the physics behind the interaction of long waves with obstacles to provide a mechanism for coastal protection. Three dimensional numerical simulation is the superior choice when numerical accuracy is concerned. However, three dimensional models are computationally very expensive. Furthermore, the large scale of the real world geophysical problems limits their applications in practice. Thus, high-fidelity depth integrated equations such as shallow water and Boussinesq type equations can be an attractive alternative for practical purposes. Shallow water equations (SWE), due to conservative and shock-capturing properties, provide us with good approximations of the wave breaking and runup. In addition, various studies have shown that the inclusion of dispersive effects before the wave breakup can be of a crucial importance. In this study, we present numerical simulation of waves' interaction with cylindrical obstacles using weakly dispersive fully nonlinear Boussinesq equations, also known as Serra-Green-Naghdi (SGN) equations. We demonstrate the capability of the SGN equations in modeling of the waves' interaction with both offshore and coastal structures while sustaining the computational performance.

Advisor: Dr. R. Weiss

PREDICTING OCCURRENCES OF ARSENIC IN GROUNDWATER IN VIRGINIA AS A TOOL FOR EXPOSURE ASSESSMENT

VANDERWERKER, Tiffany, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Arsenic (As) is a known toxin and carcinogen that can occur naturally in groundwater. Because As can be present in many types of aquifers, is odorless and colorless, and generally does not cause immediate illness, it can be difficult to evaluate if As is a concern in groundwater in a particular region. Although public supply wells are routinely tested for As and other contaminants, homeowners are responsible for testing their own wells, and may not be aware of what potential contaminants could be in their groundwater.

We have constructed a logistic regression model, using existing datasets of soils, geology, geochemistry, and hydrogeology to predict the probability of As concentrations above 10 ppb (the drinking water standard) in groundwater across Virginia. Measured As concentrations in groundwater from three datasets are used as the dependent variable. Geology, soil series and texture, land use, and physiographic province are used as explanatory variables in the model. Relationships between explanatory variables are evaluated in the model to see under which conditions As is most probable to occur in groundwater. The results will be used to create a risk assessment map in ArcGIS that will identify areas of concern in Virginia that may have elevated As concentrations in groundwater.

Advisor: Dr. M. E. Schreiber

RIVERBANK INFILTRATION INTO A GRAVEL AQUIFER AND THE IMPLICATIONS ON GEOCHEMISTRY IN PITTSBURGH, PENNSYLVANIA

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In very recent years, groundwater studies have started to look at the redox zonation of groundwater caused by the infiltration of surface water into a groundwater aquifer. Before these studies, the focus has been on the infiltration of surface water into the sediments and the hyporheic zone with the changes in geochemistry. The recent literature are identifying the introduction of dissolved organic carbon (DOC) as the main contributor to the change in the redox conditions within the groundwater aquifer. These changes in the geochemistry has affected the saturation of minerals that influences if they will precipitate or dissolve. The dissolution of the minerals could have a lasting effect on the groundwater with the mobilizing of metal contamination.

A major municipal groundwater pumping system along the Alleghany River discovered in 2010 of impacts of chlorinated Volatile Organic Compounds (VOCs) in the upgradient wells of the well field. Major cations and anions were collected for calibration purposes of a 3-D groundwater fate and transport model that was prepared for both the Pennsylvania DEP and the municipal government to understand the future of the contamination in the well field. This presentation will go into the findings of an evaluation that performed at Virginia Tech of the geochemistry collected in 2012.

The infiltration of the Alleghany River into the aquifer did not create a "redox" zonation but a "pH" zonation that was controlling the precipitation of minerals like siderite (iron carbonate), rhodochrosite (manganese carbonate), and calcite (calcium carbonate) where the river water was present in the aquifer. The wells in the well field have experienced "scaling" by hardness for decades and need regularly maintenance. Due to the presence of the VOCs, there was an abundance of iron and manganese due to oxidation-reduction reactions. The problem of scaling can become worse due to the contamination. This work will help in designing a better "cleaning" regiment for the hardness of the monitoring wells.

Advisor: Dr. T. Burbey

EFFECT OF CHEMICAL COMPOSITION ON THE HIGH-PRESSURE BEHAVIOR OF RARE-EARTH PHOSPHATES

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The rare-earth phosphate minerals monazite and xenotime are widespread accessory minerals with the chemical formula MPO_4 , where M represents the rare-earth elements. Monazite, crystallizes with the larger, lighter rare-earths (La-Gd), while xenotime crystallizes with the smaller, heavier rare-earths (Tb-Yb, Sc, and Y). The size discrepancy of the rare-earth cation causes monazite and xenotime to crystallize in different crystal classes, monazite is monoclinic while xenotime is tetragonal (Ni, Y., Hughes, J.M., Mariano, A.N. **1995**. *Am. Min.*). These minerals have long been known for their importance as geochronometers, due to their inclusion of Th and U, which decay to radiogenic Pb (Williams, M.L., Jercinovic, M.J., Hetherington, C.J. **2007**. *Annual Rev. Earth Planet. Science.*). More recently however, they are being researched as potential solid state repositories for nuclear waste, due to their substantial resistance to metamictization (Ewing, R.C., Wang, L. **2002**. *Rev. in Min. and Geochem.*).

In this presentation, we will show how the differing compositions of synthetic and natural rare-earth phosphates affect their bulk moduli and determine the pressure-induced structural changes within the monazite structure of $GdPO_4$. High-pressure single-crystal X-ray diffraction experiments on a natural Ce-monazite, a synthetic Gd-monazite, and a synthetic Tb-xenotime indicate that all three are stable with no phase transitions observed up to at least 5GPa. The bulk moduli, K, determined from a 3rd-order Birch-Murnaghan equation of state are 109.2(6) GPa with $dK/dP= 5.8(2)$, 128.1(8) GPa with $dK/dP=5.8(2)$, and 140.1(9) GPa with $dK/dP=6.2(5)$ respectively. Thus there is a trend of an increasing bulk modulus and therefore a stiffening structure across the lanthanide group from larger to smaller ionic radii, this trend also holds across the monazite-xenotime boundary (which occurs between Gd and Tb). As gadolinium is replaced by terbium the structure transitions from monoclinic to tetragonal. The monoclinic monazite structure contains PO_4 tetrahedra are cross-linked by RE^{3+} cations in 9-fold coordination with oxygen that can be described as a mono-capped square antiprism (MCSAP). Similar, is the tetragonal xenotime structure where PO_4 tetrahedra are cross-linked by RE^{3+} cations in 8-fold coordination with oxygen. However, the pressure induced structural changes seen in both Tb-xenotime and Gd-monazite are subtle. For the Gd-monazite increasing pressure has no statistically relevant effect on the PO_4 tetrahedra, only the MCSAP show significant compression.

Advisor: Dr. N. L. Ross

AN ASSESSMENT OF MELT INCLUSIONS AS A TOOL FOR QUANTIFYING VOLCANIC CO₂ FLUX

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The deep carbon cycle links shallow reservoirs like the atmosphere and oceans to deeper reservoirs including the mantle and core by the processes of subduction and volcanic degassing. Our understanding of this carbon cycle is limited but can be improved upon by quantifying carbon fluxes at the surface of the Earth. Particularly important are volcanic CO₂ fluxes, which are the result of mantle melting and subsequent degassing of crystallizing melt. This volcanic CO₂ flux is quantified by remote sensing of volcanic plumes and in situ sampling of fumaroles. Both approaches have advantages and drawbacks, but are mutually ineffective for quantifying the degassing of volcanoes that are no longer active. Thus analysis of melt inclusions trapped by volcanic phenocrysts provides an alternative source of information that is persistent in the geologic record. To evaluate the potential application of melt inclusions as a means for quantifying volcanic CO₂ fluxes, CO₂ concentrations of glassy bubble-bearing melt inclusions from the 1959 and 1960 Kilauea Iki and Kapoho East Rift Zone eruptions were compared to primary CO₂ contents estimated from remote sensing data collected from the summit of Kilauea. The maximum CO₂ concentration from the population of melt inclusions sampled (3000 ppm) is less than CO₂ concentrations inferred from remote sensing (4000-7000 ppm). This is likely because the melt sampled by the inclusions had already degassed significantly prior to trapping.

Advisor: Dr. E. Gazel

MODELLING THE MANTLE DYNAMICS OF THE GLOBAL RESURFACING EVENT ON VENUS

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

Based on the number and distribution of craters, the surface of Venus is only 500-700 Myr old. Conditions on Venus suggest that the lithosphere behaves as a stagnant lid rather than the active plate tectonics of Earth. Two hypotheses have been forwarded to explain this young age of Venus' surface; episodic catastrophic overturn of the lithosphere, and progressive volcanic resurfacing due to mantle plumes. Some numerical models suggest that a global event occurred on Venus approximately 500 Myr ago where the entire lithosphere became unstable and plunged deep within the mantle. This event was sudden, lasting only a few million years, and since then Venus has been geologically quiet. Numerical models suggest that the stagnant lid condition could have produced a number of episodic resurfacing events on Venus over solar system history. The hotspot mechanism suggests that Venus is resurfaced more gradually due to a number of mantle plumes comparable to Hawaii, rather than sudden episodic events. Venus and Earth are extremely comparable in terms of size, mass, and heat production, so a resurfacing mechanism based on processes similar to or the same as Earth's seems plausible. The estimated number of mantle plumes on Venus are comparable to those of Earth (Smrekar et al., 2010).

I will be using 3D spherical modelling to investigate the feasibility of the multiple plume scenario. I will focus on the number of plumes and the speed of resurfacing. Can plumes produce enough material to cause such a sudden and complete resurfacing event? I will also be using a relatively new code called ASPECT, which has not been widely used for 3D spherical problems. In this talk I will show preliminary work for simple convection in a 2D box. I am new to computer modelling and am using this example to familiarize myself with ASPECT and get an understanding of basic viscosity flow. I will also discuss details of the planet Venus and its mantle.

Advisor: Dr. S.D. King

DECIPHERING THE CRYPTIC NATURE OF CHEMICAL EXCHANGE BETWEEN THE SUBDUCTING SLAB AND MANTLE WEDGE: A CARBON AND SULFUR ISOTOPE STUDY

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

An estimated 2.4×10^{12} mol of sulfur (Evans et al, 2012) and $2.3 - 3.7 \times 10^{12}$ mol of carbon is subducted and recycled back into the mantle annually (Dasgupta et al, 2004). Those totals constitute a substantial portion of the global geochemical budgets and thus understanding their behavior in subduction zone settings is paramount for developing a better understanding of global geochemical budgets as a whole. Dehydration of the oceanic lithosphere leads to complex chemical exchanges between the subducting slab and overlying mantle wedge, with the interface developing as an intensely metasomatized zone. This study investigates the carbon and sulfur geochemistry of a suite of metamorphic rocks from Syros, Greece, that are theorized to represent parts of the shear zone and subducting slab. Syros hosts oceanic derived units that were subducted to eclogite facies and subsequently exhumed, and here we examine, serpentinites, talc and chlorite schists as well as metagabbros and metabasites, with the aim of better understanding the cycling of carbon and sulfur during subduction.

Ultramafic samples yielded no measurable sulfides, interpreted to be the result of oxidizing conditions at the slab–mantle interface. Sulfates are abundant in the ultramafic rocks, with $\delta^{34}\text{S}_{\text{sulfate}}$ generally suggesting interaction with Cretaceous age seawater. Some ultramafic samples exhibit slightly more negative $\delta^{34}\text{S}$ values than that of the late Cretaceous age seawater range, 15.7 ‰ compared to 18-20‰, possibly due to the mobilization of sulfides within the subduction zone. Total inorganic carbon (TIC) of the ultramafics suggests a mixing between both oceanic and mantle derived carbon sources. The combination of the total organic carbon (TOC) and TIC data for the ultramafics reflects a trend also seen in metasomatically altered oceanic ultramafics. This suggests that the carbon oceanic signature remains constant and possibly dominant throughout subduction of these lithologies.

Advisors: Dr. E. Schwarzenbach, Dr. M. Caddick, Dr. B. Gill

NEW MATERIAL OF *POPOSAURUS LANGSTONI* FROM TEXAS WITH IMPLICATIONS FOR THE EVOLUTION OF ARCHOSAURIAN LOCOMOTION

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

Understanding the interplay between skeletal morphology and locomotion is a fundamental goal of paleontologists, as animals that became extinct millions of years ago usually leave only their skeleton in the fossil record. To make predictions about how ancient animals moved and lived on land, it is critical to study the axial skeleton, which includes the backbone and ribs. Articulation structures between vertebrae are present in many groups of big dinosaurs, including long-necked sauropods and *T. rex*. These structures may be related to increased backbone rigidity and decreased flexibility of locomotion, which could have facilitated the evolution of large body size. These articulations are also present in extinct crocodile relatives called pseudosuchians ("false crocodiles"), but living crocodiles do not have them. To understand the evolution of locomotion and body size in the group that contains birds and crocodylians, I am examining the large pseudosuchian, *Poposaurus langstoni* (measured about 4 meters and possibly weighed up to 100 kilograms). Because *P. langstoni* is more closely related to crocodiles than birds, it provides critical information about the evolutionary trajectory from an ancestor related to early dinosaurs to the alligators and crocodiles living today. The first fossils attributed to this species include four vertebrae (eighth cervical, fused ninth cervical and first dorsal, and third dorsal) and two hip bones (right ilium and right ischium). Additional vertebrae and a rib fragment were collected around the same time as the original specimen and from the same quarry, but this material has only been prepared more recently. I describe this new material here in detail for the first time. These vertebrae have the complementary articulation structures commonly seen in dinosaur backbones called "hyposphene-hypantrum" that fit together like a key (hyposphene) into a lock (hypantrum) on the posterior and anterior ends of vertebrae, respectively. The presence of "hyposphene-hypantrum" articulation in *P. langstoni* may support evolution of axial skeleton morphology that allowed for species on both the crocodile and bird sides of the tree of life to reach sizes greater than any reptile living today.

Advisor: Dr. S. J. Nesbitt

GEOCLAWSED: TSUNAMI SEDIMENT TRANSPORT MODELING WITH FINITE VOLUME METHOD

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

The nonlinear shallow-water and advection-diffusion equations are commonly used for tsunami sediment transport modeling. GeoClawSed is based on GeoClaw and adds a bed updating and avalanching scheme to the two-dimensional coupled system, which is a set of hyperbolic integral conservation laws. The modeling system consists of three coupled model components: (1) the nonlinear shallow-water equations for hydrodynamics; (2) advection-diffusion equation for sediment transport; (3) an equation for morphodynamics. For the hydrodynamic part, the finite volume wave propagation methods (high resolution Godunov-type methods) are applied to the nonlinear shallow-water equations. For the sediment transport part, the advection-diffusion equation is employed to calculate the distribution of sediment in the water column. The standard Van Leer method is applied for calculating sediment flux in each direction. The bed updating and avalanching scheme are used for updating topography during tsunami wave propagation. GeoClawSed can evolve different resolutions and accurately capture discontinuities in both flow dynamics and sediment transport. The multiple grain-size classes and sediment layers are added into GeoClawSed to simulate vertical grading in tsunami deposit. Together, GeoClawSed is designed for modeling tsunami propagation, inundation, sediment transport as well as topography change. Finally, GeoClawSed is applied for one real tsunami case from 2004 Indian ocean tsunami.

Advisor: Dr. R. Weiss

UNDERSTANDING THE CAUSES OF THE LITHIFICATION BIAS: A MODELING APPROACH

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Multiple studies have demonstrated that fossil samples collected from lithified sediments exhibit lower species richness, lower evenness, and larger average specimen sizes than samples collected from un-lithified sediments. However, the question of what drives this bias has received relatively little attention. The most commonly invoked explanation is that the bias is driven by preferential dissolution of small aragonitic specimens during early diagenesis. Here we use a simple model of fossil collection from lithified sediments to test the alternative hypothesis that bias in the diversity of fossil collections can arise due to methodological issues inherent to collecting from lithified sediments. Modelling results demonstrate that biased measures of richness, evenness, and average specimen size can indeed arise from sample collection methods rather than aragonite dissolution. We further demonstrate that the effects of this bias are complex and dependent on sample specific properties. In some instances fossil collections from lithified sediments may exhibit greater richness and/or evenness than their un-lithified counterparts. Finally we show that multiple factors, such as preferential intersection of larger specimens and degree of shell exposure, can contribute to biased diversity measures of fossil assemblages. These results do not imply that aragonite dissolution does not play a role in the lithification bias, but rather suggest that the bias is the result of a confluence of factors.

Advisor: Dr. S. Xiao

EVIDENCE FOR THE RECYCLING OF SUBDUCTED LITHOLOGIES AT THE SLAB-MANTLE INTERFACE: A CASE STUDY FROM SYROS, GREECE

GORCE, Jennifer, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Subduction zones represent the only major geological environment in which material from the exterior of the planet is returned to the mantle, and the processes that occur during subduction have important implications for elemental cycles, geodynamics, mineral phase equilibria and mass transport of materials. Numerical models predict that material can move freely at the interface between the subducting slab and the overlying mantle wedge (mélange zone) independent of the motion of the subducting slab (i.e. Cloos 1982, Gerya et al 2002). This is possible because the mélange zone is comprised of rigid blocks of metagabbroic and metabasic material that can travel in a weak, sheared matrix of primarily serpentinite, talc, and chlorite. The implication of this is that blocks of subducted material now exposed in adjacent outcrops could have each experienced unique and very complex P-T-t paths, resulting from the cycling and recycling of subducted material within the mélange zone. In rare cases (Blanco-Quentero et al 2011) metamorphic rocks preserve compositions and textures that record evidence for this complex P-T-t path. Such behavior can affect the expulsion and retention of fluid during metamorphism, depending on the physical properties and location of the block in the mélange zone.

The island of Syros, Greece provides a natural laboratory for investigating the evolution of subducted lithologies, as it preserves rocks that experienced blueschist-eclogite grade metamorphism during the subduction of the Pindos Oceanic Unit. Preliminary models suggest that rocks from the island record complex P-T-t paths. Complex compositional zoning in a garnet-bearing quartz mica schist indicates that garnet crystals grew in two distinct stages. Thermodynamic models imply that the first period of growth accompanied a burial and heating path from 500°C and 21 kbars to 525°C and 23 kbars. Preliminary data suggests that the second growth phase began around 525°C and 21 kbars. The conditions of termination of garnet growth cannot be constrained with the current thermodynamic modeling, and additional techniques such as Quartz in Garnet Geobarometry (QIGG) will be employed to constrain the end of garnet growth.

Advisor: Dr. M. J. Caddick

FLUID INCLUSIONS THAT HOMOGENIZE BY HALITE DISAPPEARANCE: HETEROGENEOUS ENTRAPMENT ALONG LIQUID-VAPOR-HALITE CURVE

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Halite-bearing fluid inclusions (FIs) commonly contain an aqueous liquid, one or more solid phases, and a vapor bubble at room temperature. During heating from room temperature, the liquid-vapor homogenization (Thl-v) of a halite-bearing FI may occur at temperature higher than, lower than, or equal to the halite dissolution temperature ($T_{m_{\text{halite}}}$). Microthermometric data from FIs that homogenize by halite disappearance reflect that inclusions may have (1) trapped a high salinity, single-phase liquid at high pressure; (2) re-equilibrated, i.e., loss of H₂O from the inclusions; or (3) heterogeneously trapped solid halite together with liquid under halite-saturated conditions. Natural halite-bearing FIs that homogenize by halite dissolution are nearly ubiquitous in porphyry copper deposits, and also occur in many other ore forming environments. For most of the porphyry copper deposits, the formation pressure estimates are much lower than the pressures determined from the FIs that show $T_{m_{\text{halite}}} > \text{Thl-v}$. Additionally, published studies reported the coexistence of vapor-rich FIs with FIs that homogenize by halite dissolution, and that fluid inclusion assemblages (FIAs) with $T_{m_{\text{halite}}} > \text{Thl-v}$ show no evidence of post-entrapment modification. These results exclude scenarios (1) and (2) as major contributors to the formation of FIs that homogenize by halite dissolution.

In this study, fluid inclusions were synthesized in quartz in the presence of known brine compositions (50 wt% with KCl/NaCl=1:9) at the pressure of 250 bars, and at the temperature of 450-650°C. Then, the Thl-v and $T_{m_{\text{halite}}}$ were determined on the Linkam TS1400XY stage. At room temperature, halite-bearing FIs formed by healing fractures were concentrated along the edge of each chip where the fracturing was most intense. Halite-bearing and vapor-rich FIs coexist in the same FIAs, and few vapor FIs contain halite solid phase. Microthermometric data were obtained from 159 FIs in 5 samples. Of these, 39 inclusions homogenize by halite dissolution. These FIs should represent heterogeneous trapping of liquid and halite. An additional 53 inclusions have simultaneous Thl-v and $T_{m_{\text{halite}}}$, which indicates that FIs only trapped an NaCl-saturated liquid. The rest of the inclusions homogenize by liquid-vapor disappearance. The data suggest that FIs either trapped liquid + vapor ± halite or leakage or necking down. Petrographic and microthermometric analyses are in good agreement with previous published results of natural inclusions from porphyry copper deposits. The widespread occurrence of inclusions that homogenize by halite dissolution in porphyry copper deposits could be a direct consequence of halite saturation and heterogeneous entrapment along liquid-vapor-halite curve.

Advisor: Dr. R. J. Bodnar

IMPACT OF STRUCTURAL AND PHYSICOCHEMICAL DIFFERENCES ON CATALYTIC ACTIVITY OF TWO COMMERCIALY SOURCED PLATINUM NANOCATALYSTS

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

Platinum group element (Pt)-based nanocatalysts are important in a number of industrial and technological processes, ranging from catalytic conversion of CO, hydrocarbons and NO_x in modern automobiles to reduction of oxygen in emerging hydrogen fuel cells. These technological innovations have had - and will continue to have - a tremendous impact on our environment in terms of global climate change and soil, water and air quality.

Catalysts work by allowing the reaction to evolve through a different pathway that requires lower activation energy, increasing the reaction rate. Conservation of orbital symmetry along with d-band structure at the surface have been used in a number of works to explain the reactivity of catalytic structures in controlled systems, based on the assumption that the properties of the catalyst remained unchanged. However, the physicochemical and structural properties of real-world systems are complex, heterogeneous and dynamic. This complexity has important, yet poorly understood implications on the fundamental behavior of catalysts at their surfaces, as it influences the interaction of the catalyst with reagents, transient species and products.

This project is focused on establishing a comprehensive understanding of the relation between the physicochemical and structural properties of two commercially sourced Pt-nanocatalysts and their catalytic behavior in the decomposition of H₂O₂ at different thermodynamic conditions. Pt-nanopowder and Pt-black are chemically and structurally similar, however reactivity experiments in our lab show that the catalytic activity of Pt-nanopowder is higher than Pt-black. The activity of the two catalysts is differently affected by changes in temperature, pH and H₂O₂ concentration, which relates to differences in particle size and shape, and abundance of PtO_x at or near their surface. In addition, preliminary TEM *ex situ* analysis appears to show that an irregular phase is formed at the surface of each catalyst when in contact with H₂O₂, possibly impacting their catalytic activity in different extents.

We anticipate our work to be a starting point for a deeper understanding of the behavior of industrially produced catalysts in complex chemical environments. Research in this area will result in a better understanding of the underlying properties driving catalyst behavior in real-world conditions, which will have implications for improving the design of current and future catalysts as well as their impact in the environment.

Advisor: Dr. F. M. Michel

POSTER SESSION – Friday, February 26 1:15-2:15pm

INTEGRATING HISTOLOGY AND MORPHOLOGY TO ASSESS THE SKELETAL MATURITY OF EARLY-DIVERGING DINOSAUROMORPHS

BANO, Lauren, Dept. of Biological Sciences, Virginia Tech, Blacksburg, VA 24061

The Upper Triassic sediments of North America record the evolution of many extant vertebrate groups, including many dinosauromorphs—dinosaurs and their close relatives. Although growth is a universal biological process, developmental patterns of early-diverging dinosauromorphs are relatively unexplored because of a lack of well-preserved growth series. Additionally, our knowledge of the relationship between changes in bone tissue and morphology during growth in this group is lacking. Bone scars increase in number and size during growth in many extant reptiles, and *Dromomeron romeri*, an early-diverging dinosauromorph from the Late Triassic of New Mexico, is reported to lack large ossified bone scars in the proximal portion of the femur that are present in many other archosaurs (e.g., anterior trochanter, trochanteric shelf). In this study, we tested whether this absence of bone scars is because the reported specimens represent skeletally immature individuals, or if the lack of scarring is an evolutionary novelty by integrating histological and morphological data from a growth series of six femora of *D. romeri* (96.9 mm – 136.6 mm in length). We sampled the bone tissue of one femur and one tibia. The histology of the sampled femur, which lacks ossified muscle scars, showed characteristics of a skeletally immature individual, with a vascularized bone surface and one double annual line of arrested growth (LAG). However, the LAG may be interpreted as indicative of skeletal maturity, as multiple LAGs laid in close conjunction signal the cessation of growth. We sampled a tibia articulated with the largest femur in the growth series, but this did not possess LAGs. This suggests that size is a poor correlate with skeletal maturity in this species. If *D. romeri* does not characteristically lay down muscle scars, then histology serves as the only method of determining maturity. Size is a poor correlate with maturity in this group, which is consistent with developmental studies of early dinosaurs and dinosauriforms. Because bone scars are phylogenetically important characters, understanding how they change during ontogeny is necessary to correctly reconstruct evolutionary relationships, and *D. romeri* is different in this respect from its closest relatives. Integrated knowledge of growth patterns of early dinosauromorphs is necessary to correctly reconstruct the early paleobiology of this highly successful clade.

Advisors: C. Griffin and Dr. S. J. Nesbitt

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

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The Late Wisconsinan Glaciation, or the Last Glacial Maximum (LGM) of the Laurentide Ice Sheet in North America, significantly modified the glaciated northern Appalachians. However, 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). However, quantitative data that addresses how far south LGM periglacial conditions prevailed is sparse. The Devil's Marbleyard is a large rockfall (approximately 28,277 square meters) composed of quartzite boulders of the Cambrian Chilhowee Group (Antietam Quartzite) in the Virginia Blue Ridge province. The origin of the rockfall is generally understood to be the result of periglacial processes although neither quantitative nor qualitative data currently exist to support this theory. To address whether or not this rockfall is periglacial in origin, we will carry out a field-based comparison of the site to places with known periglacial origins. The deposit will be mapped including the morphology of the deposit overall and the distribution of different size and shape blocks, as well as fracture mapping of the bedrock scarp itself. We will also use cosmogenic isotope surface-exposure dating and lichenometry to determine if the timing of the rockfall is consistent with the LGM and could therefore be periglacial in origin. 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.

Advisors: M. Fame and Dr. J. Spotila

EFFECTS OF FUEL ADDITIVE CERIUM ON PLANT LIFE

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Nanoparticulate cerium oxide is an effective additive in diesel fuel for increasing fuel economy by 5-8% and decreasing carcinogenic particulate matter from the combustion of fuel by up to 15%. Although particulate matter in emissions decreases, the size of the cerium oxide particles resulting from combustion has been shown to increase, leading to concerns regarding the potential effects this source of Ce could have on living organisms and in turn the environment. Today even the effects of Ce on the body are unknown but in some cases large doses of Ce have been shown to lead to lung disease. This work uses diesel exhaust-generated cerium oxide particles to investigate the effects such materials are expected to have upon plants after entering the environment. Through the use of bulk chemical analyses such as acid digestions in addition to optical microscopy, this research will help determine the toxicity of cerium from a diesel additive on plants.

Advisors: Dr. M Hochella and J. Dale

UNDERSTANDING INTRAPLATE VOLCANISM BY ANALYZING OH CONTENT AND MAJOR ELEMENT COMPOSITION IN PYROXENE PHENOCRYSTS FROM BERMUDA

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The presence of water in volcanic systems can give great insight into the chemistry of the system, the source of the magma, and its eruptive history. Bermuda is one volcanic system in which not much is known, both in bulk rock geochemistry and volatile concentrations. Bermuda is an example of an intraplate volcano, and is found in the Atlantic Ocean off the coast of North Carolina. Traditionally, in the generation of intraplate volcanoes have been explained by mantle plumes. Mantle plumes are thought to be formed from an upwelling of hot material from deep within the Earth that heat the surrounding material. Hawaii is an ideal example of a mantle plume formed intraplate volcanic chain. Another theory for intraplate volcanism is known as edge driven convection which considers small convection cells within the upper mantle. Bermuda is an ideal location to test these two models of mantle melting, as it is a location that has been described by both plume and non-plume models. All previous explanations for Bermuda are derived from geophysical data. No study to date has correlated the geochemistry and petrology to melting models. By studying the water concentration of pyroxene phenocrysts from the only volcanic samples from Bermuda (the Deep Drill 1972 core) it is possible to calculate the concentration of water in the magma. Fourier transform spectroscopy (FTIR) is one technique that can measure the OH concentration in pyroxenes. Here I present water concentrations from three different sections of the Bermuda core, calculated from seven individual clinopyroxene phenocrysts. There was a notable amount of water in the clinopyroxenes ranging from 263-709ppm. A continuation of this study will include in the measuring of OH concentrations in more pyroxenes from additional sections of the core, as well as measuring major element composition of the phenocrysts to calculate the water concentration of the magma.

Advisor: Dr. Esteban Gazel

MODELING OF HYDROTHERMAL SYSTEMS AT THE MID-CAYMAN SPREADING RIDGE

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We use hydrothermal plume data and other observations to parameterize the Piccard (PHF) and Von Damm (VDHF) hydrothermal fields on the Mid-Cayman Spreading Center. The PHF is hosted in basalt at a seafloor depth of nearly 5000 m where a number of active sites vent with temperatures as high as 400°C from an area of approximately 3.5×10^4 m². A neutrally buoyant hydrothermal plume observed at a height of approximately 1000 m above the PHF yields a buoyancy flux of ~ 0.64 m⁴/s³ and a heat flux of ~ 1200 MW. Using a single-pass model, this heat output and maximum vent temperature yields a mass flow rate of ~ 600 kg/s and a crustal permeability of $\sim 3 \times 10^{-13}$ m². Heat output at PHF, if steady state is among the highest recorded at a mid-ocean ridge. This system is likely driven by a subsurface magmatic heat source.

The VDHF, hosted in ultramafic rocks near the top of an OCC approximately 13 km west of the neovolcanic zone, lies at a depth of approximately 2300 m. Venting occurs from a conical mound approximately 150 m in diameter. A plume signal at a height of ~ 300 m above the VDHF yields a buoyancy flux of $\sim 5 \times 10^{-3}$ m⁴/s³ and a heat output of ~ 100 MW. With a maximum vent temperature of 226°C, the single-pass model yields a mass flow rate of ~ 90 kg/s and a permeability of $\sim 2 \times 10^{-13}$ m². Crustal permeability at VDHF is similar to that at PHF despite its lower heat output, reflecting the lower vent temperatures and more focused discharge at VDHF.

We constructed numerical simulations in a NaCl-H₂O fluid for PHF assuming maximum bottom temperatures of 550° and 600°C and a permeability of 10^{-13} m² in a 2 km deep 2D geometry. The results show venting of phase separated fluids at temperatures approaching 400°C. Seismic data on the depth to heat sources at PHF and VDHF are needed to better constrain modeling.

Advisor: Dr. R. P. Lowell

USING VANADIUM PARTITIONING TO DETERMINE REDOX CONDITIONS IN SUBDUCTION ZONES AND CONSTRAIN MELTING PRESSURE AND TEMPERATURE

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Understanding of the redox conditions in the subduction melting environment is key to developing a precise melting model. Although it is imperative, to determine the temperatures of melting, constraining Fe^{3+}/Fe^T is challenging by standard analytical methods. In recent years, a new proxy has been developed by using the relative partitioning of Vanadium between olivine and melt ($D_V^{ol/m}$). The purpose of this project is to use the vanadium proxy to determine the redox state of subduction melts and thus the true Fe^{3+}/Fe^T .

Vanadium is present in trace to minor element concentrations in basalts, can exist in four oxidation states and its partitioning behavior can be used as an accurate oxybarometer. Once the oxidation state is determined, we can calculate the pressures and temperatures of the melting regime by using the thermobarometry calibrated to the appropriate Fe^{3+}/Fe^T . The Central American arc is the focus of the project since the subduction system is well known and samples have been well characterized, including water contents. Olivine from 23 samples from Central American volcanoes were extracted and mounted for measurements of major and trace elements (including V) by LA-ICP-MS. Vanadium and other minor/trace element concentrations in the olivine will be compared to a database of whole-rock compositions for the samples. Using the vanadium partitioning model, temperatures and depths of melting will be compared to those estimated using standard assumptions about Fe oxidation. Information about the temperature and depth of melting and equilibration, as well as potential boundaries of melt equilibration (e.g. the lithosphere-asthenosphere boundary) are important for understanding the processes that drive tectonics and volcanism. More accurate redox data could change previous models based on assumptions of state of oxidation and volatile activity.

Advisor: Dr. E. Gazel

IS THERE BIOTIC MANGANESE OXIDATION OCCURRING IN THE EPILIMNION OF A SEASONALLY STRATIFIED RESERVOIR?

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Manganese (Mn) is a naturally occurring metal that is regulated in water as a secondary drinking water contaminant at a concentration of 0.05 mg/L. Manganese can be released from geologic sources (soil, sediment, rocks) to water under reducing conditions. Falling Creek Reservoir in Roanoke, VA is a eutrophic, drinking water source that experiences reducing conditions during summer stratification, resulting in Mn release from the sediment into the water column. To alleviate the reducing conditions in the reservoir, an oxygenation system was installed to increase the amount of oxygen in the water column. The oxygenation has helped to decrease the amount of reduced Mn in the water column; however, the mechanisms that contribute to decreased Mn concentrations, including both abiotic and biotic oxidation, are not well-understood.

We investigated the role of biotic reactions in contributing to Mn oxidation using a laboratory experiment. We constructed five trials to control and isolate biotic and abiotic contributions to oxidation in particulate matter (floc). The trials were spiked with soluble Mn (Mn(II)). The concentration of Mn was then measured over the span of 18 days using ICP-AES. Our results showed that Mn oxidation occurred in the presence of floc and reservoir water, with the fastest rates occurring in the presence of floc. We did not observe any considerable abiotic oxidation within 18 days in the presence of autoclaved floc or autoclaved reservoir water. Overall, results of the study suggest that biotic oxidation is a significant process for increasing the rate of Mn in Falling Creek Reservoir.

Advisor: Dr. M. E. Schreiber

A 20-YEAR COMPARISON OF ARSENIC AND IRON IN AQUIFER SEDIMENTS OF A DYNAMIC HYDROCARBON PLUME

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Arsenic (As) in drinking water is a public safety concern, especially in areas where people rely on unmonitored wells for drinking water. If consumed, As can act as a toxin and carcinogen. It has been recently documented at an oil spill site that naturally occurring As can be released into groundwater as a secondary effect of hydrocarbon biodegradation in groundwater. In 1979, a pipeline seam split near Bemidji, Minnesota and released crude oil to the land surface, which settled on the water table and created a dissolved hydrocarbon plume. The aquifer consists of glacially derived aquifer sediments, which are the primary source for As. In aquifer sediments, As adsorbs to metal hydroxides (such as Fe) under oxic conditions, however if geochemical conditions in the sediment become reducing due to the introduction of organic carbon (such as hydrocarbons), then the Fe(III) hydroxide can be microbially reduced, releasing Fe(II) and As, which was previously adsorbed to the Fe(III), to groundwater. These coupled reactions have caused modern day concentrations of dissolved As as high as 230 µg/L. This study examines how the long-term biodegradation of the hydrocarbon plume has changed sediment-bound concentrations of Fe and As.

To examine the temporal dynamics of sediment Fe and As, sediment samples from 1993 and 2013 collected at the same three locations (86, 102 and 132 m from the oil body) were digested for As and Fe and the results compared. At 86 m and 102 m, As and Fe concentrations in sediment decreased significantly from 1993 to 2013, suggesting that active biodegradation coupled with Fe reduction and As release depleted Fe and As from sediment. Sediment samples at 132 m in 2013, near the plume's leading edge, showed that there was an increase in both As and Fe levels relative to 1993. These results suggest that the sub-oxic conditions at the plume's leading edge act as a sink for dissolved As due to the oxidation of dissolved Fe(II) and precipitation of Fe(III) hydroxides. Arsenic can then adsorb to the newly precipitated Fe(III), removing it from groundwater. This study shows the evolving plume has created spatial and temporal variations of As and Fe in aquifer sediments. As the plume continues to expand, As and Fe will be redistributed in aquifer sediments, creating zones enriched in As that may be susceptible to re-mobilization under the changing geochemical conditions of the dynamic plume.

Advisor: Dr. M. E. Schreiber

BRAINS AND BONES: AN INVESTIGATION OF THE ENDOCRANIUM OF THE PHYTOSAUR *WANNIA SCURRIENSIS*

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With increased use of virtual methods, large amounts of archosaur endocranial data have been collected focused on body size evolution, nerve pathways, and sensory systems. Archosauria is an extensive group containing dinosaurs, living birds, and crocodylians, but little is known about their common ancestor. However, there are many examples of the current sister taxon, phytosaurs, an extinct group of reptiles that superficially resemble living crocodylians. Until recently, phytosaur endocranial studies have used antiquated methods and focused on derived taxa. We provide a comparative digital examination of the internal skull anatomy of *Wannia scurriensis*, the most basal known phytosaur, using computed tomography (CT) to distinguish the morphology and evolution of the phytosaur brain, inner ear, and soft tissues. *Wannia* shows some similarities with living crocodylians and derived phytosaurs in general endocranial shape and cranial nerve innervation. *Wannia* exhibits a large hypophyseal fossa relative to brain size, which may be indicative of rapid growth. *Wannia* possibly exhibited a unique alert head position as the semicircular canals have lateral canals that are angled more than in derived taxa. Extensive facial innervation from the trigeminal nerve suggests increased facial sensitivity as in *Alligator mississippiensis*. Endocranial similarities among phytosaurs and with *Alligator* could indicate conserved ecological and functional constraints of an aquatic lifestyle on anatomy.

Advisor: Dr. M. R. Stocker

MOENKOPI COPROLITES: THEIR COMPOSITION AND PALEOECOLOGICAL SIGNIFICANCE

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Reconstructing the paleoecology of the Moenkopi Formation is critical to understanding the environment in which many major classes of animals, such as archosaurs and synapsids, radiated. This information helps reconstruct parts of the Triassic ecology of North America, namely predator-prey relationships. Inclusions of bone and other material, such as sand, gives insights into feeding habits of the producing animal, and elemental mapping data can narrow the range of minerals formed during preservation. I examined the morphology, internal structure, and composition of coprolites collected from the Moenkopi Formation of Arizona to attempt to gain insight into the feeding habits of the producing animal and the conditions in which the coprolite was preserved. Examination of the exterior surfaces of the coprolites identified some distinctive structures such as pinch marks and spiral structures, which were produced when the coprolite was originally excreted. SEM and elemental analysis provided composition data, namely the identification of areas with a high iron, phosphorous, calcium, or silicon content. Abundant iron suggests the formation of iron minerals, such as hematite or limonite, from fluids leaching into the specimen and replacing bone material. Areas of abundant phosphorous indicate bone material. Calcium-rich regions were seen to occur in linear patterns resembling filled-in cracks. Silicon was found to be abundant in round, dense spots, suggesting the inclusion of sand grains in the coprolite, perhaps ingested by the producing animal during feeding. Many of the oblong areas of high phosphorous content inside the coprolite may be ingested bone. The relative intactness of these bone pieces suggests that the prey was subjected to minimal processing before ingestion, and some fragmentation may have occurred during digestion. This may indicate that the producing animal ate their prey whole. This information is complementary to the body fossil record of the Moenkopi Formation because it provides insight into the diets of the animals that may not be apparent from body fossils.

Advisor: Dr. M. R. Stocker

SYNTHESIS AND CHARACTERIZATION OF IMOGOLITE NANOTUBES

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Imogolite is an aluminosilicate clay mineral 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 imogolite's potential application in composite materials. The pathway through which imogolite grows is currently unknown, although it is suspected that it forms via crystallization by particle attachment (CPA). In this proposed pathway, short (5-10 nm long) imogolite nanotube precursors join end to end, resulting in the long tubes that are characteristic of imogolite.

We have conducted a synthesis and characterization experiment in order to better understand the dominant growth mechanism of laboratory imogolite. A new synthesis procedure was developed that uses Ge as a chemical label. Two separate batches of short nanotube precursors, one pure silica imogolite (Si_{100} -imogolite) and one substituted with 10 mol% Ge ($\text{Si}_{90}\text{Ge}_{10}$ -imogolite) were synthesized according to the method of Levard et al. (2010). Equal volumes of the Si_{100} and $\text{Si}_{90}\text{Ge}_{10}$ -imogolite precursors were mixed into a single batch prior to the growth stage. Atomic force microscopy (AFM) shows the final solid consists of bundled aggregates of nanotube fibers that are ~2.5 nm in diameter and up to hundreds of nm in length. Low-voltage (30-60 keV) HR-TEM with high angle annular dark field (HAADF) imaging shows that different segments of a single nanotube vary in brightness along the length, suggesting variations in chemical composition. EDS of bright and dark sections of the nanotube shows the presence and absence of Ge, respectively. Dissolution and re-precipitation is expected to result in a homogenous chemical signature for Ge along the length of a single tube. Thus, we interpret the observed chemical segmentation as evidence of CPA growth. 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.

Advisor: Dr. M. F. Michel

EFFECTS OF pH, TEMPERATURE, AND H₂O₂ CONCENTRATION ON THE CATALYTIC ACTIVITY OF TWO COMMERCIALY SUPPLIED PLATINUM NANOCATALYSTS

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Platinum is a metal of interest due to its numerous applications in modern technology. From combining carbon monoxide and hydrocarbon with oxygen to form carbon dioxide and water in catalytic converters, to combining hydrogen and oxygen to produce renewable energy in hydrogen fuel cells, the industrial relevance of platinum as a catalyst is due to its notable oxidation and reduction properties. Platinum nanoparticles (Pt-nanopowder) and platinum black (Pt-black) are two platinum catalysts exhibiting high electrocatalytic activity. While both are metallic and nanosized, they differ in their synthesis methods. Pt-nanopowder is obtained through chemical vapor deposition, whereas Pt-black originates from the reduction of PtO₂, also known as Adam's catalyst. The high catalytic activities of Pt-nanopowder and Pt-black are thought to be due to their large surface area, surface chemistry, and surface structure. Despite a number of hypothesized mechanisms attempting to explain platinum catalysis, a universally accepted reaction model has yet to be established.

Our results indicate that Pt-nanopowder results in a greater hydrogen peroxide (H₂O₂) decomposition rate than Pt-black. In addition, an increased stability and dispersion in solution of the two catalysts are observed at higher pH, which is attributed to an increase in zeta potential with increasing pH. Although the starting H₂O₂ concentration affects the activity of both catalysts similarly, pH and temperature influence the activity of these two catalysts in a different way. Lastly, preliminary TEM analysis of the catalysts *ex situ* indicates the formation of an amorphous phase at the surface of the platinum catalyst during the decomposition of H₂O₂. These results are the basis for understanding the effects of environmental factors such as pH, temperature, concentration, and type of catalyst on a catalyzed H₂O₂ decomposition reaction. The purpose of this research is to further the knowledge on platinum catalysts, and ultimately catalysis itself.

Advisor: Dr. M. F. Michel

DESIGN AND FABRICATION OF MICROFLUIDICS DEVICES FOR REAL-TIME CRYSTALLIZATION STUDIES OF ENVIRONMENTAL MINERALS

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Modern crystallization science is revealing a diversity of pathways and mechanisms by which environmental minerals grow. Developing a comprehensive understanding of these processes will deepen our understanding of many low-temperature mineral-forming processes, as well as provide insights into novel synthesis methods for technological applications. Current knowledge gaps in many systems are due to the lack of experimental methodologies for making direct, real-time observations of crystallization in solution. New real-time approaches are needed to understand how varying solution chemistry and hydrodynamic conditions fits into existing crystallization models. The main objective of this project is to design and fabricate microfluidics devices that can be coupled with laboratory and synchrotron analytical characterization methods in order to study mineral growth in real time.

We have been collaborating with the Lu Lab in Chemical Engineering to fabricate device prototypes designed specifically to study the crystallization of schwertmannite, a poorly crystalline ferric hydroxysulfate nanomineral that is commonly formed in acid mine drainage. Schwertmannite is readily synthesized in the laboratory by the rapid oxidation of ferrous sulfate at acidic pH (2-4). Prior work by our group and others suggests that aggregation of precursor ferric hydroxysulfate clusters leads to schwertmannite formation, but that this process is different under turbulent versus static conditions. Microfluidic devices are an ideal way to precisely control both the chemical and hydrodynamic conditions during crystallization because they are highly customizable and have channels that are small enough to achieve laminar flow. In addition, it is possible to couple these devices with numerous analytical characterization methods, including synchrotron scattering and spectroscopy.

As this project enters its second semester, it has achieved several important milestones. First, our group is now able to use LayoutEditor to design photolithography masks suitable for printing by an outside manufacturer (e.g., FineLine). Second, we have a protocol for fabricating microfluidics chips and are able to use basic dye tests to understand flow conditions within the device channels, as well as to trouble-shoot integrity issues associated with the fabrication process. Finally, we have used a device to synthesize ferric hydroxysulfate nanoparticles in solution and evaluated the products collected ex situ using high-resolution transmission electron microscopy and powder X-ray diffraction. These results are compared to our prior studies using standard benchtop synthesis. Future milestones for the project include optimizing the devices for synchrotron scattering, computational modeling of hydrodynamics, and implementing a system for real-time monitoring of solution conditions (e.g. pH).

Advisor: Dr. M. F. Michel

TRACE ELEMENT MOBILITY FROM HYDROCARBON-RICH SHALES DURING PYRITE OXIDATION

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Shales are fine-grained clastic sedimentary rocks that form from the compaction of silt and clay-sized mineral particles. Shales that have a black color generally contain abundant organic material, along with pyrite, quartz, carbonates, clays and trace elements (i.e., copper, nickel, arsenic and vanadium) depending on location. Hydrocarbon producing shales contain between 2% and 15% organic carbon, and formed under reducing conditions. These organic-rich shales play an important role in the energy industry due to their capability to produce natural gas and/or liquid petroleum.

The Upper Devonian–Lower Mississippian Bakken Formation and the Middle Devonian Marcellus formations consist of these carbonaceous, low-density shale rocks. These rocks are known to be rich sources for oil and gas. These resources are generally extracted through hydrofracturing and horizontal drilling (aka fracking). Hydrofracturing technologies have contributed to the increase in the US production of natural gas and petroleum, but extraction can also lead to a threat to the environment and/or local communities. One potential environmental impact of fracking is the mobilization of trace elements to either surface and/or ground water.

The shales in the Bakken and Marcellus formations are locally rich in pyrite. Pyrite can oxidize when exposed to oxygen in-situ or as waste material on the surface. Furthermore, Pyrite (FeS_2) often contains numerous trace elements such as arsenic, copper and selenium. To further understand the potential of shales to generate trace elements during pyrite oxidation, five different samples were taken from the Marcellus and Bakken formations to determine their chemical composition and mineralogy. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) was used to determine trace element distribution and abundance. LA-ICP-MS was successful in measuring concentrations of V, Cr, Mn, Co, Ni, As and Se. Furthermore, X-ray diffraction was used to determine mineralogy and estimate the abundance of pyrite and carbonate minerals in each sample. X-ray diffraction was successful in identifying Albite, Muscovite, Pyrite and Quartz. These results helped to understand and predict acid rock drainage potential of the shales.

Advisor: Dr. J. Chermak

Cover Images

TOP: Minerals encrusting the eye of a silicified mayfly from the Miocene Barstow Formation of southern California.

(Drew Muscente)

MIDDLE: A plagioclase crystal that has experienced brittle deformation. The rock is a hydrothermally altered high level gabbro from the Layer 2-3 boundary in the Cocos Plate. It represents an in situ section of the oceanic crust drilled at IODP Hole 1256D by Expedition 335. (Also on back cover.)

(Jarek Trela)

BOTTOM: Amorphous coal fly ash with cenosphere in the pores.

(Rui Serra Maia)



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