

VIRGINIA TECH DEPARTMENT OF GEOSCIENCES

GEOSCIENCES STUDENT RESEARCH SYMPOSIUM 2019



FEBRUARY 21-22
KELLY HALL RM 310

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Geosciences Student
Research Symposium
at VT Geos



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24th Annual GSRS

Welcome to the 2019 Geosciences Student Research Symposium! GSRS, now in its 24th year is organized entirely by the graduate students in the Geosciences Department. The purpose of GSRS is to give students an opportunity to present their research to their peers and professors in the department. During GSRS students and faculty learn about the diversity of geoscience research that occurs in the department. Students gain practice communicating their research to a broad audience. GSRS offers a unique opportunity for students to give a professional talk in preparation for future talks at national conferences. GSRS brings the department together through scientific talks, poster sessions, and community lunches and dinners!

GSRS would not be possible without the help of many people. First, thank you very much to everyone that donated to GSRS through our Virginia Tech Crowdfunding Campaign last fall. This symposium would not be possible without your generosity. Thank you to Carol Lee Donuts, Panera Bread, The Beast of Blacksburg, Due South, and Professional Touch Catering for providing food and drinks throughout the symposium. Thank you very much to everyone in the Department of Geosciences: students, faculty, and staff for helping make GSRS possible. A special thank you goes out to members of Sigma Gamma Epsilon for helping set up for GSRS. Additionally, thank you to ICTAS at Virginia Tech for allowing us to use Kelly Hall for our symposium. We would also like to thank Dean Karen DePauw and Dean Sally Morton for attending this event. Without all this support, GSRS would not be possible!

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GSRS Schedule

Thursday, February 21	Presenter
8:00-9:00	Breakfast
8:50	Opening Remarks
	Session 1
8:55-9:10	Kristin Chilton
9:10-9:25	Kathryn Krueger
9:25-9:40	Lisa Whalen
9:40-9:55	Hao Wu
9:55-10:10	Aly Hoeher
10:10-10:25	Laura Szczyrba
10:30-12:30	Poster Session & Lunch
12:45-12:50	Announcements
	Session 2
12:50-1:05	Jessica DePaolis
1:05-1:20	Nathan Roethlisberger
1:20-1:35	Tahiry Rajaonarison
1:35-1:50	McNeill Bauer
1:50-2:05	Lowell Moore
2:05-2:20	Coffee Break
	Session 3
2:20-2:35	Selva Marroquín
2:35-2:50	Shuyang Sun
2:50-3:05	Morrison Nolan
3:05-3:20	Stacey Law
3:20-3:35	Chris Griffin
3:35-3:50	Coffee Break
	Session 4
3:50-4:05	Matt LeRoy
4:05-4:20	Grant Euen
4:20-4:35	Joshua Jones
4:35-4:50	Priyanka Bose
4:50	Closing Announcements

Friday, February 22	Presenter
8:30-9:00	Breakfast
8:55	Opening Remarks
	Session 5
9:00-9:15	Brenen Wynd
9:15-9:30	Zhen Guo
9:30-9:45	Richard Jayne
9:45-10:00	Andrew Parent
10:00-10:15	Emmanuel Njinju
10:15-10:35	Coffee Break
	Session 6
10:35-10:50	Khanh To
10:50-11:05	Shangxin Liu
11:05-11:20	Natalia Varela
11:20-11:35	Devin Hoffman
11:35-12:05	Up Goer 5
12:05-1:55	Poster Session & Lunch
1:55-2:00	Announcements
	Session 7
2:00-2:15	Calvin Mako
2:15-2:30	Graydon Konzen
2:30-2:45	Dana Korneisel
2:45-3:00	Ben Kligman
3:00-3:15	Max Schwid
3:15-3:30	Coffee Break
	Session 8
3:30-3:45	Tyler Rothschild
3:45-4:00	Michael Vadman
4:00-4:15	Amin Abbasi Baghbadorani
4:15-4:30	Yezi Yang
4:30-4:45	Alireza Namayandeh
4:45-5:00	Josh Benton
5:00	Closing Remarks
17:30 Onwards	Reception, Museum of Geosciences

Undergraduate Posters

- 1 David Belisle
- 2 Siqi Che
- 3 Roberto Gorjon-Andujar
- 4 Joshua Kling
- 5 Sarah Morgan
- 6 Devin Seran

Undergraduate Posters

- 7 Camille Do
- 8 Laura Garcia Ramos
- 9 Ronald Navarro
- 10 ThaoVy Nguyen
- 11 Jordan Pritchard
- 12 Michael Zigah

Graduate Abstracts

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

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

Two of the most dangerous events in underground mining are encountering unexpected water influx and structural instability due to excavation into undetected voids and fractures underground. The most common detection method before excavation is probe drilling, either from the mine or from the surface. Mine engineers decide on the spacing and the depth of probe drilling based on the planned excavation depth and the nature of previous voids encountered. However, drilling often misses or underestimates the size of fractures and voids between drill holes or beyond the depth of the holes. This project is working in collaboration with an underground limestone mine in the eastern United States. Excavation has unexpectedly encountered fractures and karst voids which have led to significant loss of time and resources as well as posed safety hazards.

Ground or rock penetrating radar (GPR) can detect fractures and voids within rock. GPR equipment was modified to acquire 2D and 3D data on the walls of the mine. Initial data were acquired within a 10x25x25-m triangular pillar to allow calibration of radar images to pillar walls. The data detected and imaged a karst cavern known to be >20-m³ and two smaller voids. The rough geometry of the pillar wall and the complex geometry of the voids required careful consideration of 3D geometry during data processing. Subsequently, 2D and 3D migration imaged the voids at their proper 3D locations within the pillar. Ongoing work involves synthetic radargram modeling to predict fracture aperture and infill. This research will guide future practical radar applications to detect fractures and voids prior to excavation allowing hazard mitigation.

FACTORS REGULATING THE FORMATION OF ALLOPHANE AND IMOGLITE NANOPARTICLES

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

Nanosized aluminosilicate minerals allophane and imogolite strongly control the physical and chemical behavior of soil and hold promise for technological applications. In nature, allophane and imogolite are often observed together in varying proportions. Similarly, laboratory synthesis by various methods usually does not result in pure phases. These observations suggest they form contemporaneously at a wide range of solution chemical conditions. It remains unclear what factors determine how and when these phases form in solution, which limits our understanding of their occurrence in nature and the laboratory. The objective of this study is to understand and explain what solution chemical and physical conditions control the formation of synthetic imogolite and allophane.

We have developed synthesis procedures for allophane and imogolite that mix tetraethyl orthosilicate (TEOS) into a solution of aluminum chloride hexahydrate. Idealized Al:Si ratios are set between 2 and 0.5, with initial aluminum concentrations [Al]=0.005M to 0.2M. The solution is then hydrolyzed by the controlled addition of 0.1 M NaOH to total metal:OH ratios of 1/2 to 3. The solution is stirred for 1 h at 400 rpm and heated for 7 d at 95 °C. Dialyzed products were characterized *ex situ* using powder x-ray diffraction (pXRD) and small-angle x-ray scattering (SAXS). Phase abundances were estimated from pXRD by linear combination fitting (LCF). Multivariate regression was used to simultaneously test for the influence of the variables including pH, concentration, NaOH addition rate, and elemental ratios.

Given the final synthesis product is some combination of allophane, imogolite, and amorphous silica (amSi), multivariate regression can quantify the effect that each synthesis variable has on the abundances of each of these phases. Increasing starting reagent concentration by 0.1M tended to increase the allophane proportion while decreasing the imogolite and amSi proportion at rates of +0.26 dM⁻¹, -0.22 dM⁻¹, and -0.05 dM⁻¹ respectively. Raising the initial pH to 10, from 3, which is the system without adjustment, tended to greatly increase the imogolite abundance, while decreasing the allophane and amSi abundance, by +0.5, -0.2, and -0.3, respectively. Increasing the initial Al:Si ratio from 1:1 to 2:1 decreased amSi proportion by -0.23, it also increased allophane proportion per 1 increase in ratio by +0.24, while having no impact on the proportion of imogolite. These results allow for the production of a model that can be used to optimize the synthesis of allophane and imogolite. The same approach can be applied to other types of nanoparticles.

CHARACTERIZING SUBSURFACE HYDROLOGIC FLUXES WITHIN A GLACIATED WATERSHED

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

Chemical weathering within the critical zone is an important source of solutes as elements are released from bedrock and regolith into solution. This study investigates how the spatial architecture of the critical zone influences hydrologic and solute fluxes throughout multiple sub-catchments in a glaciated, upland watershed at the Hubbard Brook Experimental Forest in New Hampshire. The overarching hypothesis is that on hillslopes, where shallow soils force water laterally through organic rich layers, there are predictable gradients in mineral depletion, solute chemistry, and weathering product accumulation.

To quantify hydrologic fluxes along this weathering gradient, which is the focus of this study, we installed transects of wells in different soil zones and bedrock at several hillslope positions in heterogeneous glacial material where groundwater occurrence is often episodic. Hydrologic flux in the soil zone is calculated using two methods: 1) Darcy fluxes, using measured hydraulic gradients and hydraulic conductivity from slug tests; 2) time-integrated fluxes measured using alcohol tracers impregnated in passive flux meters. These calculations will be coupled with measurements of solute release to estimate solute flux in different soil zones of these sub-catchments to evaluate whether patterns of mineral weathering can be explained based on knowledge of critical zone architecture.

AN APPROACH TO MODELING THE COUPLED MAGMA-HYDROTHERMAL PROCESSES AT YELLOWSTONE NATIONAL PARK

BOSE, Priyanka, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Yellowstone National Park has one of the most active and complex magma-hydrothermal systems on Earth (Fournier (1989)). The last major eruption of rhyolitic magma occurred 640,000 years ago, and geophysical data indicate that subsequent magmatic inputs, coupled with hydrothermal heat transfer, have been linked to both surface uplift and land subsidence since the last eruption (Chang et al (2007) and Wicks et al (2006)). Seismic tomography indicates the magma at Yellowstone consists of two separate partially melted magma bodies: a shallow rhyolitic magma reservoir and a deeper basaltic magma reservoir (Hurwitz and Lowenstern (2014)). Total heat output estimates from the Yellowstone hydrothermal systems are between 1.2 - 5.3 GW (Fournier (1989) and Hurwitz et al (2012)). About half of the heat output in Yellowstone comes from the northeastern vapor-dominated regions of the park (Hurwitz et al (2012)). Fournier et al (1976) used a simple heat balance argument to show the hydrothermal heat output can be derived from the latent heat and cooling of a 0.6 - 1.2 km thick magmatic sill underlying the park's 2500 km² (Fournier (1989)). This calculation doesn't account for the complex nature of the magma-hydrothermal heat transfer intimately linked to magma convection, crystallization, and magmatic replenishment processes of the coupled magma bodies, nor the heat transfer processes in the hydrothermal circulation system that is controlled by crustal permeability.

To understand the complex magma-hydrothermal system, we plan to develop models of magma convection, crystallization, and replenishment of a basaltic magma body underlying a layer of silicic crust overlain by a vigorous hydrothermal convection system. This model will be based on a code modified from Liu and Lowell (2009) with additions from Huppert and Sparks (1988) and Choi and Lowell (2015). The hydrothermal system will be modeled using the NaCl-H₂O FISHES code (Lewis, 2016). The analysis will be divided into two parts. The first part will examine how long the system at Yellowstone can be sustained if no mass or heat replenishment is added only to the shallow silicic magma chamber. How will the system evolve under these conditions? In the second part, we will investigate how much heat and mass needs to be added to the deeper basaltic magma chamber to maintain the current state of the system.

PRESERVATION OF VALLEY AND RIDGE TOPOGRAPHY VIA DELIVERY OF LARGE, RIDGE-SOURCED BLOCKS TO HILLSLOPES AND CHANNELS

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

In landscapes formed in tilted stratigraphy, such as the Valley and Ridge, topography is thought to be produced and preserved by erosional heterogeneity, with resistant lithologies supporting ridges and weaker lithologies forming valley bottoms (Hack, 1960). Recent modelling studies (Glade et al., 2017; Shobe et al., 2016, 2018) have demonstrated the additional role of resistant lithologies in preserving topography by sourcing large bedrock blocks which are delivered to surrounding hillslopes and mountain channels. There they act as armor and slow further channel lowering and hillslope steepening. This is accomplished via downslope sediment trapping on hillslopes and increasing drag/bed shielding in channels. While past workers have noted the abundance of large blocks on hillslopes (Schultz and Southworth, 1989) and in mountain channels (Mills, 1989) in the Valley and Ridge, detailed field documentation encompassing both hillslope and channel block distribution is lacking.

Here we present detailed maps of large blocks (0.5m - 4m+) on hillslopes and in mountain channels within the Valley and Ridge of Southwest VA, created using high resolution topography and aerial imagery combined with field observations. We find that blocks cover a significant portion of the mapped areas (3-9%), are concentrated in channels, and are frequently so large as to be effectively immobile (cannot be transported by plausible flows). Blocks are formed from quartz-rich sandstones and conglomerates (Cloyd, Keefer, Tuscarora) which outcrop at or near ridges and are resistant to both physical and chemical weathering, suggesting longevity once delivered to channels. These results support the findings of numerical modeling studies and represent strong field evidence highlighting an additional role of resistant lithologies in preserving Valley and Ridge topography: by stabilizing channels and hillslopes rather than just “holding up” ridges. In addition, lack of bedrock exposure currently visible at ridges suggests that delivery of the abundant blocks presently observed on hillslopes may have occurred during past periglacial climatic conditions, when soil production was slower and freeze-thaw processes enhanced block production. This suggests a mechanism by which past climatic conditions may continue to impact landscape evolution far into the future.

EXPANDING THE STRATIGRAPHIC RECORD OF TSUNAMI INUNDATION ALONG THE SEMI-ARID, SILICICLASTIC COAST OF NORTH-CENTRAL CHILE

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

On September 16, 2015, a Mw 8.3 earthquake struck offshore of the north-central Chile coast with a fault-rupture length of approximately 150 km. The earthquake triggered a tsunami that impacted 500 km of coastline from Huasco (28.5°S) to San Antonio (33.5°S), registering as much as 4.5 m on the tide gauge at Coquimbo (29.95°S) with run-up heights >10 m at a few exposed locations between Limarí (30.73°S) and Coquimbo. The tsunami provided an invaluable opportunity to examine the nature of tsunami deposit evidence in a semi-arid, siliciclastic environment, where settings suitable for the preservation of tsunami sedimentation are scarce, thereby improving our ability to identify such evidence in the geologic record. Using before-and-after-tsunami satellite imagery and post-tsunami coastal surveys, we targeted one of the few low-energy depositional terrestrial environments in the tsunami-affected area that had a high potential to preserve the 2015 tsunami deposit and older events: the Pachingo marsh in Tongoy Bay (30.30°S). We employed field and laboratory methods to document the 2015 tsunami deposit and discovered sedimentological evidence of previous tsunami inundation of the site.

The 2015 tsunami deposit and an older sand bed exhibit similar sedimentological characteristics. Both sand beds are composed of well-sorted, grey medium-to-fine-grained sand and are distinct from underlying and overlying organic silty sediments. The sand beds thinned (from ~ 20 cm to <1 cm) and fined (from medium- to fine-grained sand) inland, and fined upward. However, the older sand bed extends over 150 m farther inland than the 2015 tsunami deposit. To explore the differences in the offshore ruptures that generated the tsunamis that deposited each sand bed, we employed both a forward tsunami model (GeoClaw) and an inverse sediment transport model (TSUFLIND). Our field survey, sedimentological data, and modeling results infer that the older sand bed preserved at the Pachingo field site was produced by a larger tsunami than the 2015 tsunami. Anthropogenic evidence (copper smelter waste) constrains the magnitude and age of the older sand bed to the last 200 years. Based on historical analysis of recent tsunamis that impacted the Pachingo region, we infer a widespread tsunami in 1922 is the best candidate for depositing the older sand bed at our site, providing first geologic evidence of pre-2015 tsunami inundation along the north-central Chile coast.

VENUSIAN IMPACTS: STARTING A MOBILE LID

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

Earth and Venus are often called sister planets due to their similarities in average radii, densities, gravities, and semimajor axes. However, their surfaces bare almost no resemblance to each other. Despite the heat within Venus, we do not see plate tectonics, nor do we see any form of a dynamic, mobile lid as we do on Earth. The surface of Venus is hypothesized to be in a stagnant lid regime. The surface does show evidence of resurfacing despite its quiescent nature. There are two prevailing hypotheses for this resurfacing: a progressive process similar to hotspot volcanism on Earth and a cataclysmic event which triggers melting and resurfacing. Recent work has shown that the mobile lid regime requires a component of degree-1 density structure. Without this degree-1 structure, Venus models remain in a plume-dominated, stagnant lid regime. This suggests the need for a mechanism to introduce the degree-1 structure in order to trigger mobile lid behavior. It has also been proposed that a large planetary impact was the trigger that initiated plate tectonics on the early Earth. Conditions on early Earth are hypothesized to be similar to modern-day Venus. Here we investigate the role of impacts on the development of mobile lid convection on Venus.

AN EXCEPTIONAL NEW LATE TRIASSIC (FOSSIL ASSEMBLAGE FROM ZIMBABWE AND THE BIOGEOGRAPHY OF THE EARLIEST DINOSAURS ACROSS PANGEA

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

Following the end-Permian Mass Extinction, most surviving species were geographically widespread across Pangea until the Carnian Stage of the Late Triassic (~235 Ma), when levels of endemism—species being geographically unique and not widespread—reached pre-extinction levels. This endemism has been hypothesized to have been driven primarily by strong latitudinal gradients across Pangea, with environmental, not geographic, barriers preventing worldwide dispersal of terrestrial taxa across the supercontinent. Because the oldest dinosaur material is known exclusively from a few Carnian-aged deposits of eastern and western Gondwana (Brazil, Argentina, India), the origin and early evolution of dinosaurs may be tied to the broader biogeographic trend created by this confluence of endemism and paleoclimate across Pangea. Here, I report an exceptional new vertebrate assemblage from the Pebby Arkose Formation of northern Zimbabwe, with hundreds of skeletal elements collected from a single locality. Our team preliminarily dates the new locality as ?late Carnian by the presence of hyperodapedontid rhynchosaur reptiles, an important “index taxon” for the Carnian. In addition to the abundant rhynchosaur material, we collected extinct mammal relative (cynodont) and extinct crocodylian relative (pseudosuchian) remains. We recovered a nearly (~90%) complete individual and other associated remains of a small (2-3 m length) sauropodomorph dinosaur, the oldest definitive dinosaur known from Africa and roughly equivalent in age to the oldest known globally. This individual can be identified by diagnostic sauropodomorph features (e.g., hatchet-like crest of the humerus) and the postcranial skeleton is strikingly similar to that of the sauropodomorph *Saturnalia* from the late Carnian of Brazil. The cranium appears to possess more derived character states shared with later taxa like *Plateosaurus* (e.g., angle of the upper jaw bone) rather than the earliest sauropodomorphs with cranial material. Because this assemblage is at roughly the same paleolatitude (~45°) as coeval rhynchosaur-dominated, cynodont- and dinosaur-bearing sediments from India and South America, this formation geographically links these previously known assemblages, allowing sampling across a latitudinal band spanning Pangea. The similarities of these assemblages, and the dissimilarity of assemblages further north and south, supports the influence of climatic bands on the paleobiogeography of post-extinction Pangea. These conditions played a major role in the early evolution and spread of dinosaurs across the world by restricting the geographic availability of suitable environments to a portion of southern Pangea.

Advisor: Dr. S. J. Nesbitt

AN EXAMINATION OF AMPLIFICATION AND ATTENUATION EFFECTS IN THE ATLANTIC AND GULF COASTAL PLAIN USING SPECTRAL RATIOS

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

The Atlantic and Gulf Coastal Plain in southern and southeastern United States contains extensive Cretaceous and Cenozoic sedimentary sequences of variable thickness. We investigate the difference in response of sites in the Coastal Plain relative to sites outside that region using spectral ratios from 17 regional earthquakes occurring in 2010-2018 recorded by the EARTHSCOPE transportable array and other stations. We find that Coastal Plain sites experience amplification of low-frequency ground motions and attenuation at high-frequencies relative to average site conditions outside the Coastal Plain. We use stacked coda and Lg spectra for sites outside the Coastal Plain as a reference. The spectral ratios at high frequencies give estimates of the difference between kappa at Coastal Plain sites and the reference condition. Kappa values determined from the coda are strongly correlated with the thickness of the sediment section and agree well with previous estimates determined from Lg. Averaged estimates of kappa reach ~ 120 ms at Gulf coast stations overlying ~12 km of sediments. Relations between Lg spectral ratio amplitudes versus sediment thickness in successive frequency bins exhibit consistent patterns, which were modeled using piecewise linear functions at frequencies ranging from 0.1 to 2.8 Hz. For sediment thickness greater than ~ 0.5 km, the spectral amplitude ratio at frequencies higher than approximately ~3 Hz is controlled by the value of kappa. Fourier amplitude spectral ratios at frequencies between ~1.0 and 0.1 Hz are strongly dependent on thickness. At 0.1 Hz, the mean Fourier amplitude ratio (Coastal Plain/reference) is about 2.7 for sediment of 12 km thickness. Analysis of residuals between observed and predicted ground motions suggests that incorporating the amplification and attenuation as functions of sediment thickness may improve ground motion prediction models for the Coastal Plain region.

INVESTIGATING IMPACTS OF pH AND ION RATIO ON THE SHORT-RANGE STRUCTURE OF AMORPHOUS CALCIUM PHOSPHATE BY UTILIZING *IN SITU* TECHNIQUES

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

The crystallization pathway of hydroxylapatite has been a focus of study for over forty years, specifically (carbonated) calcium phosphate bone minerals. This makes synthetic hydroxylapatite an ideal proxy for investigating biominerization processes and for the development of bone replacements materials. Crystallization of hydroxylapatite commonly proceeds through the formation of amorphous calcium phosphate (ACP), which has been a focus of many investigations. Attempts to examine the short-range order of atoms in ACP have primarily fallen into two categories; *ex situ* investigations of dried samples or *ab initio* molecular dynamic models. A limited number of experimental studies of calcium phosphate precursors have attempted to examine the ACP in its native hydrated form.

In our investigation we use a novel mixed-flow reactor (MFR) synthesis method to examine the precursor phases *in situ*. The precipitate flows through the x-ray beam while still in solution and high intensity synchrotron x-ray total scattering is used to collect structural information. The MFR set-up enables precise control of system chemistry and sample age, without concern of sample evolution during data collection. Data are collected soon after initial mixing and sample precipitation, allowing investigations into the structural developments and phase formations that occur early in the crystallization process. Our investigation focuses on how initial solution conditions, like pH or the ratio of calcium to phosphate during mixing, can affect the structure and evolution of the precursor phases.

Results show the synthesis of hydroxylapatite and its precursor phases by this method is consistent between replicates and highly adaptable to various initial conditions. By varying the system pH and initial Ca/P ratio, the bonding geometry between calcium and phosphate is either predominantly bidentate, a mix of bidentate and monodentate, or predominantly monodentate geometries. This supports a literature hypothesis that there are multiple types of ACP, which was proposed with morphological differences, but no structural evidence has ever been presented. In addition, the presence or absence of bidentate geometries influences the crystallization kinetics. Samples with only monodentate geometries evolve to hydroxylapatite, while samples with bidentate geometries evolve to brushite. Future work will focus on modeling the end member structures with published theoretical models of ACP.

Advisor: Dr. F. M. Michel

ECOLOGICAL RECOVERY FOLLOWING THE END-PERMIAN MASS EXTINCTION RECORDED IN MIDDLE TRIASSIC TOOTH ASSEMBLAGE

HOFFMAN, Devin, Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061

Mass extinctions provide a biological “reset” often linked to subsequent biological radiations, generating a repeated macroevolutionary pattern. The end-Permian Mass Extinction, largest of the “Big Five,” decimated ecosystems and environments. Following the extinction, archosauromorphs (group including birds, crocodylians, and their extinct relatives) rapidly evolved into numerous distinct species, expanded globally, and, by the Late Triassic, had filled a wide array of ecological niches. It is unclear if the species diversification of archosauromorphs in the Early and Middle Triassic was co-incident with the ecological specializations present by the Late Triassic, or if ecological disparity occurred after lineage splitting. One measure of ecology in the fossil record is teeth which have a direct link to ecology through diet, although Early and Middle Triassic tooth assemblages are rare, limiting utilization of tooth morphology during this critical time. However, recent fieldwork (2007-2017) in the Middle Triassic Manda Beds of the Ruhuhu Basin, Tanzania has revealed a tooth assemblage that partially fills this gap. To reconstruct the species composition of the assemblage we used teeth within jaws of known taxonomic assignment (e.g., *Nundasuchus*, *Parringtonia*, and one undescribed species) and expanded with 31 isolated teeth of unknown species affiliation. We analyzed this dataset using both continuous measurements (PCA) and discrete tooth characters (non-metric multidimensional scaling, NMDS) using the software R and PAST. Continuous measurements (observations = 71) produced a linear relationship of tooth height predicting tooth base ratio (=base length/base width). Using this relationship, we generated a morphospace in which the majority of isolated teeth fell within a zone of overlap shared by several Manda species (four of five taxa). Several isolated teeth fall outside of the known taxa morphospace and two teeth fall exclusively within the space of *Pallisteria* though this may be the result of size. The discrete NMDS method (observations = 67) of eleven binary characters removed the potential influence of size and reduces overlap among species (significant overlap in two of five taxa). The majority of the isolated teeth fall within the *Nundasuchus* morphospace and two are within *Pallisteria* morphospace. The significant overlap of tooth shape among species and overall similarities indicate that ecological diversification lagged behind species diversification in archosaurs, a pattern predicted in Simpson’s 1944 “adaptive zones” model. Though this represents a single locality, the methods used herein offer a promising lens to reconstructing ecological radiations and are readily transferable across a broad range of Earth history.

Advisor: Dr. S. J. Nesbitt

CO₂ SEQUESTRATION PROJECT IN A HIGHLY HETEROGENEOUS BASALT RESERVOIR

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

To understand the implications of permeability uncertainty in basalt-hosted CCS reservoirs, this study investigates the feasibility of industrial-scale CCS operations within the Columbia River Basalt Group (CRBG). It is generally accepted that plausible constraints on in situ fracture-controlled permeability distributions are unknowable at reservoir scale. In order to quantify the effects of this permeability uncertainty, stochastically generated and spatially correlated permeability distributions are used to create 50 synthetic reservoir domains to simulate constant pressure CO₂ injections. Results from this research illustrate that permeability uncertainty at the reservoir-scale significantly impacts both the accumulation and distribution of CO₂. After 20 years of injection the total volume of CO₂ injected in each simulation ranges from 2.4 MMT to 40.0 MMT. Interestingly, e-type calculations show that the mean CO₂ saturation over the ensemble of 50 simulations is concentric around the injection well, however, ensemble variance shows an ellipse of uncertainty that trends in the direction of maximum spatial correlation (N40°E). These results indicate that a priori knowledge of permeability correlation structure is an important operational parameter for the design of monitoring, measuring, and verification strategies in highly heterogeneous CCS reservoirs.

Advisor: Dr. R. M. Polleyea

EVIDENCE FOR SLIP ON A BORDER FAULT TRIGGERED BY MAGMATIC PROCESSES IN AN IMMATURE CONTINENTAL RIFT

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

Continental rifting evolves through repeated tectonic and magmatic processes. In this work, we investigate the 2007-2008 Northern Tanzania rifting episode to understand the interactions between magmatism and border fault slip during immature continental rifting. We compare modelled stress changes with geodetic observations from the western adjacent border fault. We model 6 distinct phases of the rifting episode, including the subsequent eruption of Ol Doinyo Lengai. The southern segment of the border fault experienced a positive cumulative Coulomb stress change, consistent with newly processed Global Positioning System (GPS) data showing a distinct instance of slip during this time period. Our work suggests active volcanism and faulting are correlated in time, indicating magmatism associated with volcanic activity influences slip on the border faults in immature continental rifts.

NEW LATE TRIASSIC REPTILES FROM ARIZONA SUPPORT EVOLUTIONARY RADIATION OF TERRESTRIAL TETRAPODS AFTER END PERMIAN EXTINCTION

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The Permian-Triassic Extinction Event (~251 Ma) caused significant extinctions in terrestrial tetrapod lineages, especially synapsids. Evolutionary and geographic radiations in many reptile groups including non-archosaur archosauromorphs, archosaurs, and testudines are hypothesized to have occurred in the Triassic in response to opening of niche space after the extinction event. Lepidosauria, which includes lizards and their closest relatives the rhynchocephalians, is another reptile lineage which is hypothesized to diversify during the Triassic in the aftermath of the Permian-Triassic Extinction. Fieldwork over the past five years in the Chinle Formation (Norian) of northeastern Arizona in Petrified Forest National Park has yielded abundant rhynchocephalian material from multiple localities. This new material, consisting mostly of isolated jaws, represents at least four new rhynchocephalian taxa. Recent U-Pb detrital zircon dating of the Chinle Formation has produced absolute dates for most rock units in the Chinle Formation, making these new taxa the only Triassic rhynchocephalian fossils globally to have precise age control. The new taxa also make up most of the known equatorial diversity of rhynchocephalians in the Triassic, given the low paleolatitude of the Chinle Formation.

A phylogeny with divergence dates for Rhynchocephalia was estimated using a Bayesian total-evidence analysis with fossilized birth-death process dating approach in the phylogenetic software package BEAST 2. Two datasets for known rhynchocephalian taxa, including the four new taxa from the Chinle, were used in this analysis. One data set includes morphological data, and the other includes stratigraphic (age) ranges for all fossil taxa. Results support a Permian origin of the lepidosaur lineage, and an Early/Middle Triassic radiation of rhynchocephalians. This analysis adds to the quantitative evidence that the Permian-Triassic Extinction Event acted as a reset for tetrapod evolution, allowing for lineages that survived the extinction to diversify into open niche space in the Triassic. The geographic location of these new taxa show that this diversification event was global in nature.

Advisor: Dr. M. R. Stocker

HYDROGEOLOGY OF LONG-RANGE PRESSURE MIGRATION DURING OILFIELD WASTEWATER DISPOSAL

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Earthquake occurrence in north-central Oklahoma increased from an average of two M3+ earthquakes per year before 2009 to a peak of >900 in 2015 (Kroll et al. 2017). This increased rate of seismicity has been strongly related to oilfield wastewater disposal into deep geological formations, particularly into the underpressured Arbuckle formation. The Arbuckle is hydraulically connected to Precambrian basement through an extensive fracture system, which transmits pressure perturbations from high-density wastewater injections to seismogenic depths. Geostatistical cross correlation by Polleyea et al. (2018) and observational data from the Kansas Geological Survey (Peterie et al. 2018) show earthquake occurrence at length scales of up to 90 km from high-rate injection wells along the Oklahoma-Kansas border. A numerical groundwater modeling study tests the hypothesis that the hydrogeologic principle of superposition provides a physical explanation for these long-range pressure accumulations and earthquake triggering. Based on structure contour data from the Oklahoma Geological Survey, the model domain represents the Arbuckle Formation and underlying Precambrian basement to include parts of the Anadarko and Ardmore Basins, the Anadarko Shelf, and the Cherokee Platform. Simulation results are geostatistically analyzed to quantify the length-scale at which change in fluid pressure is spatially correlated and change in fluid pressure and earthquake occurrence are spatially cross-correlated.

Advisor: Dr. R. M. Polleyea

INTRODUCING A NEW WEST VIRGINIA FOSSIL LOCALITY: THE FIRST VERTEBRATE FROM THE HINTON FORMATION

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Plants and invertebrates had thoroughly colonized land by the Silurian, developing rigid structures and organs like the book lung to adapt to their new environment (Wellmen et al. 1993, Jeram 1990). These evolutionary innovations precipitated a massive change in Earth's ecology, eventually leading to the lush coal swamps which gave the Carboniferous its name. Tetrapods, relatives of amphibious lobe-finned fishes, followed later, and their descendants make up much of the rich diversity of vertebrate life on our planet today. Relationships between these early amphibious and terrestrial animals are still poorly understood, and fossil material is concentrated in just a few modern localities and time periods, so each new locality has the potential to shed light on the evolution of terrestrial vertebrates.

The Mauch Chunk group in West Virginia has a long history of fossil finds from the upper Mississippian and lower Pennsylvanian. This group is made up of the Bluefield, Hinton, and Bluestone formations which record a transition from a fully marine environment to a terrestrial deltaic setting. The youngest segment, the Bluestone formation, is largely terrestrial with very few marine transgressions and has yielded a few excellent fish fossils (Mickle 2018) and tetrapodomorphs (Romer 1969 & 1970, Hotton 1970). In the underlying Hinton formation, marine sediments give way to a series of fossiliferous beds containing freshwater invertebrates and plant fossils. The Hinton locality was originally described as containing "the earliest land vertebrates of this continent" but was thought until recently to bear only very fragmentary fossils, pointing the attention of researchers elsewhere (Romer 1941).

An unusually complete left tetrapodomorph dentary is the first vertebrate fossil described from recent field work at a quarry in the Hinton Formation, the same locality described by Romer in 1941. There is more material to be prepared and likely much more to be discovered, so this specimen represents the beginning of a new vertebrate assemblage defining near-shore Mississippian Appalachia. Its dentition and anatomy bear a striking resemblance to both known Rhizodonts (tetrapodomorph lobe-finned fishes) and Anthracosaurs (amniote-line tetrapods) from the area, placing it in the middle of an exciting period of evolutionary innovation as aquatic animals began to colonize the land and adapt to terrestrial life. Animals like this one set the stage for a world much like the one we know today as Earth approached the end of the Paleozoic.

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

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Elevated concentrations of soluble iron (Fe) and manganese (Mn) in drinking water degrade water quality by affecting taste, odor, and color. Under oxic conditions (dissolved oxygen (DO) >2 mg/L), Fe and Mn occur naturally in their insoluble forms in sediments. However, the development of low DO in the hypolimnion of some lakes and reservoirs during thermal stratification can lead to the reduction of oxidized, insoluble Fe and Mn, in the sediments, to soluble forms, which are then released into the water column. In response, many water utilities have installed hypolimnetic oxygenation (HOx) systems to control metal concentrations *in situ* in drinking water reservoirs. However, previous research has found anoxic (DO < 0.5 mg/L) conditions still develop within sediments, even with operational HOx systems, allowing for the reduction/release of soluble Fe and Mn into the water column. To examine the drivers of metal release from the sediments in varying redox conditions, we conducted sediment flux chamber experiments to directly quantify Fe and Mn fluxes at the sediment-water interface in a small, eutrophic reservoir at different times throughout the summer stratification period. In our experiments we deployed three sediment flux chambers in the deepest part of the reservoir and measured metal fluxes during two ten-day experiments in June and August. Throughout the experiments, we monitored DO, ORP, temperature, and pH and sampled for total and soluble (filtered, 0.45 micron) metals. During the June experiment, total and soluble Mn had a highly variable flux while the total and soluble Fe fluxes were 364 (\pm 52) and 338 (\pm 58) mg/m²·day, respectively. During the August experiment, total and soluble Mn fluxes were 34 (\pm 2) and 34 (\pm 2) mg/m²·day, and total and soluble Fe fluxes were 597 (\pm 37) and 561 (\pm 17) mg/m²·day, respectively. Sediment oxygen demand (SOD) was 467 (\pm 101) mg/m²·day in June and 703 (\pm 225) mg/m²·day in August. The water column chamber did not show any significant fluxes during the experiments. The Fe and Mn fluxes, as well as SOD, are similar to rates measured in other eutrophic, freshwater sites. The next step of this project is to estimate the fluxes indirectly, using water column data, which will allow for a more robust statistical comparison of fluxes between seasons as well as to analyze the drivers of metal fluxes (i.e. temperature, DO, pH).

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

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Classification and modeling of fractured systems is highly challenging due to the heterogeneous nature of the materials in conjunction with the often complex subsurface structure. We investigate the fractured crystalline-rock aquifer system near Ploemeur, France, by characterizing infiltration and groundwater flow using time series hydraulic head and precipitation data analyzed at daily, monthly, yearly, and decadal intervals. The recharge sites are of particular significance; annual withdrawal from the system nears 1 million m³ with minimal observed drawdown, raising questions as to the origins of the recharge. Extensive monitoring has shown a roughly two-month lag between seasonal water levels and monthly precipitation, posing additional queries about groundwater movement through the unsaturated zone and underlying crystalline-rock aquifer system.

The primary objective of this study is to evaluate the mechanisms constraining recharge and the lag between hydraulic head and precipitation via unsaturated zone modeling of the Ploemeur system using MODFLOW and geostatistical tools. The eventual addition of subsurface structural elements and surface deformation measurements will be imperative to the accuracy of the model, and will be implemented in the final stages of work in order to distinguish the fracture geometry and provide insight to the structural and poromechanical controls on the system.

Advisor: Dr. T. J. Burbey

A MULTI-BASIN COMPARISON OF IRON SPECIATION RECORDS OF THE CAMBRIAN SPICE EVENT

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The late Cambrian SPICE (Steptoean Positive Carbon Isotope Excursion) is recognized as a global oceanographic event recorded as positive shifts in the carbon ($\delta^{13}\text{C}$), and sulfur ($\delta^{34}\text{S}$) isotopic records that are linked temporally with marine extinctions on several paleocontinents. While these trends are thought to result from an increase in the areal extent of marine anoxia and possibly euxinia (water-column H_2S), relatively little work has focused directly on characterizing the (local) redox conditions during the event. Here we employ iron speciation analyses to explore the redox history of the SPICE event from four different basins representing a range of depositional conditions (e.g., sedimentation rate, biological productivity, paleobathymetry, etc.) in an effort to tease apart local controls from its broader global expression. Specifically, we examined successions from Avalonia (central England), Baltica (southern Sweden), Laurentia (eastern U.S.), and North China (South Korea). Our iron speciation analyses broadly indicate a shift towards more reducing conditions during the SPICE at each location. However, with the exception of the location in Baltica, where persistent euxinia accompanied the event, the anoxic conditions we record elsewhere are dominantly ferruginous (water-column Fe^{2+}) suggesting euxinia likely remained limited to areas where conducive environmental conditions existed. Importantly only the succession in Laurentia, deposited in a relatively shallow intrashelf basin, records a local shift from oxic to anoxic conditions during the SPICE. Intriguingly, Laurentia is also the lone paleocontinent of the four compared here to experience a significant pulse of marine extinction at this time, suggesting that the deoxygenation of shallower marine environments may have been a factor driving this event. These results provide a more nuanced picture of the heterogeneous redox conditions that accompanied the SPICE along with illustrating an important environmental mechanism that may help explain the observed pattern of biological turnover.

TRANSITION ZONE STRUCTURES BENEATH THE EASTERN US

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The complex tectonic history of the eastern US over the past billion years includes episodes of subduction and rifting associated with two complete cycles of supercontinent assembly and breakup. Whether and how these geologic processes relate to the deeper mantle structures remains unknown. The unsolved problems include the structure of the transition zone that may influence upper mantle flow and interact with the shallower geological processes. The Mid-Atlantic Geophysical Integrative Collaboration (MAGIC) project deployed 29 broadband seismometers in a dense linear transect across Virginia, West Virginia, and Ohio, providing an opportunity to image small-scale high-resolution deep mantle structures throughout the Appalachian region of the eastern US. Combined with the neighboring EarthScope USArray Transportable Array (TA) stations, we use receiver functions to investigate the undulations of 410-km and 660-km discontinuities beneath the MAGIC array from the Atlantic coast to the eastern continent interior. Our preliminary results show that the 410 discontinuity deepens from the inland to the coastline, consistent with previous results (Gao & Liu 2014; Wang & Pavlis 2016). The 660-km discontinuity slightly deepens along the middle part of the MAGIC profile beneath Appalachia, while the previous results (Gao & Liu 2014; Wang & Pavlis 2016) show a largely flat 660. These observations indicate that hydration resulting from dewatering of the Farallon slab (van der Lee et al., 2008) and edge-driven convection (King, 2007) are possible but, evidence for both is weak. Cooler mantle beneath the western half of MAGIC array is not consistent with ‘thermal blanketing’ of cratonic lithosphere (Grigné and Labrosse, 2001). The smooth 410 and 660 indicate that the ‘missing’ Harrisonburg lithospheric block is not in the transition zone.

CONTRASTING RECORDS OF MONAZITE FLUID ALTERATION IN NORTHERN SCOTLAND

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Monazite is an extremely useful mineral for quantifying the timing and conditions of metamorphism using U-Pb geochronology and trace element compositions. In addition to participating in metamorphic reactions, monazite is also known to undergo dissolution and reprecipitation in the presence of fluid, thereby providing an opportunity to understand fluid infiltration events in metamorphic rocks. We present monazite data from the Sgurr Beag nappe in northeastern Scotland that preserve evidence for two different signatures of fluid recrystallization. Initial crystallization of monazite throughout the Sgurr Beag nappe occurred at c. 750 Ma. All dated samples experienced subsequent partial isotopic resetting toward younger ages (600 Ma and younger), likely as a result of fluid-mediated reprecipitation. A fluid-mediated resetting mechanism is indicated by textures observed in monazite. These typically show homogenized rims that truncate more complex interior zoning. Monazite cores are often more porous than rims, which typically indicates dissolution-reprecipitation reactions. Furthermore, many partially reset monazite are entirely included within garnets that are interpreted to have grown at c. 750 Ma based on consistent parageneses with monazite and xenotime. In such a situation it is more likely that was monazite reset by reprecipitation rather than renewed growth or Pb loss.

Although monazite textures, geochronologic data and metamorphic assemblages are broadly similar across the Sgurr Beag nappe, there are two clearly different compositional signatures in these monazite. In four samples, partially reset monazite is high in Y and heavy rare earth elements (HREE) and has relatively low Th/U ratios of 3-4. In two samples, partially reset monazite is low in Y+HREE and has high Th/U ratios of 5-11, likely resulting from U loss. This latter compositional signature is similar to that produced by experimental fluid alteration of monazite. These two compositional trends in monazite appear to be associated with distinct metamorphic textures in thin section. Samples with high Y+HREE monazite consistently exhibit garnet breakdown to plagioclase, quartz and biotite, which is often interpreted to indicate decompression. Samples with low Y+HREE monazite typically have garnet breaking down to chlorite, which indicates hydration. We therefore interpret the low Y+HREE, high Th/U monazite to have formed by fluid-mediated reprecipitation during chlorite-grade hydration, while high Y+HREE monazite resetting occurred at higher temperatures.

EVALUATING ORGANIC MATTER SULFURIZATION AS A MECHANISM OF ENHANCED BURIAL OF REDUCED CARBON AND SULFUR ACROSS THE TOARCIAN OCEANIC ANOXIC EVENT

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Mudrocks with high organic carbon contents have been the focus of intensive study since they are key economic resources as well as frequently reflecting past intervals of extreme environmental change. In particular, the Mesozoic is known to contain multiple instances of the widespread deposition of organic-rich mudrocks that are associated with the expansion of oceanic anoxia called Oceanic Anoxic Events or OAEs. A fundamental debate exists as to what mechanism exerts dominant control on the formation of organic-rich mudrocks: enhanced organic matter production or preservation. However, organic matter preservation is not governed solely by anoxia and may be controlled by other factors. Organic matter sulfurization (OMS) is one such preservation mechanism that operates rapidly within euxinic environments (e.g. anoxic with free hydrogen sulfide). Therefore, it may act as a significant mechanism for organic matter preservation in anoxic environments.

Here we investigate OMS as a potential pathway of enhanced preservation of organic matter during an OAE. Specifically, we investigated this process across the Toarcian Oceanic Anoxic Event (T-OAE, ~183 Ma) of the Early Jurassic. We will present $\delta^{34}\text{S}_{\text{org}}$ and organic matter S:C ratio data from the event as recorded within three basins of the European epicontinental seaway: the Cleveland Basin (UK), the Paris Basin (Luxembourg), and the Southern German Basin (Switzerland). The data generated within these basins are used to evaluate the influence of OMS on organic matter burial across the T-OAE. The broader goal of this work is to determine whether sulfurization acts as a significant preservation mechanism of organic matter when widespread anoxia or euxinia develops in the oceans and if so, then how this may influence our understanding of carbon and sulfur cycling across oceanic anoxic events.

THE VOLATILE SOLUBILITY AND QUENCHABILITY OF HYDROUS BASALTIC MELTS: INSIGHTS FROM RAMAN SPECTROSCOPY

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Volatile elements dissolved in silicate melt influence a range of geologic processes, which include the transfer of volatiles into and out of the deep earth, the release of energy by explosive volcanic eruptions, and the concentration of valuable elements into ore minerals during magmatic boiling. For example, the concentration of H₂O in primary melts associated with subduction zone volcanoes provides a constraint on the amount of H₂O released from the subducting slab. This parameter is in turn constrained by the volatile contents of melt inclusions, droplets of melt trapped by growing phenocrysts. However, the usefulness of primary H₂O concentrations determined using melt inclusions depends on the likelihood that the inclusions have trapped and preserve a representative sample of the melt in question. While many primitive volcanic deposits contain glassy melt inclusions with ~4 wt% H₂O, petrologic evidence suggests that primary melts may have H₂O contents of 10 wt% or more. However, it is not clear whether melts with a sufficiently high concentration of H₂O can be quenched to a homogenous glass, which could be preserved in a melt inclusion and analyzed to estimate the composition of the pre-eruptive melt. Thus, it is possible that the melt inclusion record is biased toward melt compositions that with sufficiently low H₂O concentrations to be quenched to a glass during eruption.

In this study, we explore the limits of melt “quenchability” by analyzing experimental run products synthesized at conditions similar to those under which primitive melt inclusions are likely to be trapped (1 GPa, 1300 °C, 1-7 wt% H₂O). We used Raman spectroscopy to determine how H₂O is distributed within quenched samples of hydrous basaltic melt. Raman analyses yielded H₂O concentrations in glasses that are systematically lower by up to ~1 wt% than total H₂O contents determined using thermogravimetric analyses. This indicates that additional H₂O is contained in bubbles or minerals which form during quenching. We did not detect any additional H₂O at the wetting surface of bubbles or as H₂O when bubbles analyzed in situ and heated to 150 °C. However, nahcolite (NaHCO₃) and additional alteration minerals were detected at the surface of some of the bubbles. This suggests that the bubbles contain a small but significant amount of H, which likely exsolves from the melt during quenching and is sequestered in alteration minerals like nahcolite. Therefore, glassy melt inclusions with compositions similar to the synthetic basalts used in this study may significantly underestimate the primary H₂O contents of the magmas they sample.

THE ROLE OF OXYANION ADSORPTION ON THE SURFACE REACTIVITY AND PHASE TRANSFORMATION OF FERRIHYDRITE

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Ferrihydrite (Fh) is a semicrystalline iron oxy-hydroxide pervasive in soil and groundwater systems. Its highly reactive surfaces are commonly adsorbed with oxyanions of metal and metalloid contaminants such as zinc, arsenic, selenium, nitrate, and phosphate. Fh metastability causes it to eventually transform to less hydrated and more stable minerals such as goethite (FeO(OH)) and hematite (Fe_2O_3). The transformation can cause complexes to be released from the particle surfaces, thereby impacting their transport, fate, and environmental impact. The effects that surface complexes of common groundwater constituents have on Fh stability and reactivity are also not fully understood. New information on how important types of surface complexes affect Fh transformations is needed to reach a more quantitative and predictive understanding of the role Fh plays in environmental systems.

Using flow adsorption microcalorimetry (FAMC), we recently showed that the molar enthalpy (ΔH) of the oxyanions adsorption on Fh follow the modes of surface complexation (i.e., $\text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-} < \text{H}_2\text{PO}_4^- < \text{H}_2\text{AsO}_4^-$) from electrostatic outer-sphere in $\text{Cl}^- < \text{NO}_3^-$, a mixture of outer-sphere and inner-sphere complexations in $<\text{SO}_4^{2-}$, monodentate-bidentate inner-sphere in $<\text{H}_2\text{PO}_4^-$ to bidentate inner-sphere in H_2AsO_4^- . Furthermore, the heat of exchange and irreversibility followed the same trend, increasing with increasing molar enthalpy across the oxyanions. It currently remains uncertain if the phase transformation kinetics and pathway of Fh also depend on the mode of surface complexation and molar enthalpy. Thus, we are currently examining the impact of three oxyanions (nitrate, sulfate, and arsenate) adsorption on the phase transformation of Fh using a combination of powder x-ray diffraction (pXRD), small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM). Overall, a systematic study of the interaction of Fh with these oxyanions will provide insight into the fate and transport of toxic metals and metalloids in natural environments.

3D EDGE-DRIVEN CONVECTION AND LITHOSPHERIC DEFORMATION IN THE MALAWI RIFT: IMPLICATIONS FOR RIFTING PROCESSES IN MAGMA POOR RIFT SYSTEMS

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The physical processes driving magma-poor rifting remain elusive. The East African Rift Systems encompasses an ideal natural laboratory, the Malawi Rift, to explore competing hypotheses. Recent seismic tomographic models image a low-velocity zone (LVZ) beneath the magma-poor Malawi Rift and the adjacent Rungwe Volcanic Province (RVP) in East Africa. Although this LVZ does not extend below 300 km, it is interpreted to be due to the flow of warm, superplume mantle from the southwest, suggesting that plumes play an important role in transporting magma beneath the Malawi Rift. Alternatively, the LVZ may be due to passive upwelling in the magma-poor rift that can also results in the transport of melts along the base of the rift. We test the hypothesis that the anomalous LVZ is due to passive asthenospheric mantle upwelling from edge-driven convection (EDC) due to lithospheric thinning with numerical experiments. We present a three-dimensional (3D) EDC model of the lithosphere-asthenosphere system for the Cenozoic Malawi Rift that is constrained by gravity-derived lithospheric structure. 3D-EDC modeling shows relatively rapid (~3 cm/yr) mantle upwelling beneath the northern Malawi Rift and RVP that is coupled to the crust likely producing the elevated topography. The mantle flow patterns suggest that decompression melts of upwelling mantle materials migrate southward (~1 cm/yr) beneath the amagmatic central and southern Malawi Rift segments where the thick crust is decoupled from the lithospheric mantle and northwestwards along the Western Branch towards the RVP. This work suggests passive upwelling due to EDC can transport melts at depths yet to reach the surface that may influence continental rift initiation in magma poor rifts.

Advisor: Dr. S. Stamps

IMPROVING STRATIGRAPHIC CORRELATION OF EDIACARAN BLACK SHALES IN SOUTH CHINA USING MERCURY CONTENT, $\delta^{13}\text{C}_{\text{ORG}}$ AND $\delta^{15}\text{N}_{\text{ORG}}$ DATA

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The Doushantuo Formation of South China provides significant detail about the Earth and life in the late Ediacaran Period. Exceptionally preserved fossils and geochemical data from this formation have been useful in reconstructing regional and global climate conditions as well as eukaryote evolution. Understanding these histories requires stratigraphic correlation between sections of the Doushantuo Formation, especially the correlation among different black shale units (Member IV, the Miaohe Member, and the Lower Black Shale) described at different sections. Building on current lithologic and stable isotopic correlations, we seek additional chemostratigraphic tools: mercury [Hg] content, organic carbon isotope composition ($\delta^{13}\text{C}_{\text{org}}$) and organic nitrogen isotope composition ($\delta^{15}\text{N}_{\text{org}}$) of these black shale units. Mercury accumulates in organic material, making black shales a good target for [Hg] analysis, especially given that [Hg] is influenced by global volcanic input and local redox conditions. $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{org}}$, along with existing Fe speciation data, can be used to infer local redox conditions. Together, these geochemical data will help us to resolve both local redox conditions and global Hg flux, the latter of which could facilitate stratigraphic correlation between sections. By integrating these data with existing geochemical, biostratigraphic, and geochronological data, the depositional age of these black shale units of the Doushantuo Formation can be better constrained. With a solid chronostratigraphic framework, we can better constrain the evolutionary and environmental events in the Ediacaran Period. For example, the age of the Shuram Excursion, which represents the largest negative carbon isotope excursion in Earth history and is recorded in the Doushantuo Formation, can be constrained. Preliminary data generated so far suggest two correlatable mercury excursions: in the uppermost Member IV and Miaohe Member; and in the basal Member IV and the Lower Black Shale.

POST-RIFT GEOLOGIC EVOLUTION OF THE APPALACHIANS AND MID-ATLANTIC U.S. CONTINENTAL MARGIN: INSIGHTS FROM EARLY CRETACEOUS SEDIMENTARY SYSTEMS

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Geologic evolution of the U.S. Atlantic passive margin remains poorly constrained and understood. Here, I apply both detrital zircon U-Pb and (U-Th)/He geo-thermochronometers to Early Cretaceous onshore to offshore sandstones of the mid-Atlantic (U.S.) passive margin. Fluvial sandstones of the Lower Cretaceous Potomac Group are abundant in the subsurface of the coastal plain. Sandy turbidites of the Hatteras Fan, equivalent with the Blake-Bahama Formation, were cored during DSDP Leg 93 from the outer continental rise, offshore North Carolina. This study will directly test hypotheses regarding provenance and the overall source-to-sink system put forth following the discovery of the Hatteras Fan. Heavy mineral analysis through fan stratigraphy revealed a marked change in source area, though no definite tectonic terranes were cited as dominant source areas. Isopach maps from wells and seismic-reflection revealed an apparent relationship between the paleo-Susquehanna River and the Hatteras Fan, which led to interpretations of the overall fluvial-to-basin floor system.

Detrital geochronology and thermochronometry are becoming increasingly valuable in sedimentary basin analysis as a result of the ability to analyze hundreds of grains per sample efficiently and relatively inexpensively. Though many isotopic systems have emerged in recent years for various applications, U-Pb dating of detrital zircons (DZ) is common due to the high closure temperature of the U-Pb system, indicative of crystallization age. In addition to U-Pb, individual zircon grains can be “double-dated” using other isotopic systems, such as (U-Th)/He (ZHe). ZHe ages indicate timing of cooling and exhumation as closure temperature is much lower than U-Pb (~210°C, which is ~7-8.5 km deep in the crust). Together, these geo-thermochronometers provide valuable insight to processes acting in the source area, the basin, or both. Coupling DZ and ZHe will help further elucidate the evolution of the mid-Atlantic sedimentary system operating during the Early Cretaceous, heretofore understood through mapping of widely-spaced vintage 2-D seismic-reflection data and sparse well coverage. Additionally, outlining a potential paleo-catchment can provide constraints on sedimentary system segment scaling, holding major resource assessment potential for this frontier basin.

EDGE DRIVEN CONVECTION INDUCED SEISMIC ANISOTROPY BENEATH MADAGASCAR

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Over the past few decades, azimuthal seismic anisotropy measurements have become a widely used proxy to study past and present-day internal deformation of the lithosphere, as well as, to characterize convective motion in the mantle. Recently, shear-wave splitting measurements in Madagascar indicate a complex pattern of azimuthal anisotropy that cannot be entirely explained by the surface geology and the direction of absolute plate motion. The source mechanisms of these complex patterns of anisotropy remain poorly understood. Herein, we test the hypothesis that the majority of the observed seismic anisotropy observations are due to Edge Driven Convection (EDC) generated strain beneath Madagascar. In this work, we use the numerical code Advanced Solver for Problems in Earth's ConvecTion (ASPECT) to model 3D EDC model beneath Madagascar and surroundings using shear wave tomography derived lithospheric thickness. Our modeling results show that EDC develops at the transition from thick to thin lithosphere forming three convection cells beneath Madagascar, and one convection cell between East Africa and the Comoros. The asthenospheric upwellings of the convection cells coincide with the location of intra-plate Cenozoic volcanism in central and northern Madagascar and at the Comoros volcanic chain. We then calculate finite strain ellipsoids accumulated along pathlines of the convective flow beneath seismic stations where measurements exist and use them as a proxy for seismic anisotropy. Predicted anisotropy aligns mostly with observations in the northern and southern regions of the island. NE oriented anisotropy in northern Madagascar fits with predicted LPO at 125 km with an average misfit of $\sim 18^{\circ}$. We also find a good fit in south central Madagascar at 200 km with an average misfit of 21° where the source of anisotropy has been proposed to be linked with the underlaying crustal ductile shear zone. This indicate that those anisotropy might be sourced from combination of deeper convective flow and shallow fabrics. Our study suggests that EDC play important role in the mantle dynamic beneath Madagascar.

A TIME-SERIES ANALYSIS OF SUBSIDENCE IN THE SOUTHERN COASTAL PLAIN OF VIRGINIA BY AQUIFER/AQUITARD COMPACTION FROM GROUNDWATER PUMPING

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The Coastal Plain in the southern Chesapeake Bay area is becoming increasingly susceptible to nuisance flooding as a result of the combination of sea-level rise and land subsidence associated with aquifer compaction from excessive groundwater pumping. Detailed time-series compaction data (land subsidence) from three USGS deployed extensometers in the region provide evidence for periodic seasonal variations in land subsidence that reflects the nature of the complex multi aquifer/aquitard system in the Coastal Plain. Earth and ocean tide data can also be observed in the newest and most sensitive of the three extensometers. Regional municipal planners can use subsidence rates to update models and make decisions on how and where to mitigate expensive consequences of subsidence in the region (e.g. nuisance flooding). MATLAB software is used to import extensometer data that contains earth and ocean tidal data for isolation and removal of the tidal data by frequency analysis. Removal of tidal data will identify the magnitude of the subsidence. Additionally, aquifers can be characterized by analyzing the cyclical compaction records along with local piezometer data. The early processing of the extensometer data shows a net increase of subsidence by compaction though the magnitude of this increase has yet to be determined. An updated model describing the nature and extent of subsidence by aquifer compaction in Southeastern Virginia is the desired outcome of the study as detailed analysis of the seasonal compaction records together with the time-series water-level records can provide important information about the aquifer and aquitard properties in the region.

Advisor: Dr. T.J. Burbey

MICROSTRUCTURAL, STRAIN AND CRYSTAL FABRIC ANALYSES OF FRIES THRUST FAULT MYLONITES FROM RINER TO ROANOKE, SW VIRGINIA

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The Fries fault zone is a large tectonic discontinuity in the Blue Ridge Province of southwest Virginia carrying crystalline basement core rocks over meta-sedimentary cover rocks. The fault bends around the Roanoke recess and is structurally linked with major orogen-scale faults to the north and south within the Central and Southern Appalachians, respectively. The northeast striking, southeast dipping fault zone locally ranges from 1 to 2.5 km in width, with estimates of reverse fault displacement ranging from 30-100 kilometers. Progressive sub-simple shear is dominant with flattening increasing through four stages of Paleozoic deformation. Mylonites in the hanging wall and footwall of the shear zone are derived from hydrous and anhydrous rocks, respectively, of Precambrian to Cambrian age. The hanging wall, termed the Lovingston basement terrane, is composed of biotite granofels and biotite granulites. The footwall, termed the Pedlar basement terrane, contains charnockites and pyroxene granulites. Within the fault zone, mylonites are variably developed under greenschist to amphibolite facies conditions, with disputed extensional and contractional kinematic indicators developed at local and regional scales.

In order to constrain the structural framework and kinematic history of the fault zone, field mapping and collection of oriented samples will be conducted in a series of transects across the Fries fault zone from Riner northeastwards to Roanoke, Virginia, and followed by microstructural, 3D strain and quartz c-axis fabric analyses on the samples collected. Additional fieldwork will involve field mapping of the less conspicuous northeastern along-strike continuation of the Fries fault zone, located to the north of Roanoke, near Suck Mountain in Botetourt and Bedford counties.

PALEOCEANOGRAPHY OF AN EDIACARAN PHOSPHORITE: GEOBIOLOGICAL INSIGHTS FROM THE DOUSHANTUO FORMATION IN HUBEI PROVINCE, SOUTH CHINA

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Phosphorous-rich sedimentary rock (i.e., phosphorite) of the Ediacaran Doushantuo Formation (635–551 Ma) in South China was deposited immediately after a Snowball Earth glaciation, contemporaneous with increases in atmospheric oxygen concentration, and prior to the Cambrian Explosion. This formation hosts proxies for nutrient and oxygen levels in ancient oceans in the form of sedimentary phosphate minerals that also preserved microbial and eukaryotic organisms. Extensive Doushantuo phosphorites are exposed at the Wanjiagou section in western Hubei Province, which offers a temporally significant record of ecological and environmental drivers and feedbacks during the Ediacaran Period. Although this section has been studied previously, mechanisms of sedimentary phosphate mineral formation remain enigmatic as a result of poor constraints on past oceanic chemical species/nutrient concentrations (oxygen, phosphorous, nitrogen, and carbon), the biological diversity of organisms cycling these nutrients, and paleogeographic settings. To determine the nature of the environmental conditions that led to phosphate mineral formation and fossil preservation, sedimentological, geochemical, and paleobiological approaches are necessary. Outcrop and hand sample observations in conjunction with petrographic analyses of samples collected from the Wanjiagou section at a decimeter scale differentiate two types of phosphorite textural patterns: pristine phosphorite deposited near the seafloor (authigenic) and reworked or winnowed phosphorite. Representing different hydrodynamic energy levels of the ocean when they formed, pristine intervals were precipitated in relatively shallow and calm waters as a by-product of chemosynthetic bacteria, whereas reworked intervals indicate increased hydrodynamic activity. Petrography and X-ray diffractometry (XRD) reveal a complex history of mineral alteration during diagenesis, with multiple episodes of phosphate mineral recrystallization, dissolution, remobilization, and stabilization. In addition, several other authigenic minerals (e.g., pyrite, barite, quartz) exhibit evidence for alteration and/or overprinting, affecting chemical signatures and complicating their paleoenvironmental interpretations. Documentation of these characteristics is foundational to sample selection for higher resolution electron microscopic, energy dispersive spectroscopic, and isotope geochemical analyses, ultimately to establish the original chemical signatures of the phosphate minerals and morphologies of fossils. Petrographic and XRD results will be synthesized with future chemical and paleontological data to further delimit the physical and biogeochemical state of the ocean, phosphogenesis mechanisms, organismal affinity, and biodiversity in the Doushantuo Formation.

Advisor: Dr. S. Xiao

IMAGING THE SHARPNESS OF THE LITHOSPHERE-ASTHENOSPHERE BOUNDARY (LAB)

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The lithosphere is the outermost shell of the earth. The lithosphere-asthenosphere boundary (LAB) divides the cold, rigid shell from the underlying weaker mantle and is fundamental in plate tectonics. However, its depth and defining mechanism are currently being debated. Imaging the sharpness of the lithosphere-asthenosphere boundary (LAB) is important for understanding its nature. It has been suggested that the LAB beneath continents is probably a sharp discontinuity (over <30 km) associated with partial melting, and, SS precursors with a dominant period of 20 seconds are consistent with such model. In this study, we compare seismograms generated in 1-D reference earth models with varying discontinuity sharpness to investigate seismic signals that are sensitive to discontinuity structure. At 10 to 100 seconds periods, travel times of SS precursors show negligible differences when a first-order discontinuity is replaced by a gradient zone over 50 km, as long as the average S wave speed over the depth range remains the same. It shows that surface wave overtones at those periods are most sensitive to the sharpness of the discontinuity and can be potentially used to better constrain the LAB. We measure the travel time differences of SS precursors and higher-mode surface waves between observed and synthetic seismograms for one seismic event. The preliminary results are overall consistent with a shallower LAB depth in the Pacific Ocean.

EXPLORATORY DATA SCIENCE ANALYSIS OF THE PRESERVATION POTENTIAL OF COASTAL STORM DEPOSITS

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Observations of sediment overwash deposited in the Florida Keys by Hurricane Irma provide an opportunity to explore the application of data science techniques, such as machine learning, to sparse data. Depending on the environment, hurricane signatures in coastal deposits can potentially be archived in the sedimentary record and used to understand Holocene storm frequencies, intensities, and climate evolution at different locations. This information is extremely valuable since the current written record and observations of hurricanes are too limited to make statistically robust return period and magnitude predictions. However, before these prehistoric storm deposits can be used a reliable tool to better understand storm history and climate phases, the factors that modify these deposits over time need to be thoroughly studied. Physical and biological post-depositional processes rework the sediment, often resulting in the blurring and thinning of event signals. Because of these alterations, not all hurricane signatures are preserved in the geological record, which may lead to underestimations or misinterpretations of paleostorm chronologies. Few studies have explored the evolution of modern storm deposits through time in an effort to quantitatively model the thinning of the sediment layer.

The data in this study were employed to quantify the evolution of Hurricane Irma storm deposits through time, especially how the deposit thickness decays, and theoretically predict the point at which the event signal disappears from the geologic record. First, the data were cleaned and physically constrained according to several key assumptions. Machine learning algorithms were then trained and fitted to the data to create multiple models. The Python Scikit-learn machine learning library was used to generate linear, polynomial, and exponential decay univariate equations that were evaluated for fit using the coefficient of determination. The results show that the linear model performed best, followed by the exponential decay and then the polynomial models. However, R-squared values for all models were too low to make reliable and precise predictions. This study demonstrates the potential of machine learning applications in geoscience as well as the importance of having an adequate amount of high quality data to train machine learning algorithms. However to fully unleash the power of data science techniques for sparse geoscientific data, such as machine learning, we need to find better theoretical models that adequately describe and quantify post-depositional processes. While such models can be simple (linear), field data can be employed to introduce natural variability in the model results.

UNDERSTANDING CRANIAL KINESIS IN BIRDS UTILIZING MODERN SPECIES AND THE ALTRICIAL-PRECOCIAL SPECTRUM

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In living birds, cranial kinesis (the movement of skull bones relative to the braincase) enhances the mobility and dexterity of the bill, which allowed them to diversify in multiple aspects. One of those aspect is the wide spectrum of life-history traits, the altricial-precocial spectrum of the independent behavior of hatchlings. Precocial birds are more independent of their parents and forage by themselves early, whereas altricial birds are dependent on parental care for food. This dichotomy in feeding behaviors in avian hatchlings is expected to be reflected in the jaw and its musculature, providing a direct relationship between morphology and behavior. All living birds exhibit one of three types of 4-bar linkage cranial kinesis, which all differ depending on their dorso-flexion zone. The associated morphological traits of this jaw flexion are not seen in their non-avian dinosaur relatives. The evolutionary mechanism of transitioning from akinetic non-avian dinosaur skull to kinetic bird skull is poorly understood. This is complicated by the fragility of a kinetic skull, which often becomes flattened and disarticulated in the fossil record. Additionally, a gap in understanding the musculoskeletal configuration of small living birds has made identifying any distinct bony correlates of those feeding muscles even more difficult. However, bird ontogeny (growth) represents a full range of morphological variability that has not been utilized as an analog for studying the cranial kinesis transition.

We used diffusible iodine-based contrast-enhanced computed tomography (CT) to examine examples of altricial (black-throated finch) and precocial (domesticated chicken) birds. Our data presented more complexity than expected. One of the muscles, the *Musculus pseudotemporalis superficialis*, had different attachment sites between the altricial and precocial exemplar. This may have been related to taxonomic differences or variation on the prokinetic jaw musculature configuration. The altricial exemplar presented extremely partitioned musculatures that we deemed were not informative enough to be seen in fossils. Variations in muscle growth and development might be affected by breeding seasons, especially in the altricial exemplar. While using the domesticated chicken in this study supported prior studies that chickens are more likely to be representative of the ancestral condition of jaw musculature, domesticated species might not have or have more cranial musculoskeletal features than their wild ancestors. This highlights the need to expand our taxonomic sampling to encompass both living bird diversity and the whole altricial-precocial spectrum in order to accurately interpret the fossil record by using modern species.

MEASURING THE DISTRIBUTION OF ASEISMIC DEFORMATION ACROSS THE PARKFIELD SECTION OF THE SAN ANDREAS FAULT, CALIFORNIA THROUGH DIFFERENTIAL TOPOGRAPHY

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High-resolution, space-based tools have greatly improved the ability to measure millimeter scale displacements across actively deforming regions. However, they lack both spatial and temporal coverage. We are limited to measurements acquired in the last ~25 years, since the advent of GNSS networks and InSAR capabilities. Recently, increased lidar densities have allowed for the generation of high-resolution differential topography in areas with multiple lidar swaths. While differential lidar topography studies are becoming increasingly common in areas with coseismic deformation, they are not used for creeping/aseismic faults. Therefore, I am investigating the creeping Parkfield segment of the San Andreas fault using multiple lidar datasets as well as historical aerial photographs.

To constrain the along and across strike strain/ slip gradients, as well as temporal changes in the distribution of strain accumulation, I use an Iterative Closest Point algorithm to difference the 2005 B4 lidar dataset against the recently flown 2018 Parkfield NCALM dataset. This algorithm sequentially determines the rigid transformation for 50m patches across the study area between the point clouds. My differential lidar analysis shows creep rates comparable with published rates (e.g., Titus et al., 2006) but with much greater spatial density. Additionally, I will use dense point clouds derived from aerial photographs as additional datasets with which to reference against both the lidar datasets and each other. Historical aerial photographs allow for greater temporal coverage, extending back to the 1930s along the Parkfield segment.

Advisor: Dr. S. P. Bemis

PLIOCENE-PLEISTOCENE VARIABILITY OF ANTARCTIC BOTTOM WATER (AABW)
PRODUCTION, HILLARY CANYON, ROSS SEA (IODP SITES U1524 AND U1525)

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Antarctic Bottom Water (AABW) is the coldest (-1° C) and deepest (> 2000 m) water mass in the modern ocean, and it plays a key role in the global meridional overturning circulation (MOC) as it creates the vertical motion due to changes in density. These processes influence oxygen and carbon exchange between the atmosphere and the deep ocean. In the Ross Sea, however, over the last 40 years, the AABW has warmed and freshened, mostly to the interaction with the West Antarctic Ice Sheet (WAIS), currently retreating as a result of the wind-driven oceanic currents that transport warm waters toward the ice margin. In order to understand the evolution of the WAIS in the context of climate and oceanic change over the Neogene and Quaternary, IODP (International Ocean Discovery Program) Expedition 374, which sailed in January-February 2018, drilled five sites and recovered sediments from the outer continental shelf to rise in the eastern Ross Sea. The two sites studied here (U1524 and U1525) characterize sedimentary successions from the continental rise of Plio-Pleistocene age. The sedimentary sections recovered are positioned on the levee of the Hillary Canyon, which is one of the largest conduits of AABW delivery from the shelf into the abyssal ocean along the Antarctic margin. The levee of this 40 km wide by 30 m deep submarine canyon-channel system thus contains an archive of pulsed AABW production. The sedimentological analysis includes the count of over 3,000 thin (<1 cm) turbidite beds and the grain size analysis of 150 samples and will allow the reconstruction of the AABW paleocurrent strength and variability, in the context of a multidisciplinary effort to assess the relationship between sea level change, sea surface temperature, and ice sheet advance/retreat history.

CONSTRAINING THE TIMING OF HEATING WITHIN THE CORE OF NANGA PARBAT

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The thermal evolution of the Nanga Parbat massif (NPM), the 9th tallest mountain on Earth is investigated through a 10 μm lens. Located at the western syntaxis of the Himalayan chain, the NPM is the site of extreme relief and rapid erosion. The core of the massif exposes the youngest dated migmatites and granites (between 1-3 Ma) suggesting very fast cooling from peak temperatures (Crowley et al., 2009). High resolution laser ablation split-stream (LASS) data collected on *in-situ* monazite and xenotime accessory phases (with a beam size of $\sim 10 \mu\text{m}$) from samples from the core of the NPM confirms these young ages. These data show a phase of partial melting indicated by garnet growth (~ 2.2 Ma) followed by rapid cooling indicated by garnet breakdown ($\sim 1.3 - 0.75$ Ma). This data represents the first timing constraints on the prograde heating path for the massif. The next phase of the project will be to further constrain the prograde path utilizing thermodynamic modelling as well as garnet geospeedometry. The tectonic aneurism model of Zeitler et al. (2001) explains this anomalously fast exhumation as a positive feedback system between high topography, erosion, and decompression melting. Alternatively, a deep crustal heat source, such as an asthenospheric upwelling could explain the rapid uplift and melting. Additionally, it may be a combination of these two models that best explain the NPM.

Advisor: Dr. M. Caddick

QUANTIFYING PERMEABILITY ALTERATION EFFECTS TO CO₂ STORAGE POTENTIAL IN A BASALT FRACTURE NETWORK

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Anthropogenic CO₂ emissions are strongly implicated in increasing global temperatures and other serious environmental issues. Carbon capture and sequestration (CCS) is considered as an engineering-based approach designed to reduce the total mass of atmospheric CO₂ releases. In the context of CCS, there are four types of trapping mechanisms for CO₂ storage. Mineral trapping is one of the mechanisms that plays an essential role on CO₂ migration and accumulation and eventually effects the overall success of CCS project. In basalt reservoirs, CO₂ dissolution in formation water releases H⁺ to drive mineral dissolution of olivine and pyroxene, which releases divalent cations (Ca²⁺, Mg²⁺, Fe²⁺) that react with bicarbonate to form secondary mineral phase, e.g., calcite, magnesite, siderite.

In this study, a Monte Carlo numerical model is designed to simulate a supercritical CO₂ plume infiltrating a low-permeability flood basalt entablature. The fracture network model is based on LIDAR mapping of the Columbia River Basalt Group in southeast Washington State and spatial fracture permeability distribution is randomly drawn from a basalt aperture distribution. CO₂ reactive transport behavior is simulated in 50 equally probable realizations of the fracture network. Non-reactive model results after 10 years simulation reveal that CO₂ flow converges on a single dominant flow path and CO₂ accumulates at fracture intersections before diverging into branching fractures. This leads to the situation that CO₂ relative permeability is low in branching fractures and it is possible for carbon mineralization. As a result of carbon mineralization, the fracture permeability along primary flow paths reduces and it slows the vertical migration of CO₂. This study tests the hypothesis that CO₂ mineralization will effectively seal the fracture network by simulating reactive CO₂ flow within the basalt fracture network, and analyzing the ensemble of realizations with e-type statistics. Reactive CO₂ flow is modeled using a newly developed kinetic rate equation for basalt dissolution, and alteration products (carbonate, zeolite, and clay phases) form on the basis of local equilibrium. The results have implication to understand the self-sealing basalt fracture system resulting from carbon precipitation.

HIGH CRANIAL DISPARITY IN THE CLOSE RELATIVES OF ARCHOSAURS AS
DEMONSTRATED IN *DOSWELLIA SIXMILENSIS* (ARCHOSAURIFORMES:
PROTEROCHAMPSIA)

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The Triassic Period (252 – 200 Ma) records a great expansion of reptile diversity and disparity, particularly in skull morphology. There is a growing consensus that close relatives of archosaurs (group including crocodiles and birds) exhibit substantial range in skull shape (cranial disparity), especially by species either shortening or elongating the skull. This disparity is exemplified in the North American Late Triassic proterochampsians by the ‘short-faced’ *Vancleavea* and the ‘long-faced’ doswelliids. To critically investigate skull elongation and character evolution in these proterochampsians, we evaluate the enigmatic taxon, *Doswellia sixmilensis*, known from much of a skull, neck vertebrae and bony armor plates from the Bluewater Creek Formation of New Mexico. I redescribe *D. sixmilensis* on the basis of extensive repreparation of the skull material to identify cranial elements, morphological details previously not described, and cranial suture patterns. As such, I reinterpret what was previously regarded as the antorbital fenestra to be the orbit and, as a consequence, the identification of bones and the diagnosis of the taxon must be substantially modified. For the first time, I scored *D. sixmilensis* into the phylogeny of archosaurs and their close relatives, consisting of 676 characters and 109 species. I analyze this dataset using Bayesian inference and as such, recover *D. sixmilensis* as the sister (closest relative) species of *Doswellia kaltenbachi* nested within the clade Doswelliidae. We recover Doswelliidae as a monophyletic clade sister to *Proterochampsia*, nested within the Proterochampsidae, a previously only South American group. This topology challenges previous interpretations of the Doswelliidae as being the close relatives of, but not nested within, the Proterochampsidae and suggests previously unrecognized cranial disparity within the Proterochampsidae. To reconstruct archosauromorph cranial disparity, I place *D. sixmilensis* and other proterochampsians into a similarity analysis of 36 species and 42 cranial characters using a non-metric multidimensional scaling ordination plot. I find that early diverging proterochampsians explore regions of the morphospace unexplored by other archosauromorphs, but all long-snouted taxa (archosaurs and their close relatives) cluster together in the same area of morphospace, disparate from all other skull forms. From this it is clear that archosaur relatives experimented with the anterior half of their skulls with a combination of unique and convergent character states present in the earliest true archosaurs.

INVESTIGATING AN OCEANIC ANOXIC EVENT IN THE LATE EARLY CAMBRIAN
VIA CHEMOSTRATIGRAPHIC ANALYSIS OF THE SOUTHWESTERN VIRGINIA
SHADY DOLOMITE

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Oxygen availability plays a significant role in animal diversification, evolution and extinction (e.g., Sperling et al., 2013), and abrupt, widespread oceanic anoxic events are one of the common causes of mass extinctions (Barnosky et al., 2011). Major volcanic eruptions are suggested to have triggered marine anoxia and subsequent biotic crises (Hough et al., 2006).

The Precambrian-Cambrian radiation of biodiversity was quickly followed by a two-phased late Early Cambrian extinction, consisting of the mid-Botomian Sinsk Event and the later early Toyonian Hawke Bay Transgression Event (Zhuravlev, 1996). The early phase of the extinction, the Sinsk Event, is suggested to be linked with an oceanic anoxic event based on the presence of extensive black shale deposits worldwide (Zhuravlev and Wood, 1996). Carbon isotope stratigraphy done on the Nemakit-Daldynian to Toyonian strata in northern Siberian record an abrupt negative excursion that coincided with the Sinsk event in mid-Botomian, suggesting a sudden decrease in oxygen concentration (Brasier et al., 1994; Zhuravlev and Wood, 1996). A sharp increase in francolite-bound sulfate $\delta^{34}\text{S}$ in Australia also suggests an oceanic anoxic event which enhanced anoxic microbial sulfate reduction, and is argued to be linked with CO₂ emission of the Kalkarindji Large Igneous Province (Hough et al., 2006).

To assess the global nature of the isotope perturbations in the northern Siberian sequence, I will generate carbon isotopic data of the Early-Middle Cambrian transition from carbonates in the Upper Shady Member of the southwestern Virginia Shady Dolomite, USA as a Laurentian equivalent. I will also construct a carbon cycle box model to explore the impact of an additional volcanic influx on the oceanic carbon reservoir and the carbon isotopic signature ($\delta^{13}\text{C}$) of dissolved inorganic carbon. The new record in Laurentia and the modeling results will further serve as a proxy to assess the extent of the mid-Botomian oceanic anoxic event, determine the drivers behind the excursions in the Cambrian carbon cycle, and investigate their relationship to the late Early Cambrian extinctions.

Advisor: Dr. B. C. Gill

Undergraduate Abstracts

SYNTHESIS AND CHARACTERIZATION OF IRON NANOMINERAL COATINGS ON CALCITE

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Mining activities that expose pyrite (FeS_2) and other metal sulfide minerals to wet and oxidizing conditions on the Earth's surface, initiates a series of chemical reactions that create low-pH systems enriched in iron, sulfur, and a variety of potential contaminants. The most common method to remediate acid mine drainage (AMD) is to capture the water and pass it through a trench filled with crushed limestone to neutralize the acidity. Although effective, the pH increase causes various insoluble ions to precipitate as coatings that inhibit the interaction between the limestone and the hydrogen ions (H^+), thus limiting treatment efficiency. New research is needed to understand the physical and chemical characteristics of the coatings, as well as how their formation is affected by AMD solution chemistry.

To model the system, a 3D-printed mixed flow reactor (MFR) was used to react acidic ferric sulfate solution with crushed calcite (0.8-1 mm) resting on a permeable platform. Ferric sulfate (1-10 mM) was passed through the reactor via peristaltic pump at a rate of 0.95 ml/min while the reactor was gently stirred. Effluent pH was monitored and recorded continuously using a custom 3D-printed in-line flow cell. Effluent samples were collected in nine-minute intervals for chemical analysis by inductively coupled plasma optical emission spectrometry (ICP-OES). Mineral coatings on the calcite were recovered and characterized by powder x-ray diffraction (XRD) and small-angle x-ray scattering (SAXS).

Dissolution of calcite by acidic ferric sulfate (pH 2-3) and formation of bicarbonate causes a rapid increase in pH at the beginning of the experiment. As a result, dissolved Fe^{3+} become unstable and precipitates as an orange-colored coating on the calcite surfaces. With the development of the coatings over time, the pH of the system steadily decreases. SAXS and powder XRD analysis showed that the coating is poorly crystalline schwertmannite, a nanosized (1-2 nm) ferric iron-oxyhydroxysulfate commonly formed in AMD systems at pH <4.5. ICP-OES showed changes in dissolved Ca, Fe and sulfate concentrations that were consistent with coating development. This approach can be used to systematically test how different solution chemistries or substrates (e.g., limestone, dolomite, etc.) affect coating development. The results will benefit future development of passive AMD treatment systems.

APPLYING GARNET-MONAZITE THERMOMETRY TO SCANDIAN THRUST SHEETS IN NORTHWEST SCOTLAND

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Northwest Scotland features a series of east dipping ductile thrust faults cutting the metasedimentary Moine Supergroup. From the structurally lowest Moine thrust in the foreland to the most hinterland-positioned Naver thrust, there is a continuous increase in metamorphic grade from greenschist facies to sillimanite-bearing amphibolite facies. To further understand the tectonic history of this area, it is essential to establish temperature-time constraints for individual thrust sheets. Electron microprobe and laser ablation ICP-MS are used to analyze trace elements and U-Pb isotopes in samples throughout the study area. Some of our samples show clear REE zoning in garnet and monazite. In two samples from the leading edge of Naver thrust sheet, monazite crystals typically have low Y domains, which are likely to be in equilibrium with garnet crystals that display relatively flat REE zoning. Temperatures based on the garnet-monazite thermometer of Pyle et al. (2001), are estimated at 540-560 °C, in good agreement with other petrological constraints. Concordia ages of low Y monazite from these two samples are 426±2 and 425±4 Ma. Another sample from the leading edge of the Naver thrust sheet contains two distinct groups of garnet, each with distinct textures and REE zoning patterns. Which is challenging to interpret, but the full range of garnet compositions are consistent with temperatures of 620-680 °C, if garnet and monazite are in equilibrium. The concordia age of monazite in this sample is 420±2 Ma. One sample from the underlying Moine thrust sheet has distinct and consistent high Y garnet rims, which we interpret to be in equilibrium with monazite. Garnet-monazite temperature estimates for this sample are 580-590 °C, also consistent with other petrological constraints. The concordia age of monazite in this sample is 416±2 Ma. Importantly, previous geochronology (Goodenough et al., 2001) has suggested that transitional ductile-brittle deformation (300-400 °C) in the structurally underlying Moine thrust zone occurred at *c.* 430 Ma. In contrast, our results imply that the rocks in the ductilely-deformed hanging wall to Moine thrust were buried much deeper than those in the footwall until at least 420-415 Ma. Therefore, final movement on the Moine thrust likely occurred long after 430 Ma and perhaps even later than 415 Ma.

Advisor: M. Caddick

CORRELATION OF INORGANIC AND ORGANIC NITROGEN AND CARBON ISOTOPES AND MERCURY CONTENT IN SEDIMENTARY BASINS

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By studying the geological record of past climate proxies, we are able to understand modern environments by studying ancient environmental chemistry that was critical to the buildup of the Cambrian Explosion. The objective of this research is to understand the redox conditions in an Ediacaran sedimentary basin, specifically the Doushantuo Formation located in Hubei Province, China by using geochemical data measured from the region's black shales. To generate the geochemical data, powdered and decarbonated black shale samples will be analyzed by a mass spectrometer and Teledyne Leeman Labs Hydra II analyzer, which will help determine mercury concentrations and organic carbon/nitrogen isotope compositions. Through studying these isotopes and concentrations, we can enhance our understanding of changes in ancient environmental chemistry to inform the current understanding of modern environmental chemistry changes.

Generally, the inorganic and organic carbon isotopes in chemostratigraphic profiles has coupling trends that are negative values. The Doushantuo Formation was chosen for this study because of its unique decoupling trend between inorganic and organic carbon, which suggests unknown abnormalities in this chemical environment. Organic carbon isotopes in the rock record generally has negative fractionation (isotope of interest compared to common isotope). In the Doushantuo Formation, organic carbon isotopes have relatively large negative fractionation values, while its inorganic counterpart nears low negative values to zero fractionation. When negative fractionation occurs in inorganic carbon isotopes, it is usually for a short period. The highly negative fractionation of the inorganic carbon isotope in the Doushantuo Formation is unusual because it lasts for a long time and strays from the parallel inorganic and organic carbon isotope trends (decoupling). This fractionation is influenced by ancient bacteria and microbial life, which can give us a glimpse at the chemical environment of the Doushantuo Formation during the Ediacaran.

STAUROLITE-GARNET RELATIONSHIPS IN THE NELSON AUREOLE METAPELITES (BRITISH COLUMBIA)

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Garnet and staurolite are two phases that are common in pelitic metamorphic rocks. They are often texturally related to each other. In this study, we use samples from the Nelson Aureole, British Columbia to characterize the textural relationships between both phases. The Nelson aureole metapelites present chemical and textural features that do not match with the thermodynamic models. Particularly, the garnet formation is delayed and the garnet and staurolite porphyroblasts are relatively unreactive. This may reflect the effect of other factors that are not taken into account currently. As described in Foster (1986), the spatial distribution of the reacting phases may play an important role in the development of the mineral textures and compositions. While garnet and staurolite are commonly textural related in metamorphic rocks, the reasons for this relationship have not been studied in detail. This study focuses in the spatial distribution of garnet and staurolite porphyroblasts and the textural, crystallographical and chemical relationships between both phases. We carried out a petrographic analysis of three selected thin sections from the staurolite-andalusite zone of the Nelson Aureole (CW-93-10a, CW-93-10b and CW-93-9). We identified three textural relationships between garnet and staurolite: a) Inclusion: garnet porphyroblasts in staurolite, b) Boundary: garnet porphyroblasts in contact with staurolite, c) No contact: garnet-free staurolite/garnet porphyroblasts in matrix. Type C is significantly the most common in these rocks, while type A is mainly restricted to CW-93-9. Type B and C occur surrounded by a chlorite halo that formed during retrograde metamorphism. The garnet porphyroblasts are subidiomorphic and present fractures and inclusions, whereas the type A garnets are smaller, clean and idiomorphic. Further TEM analysis could help to investigate the mass transfer processes acting at the boundary between staurolite and garnet to discern their relationship on the nanoscale.

Advisor: Dr. M. J. Caddick

ANALYSIS OF GPS MONUMENTATION FOR THE EAST AFRICAN RIFT SYSTEM

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Poor GPS monumentation can result in non-tectonic signals being observed at the station. In this work, we aim to analyze the monumentation of GPS instruments in East Africa to potentially isolate data that has been affected by sources other than tectonic displacement. The types of monumentation can be organized into 4 main groups: (1) instruments positioned in bedrock, (2) instruments placed on concrete slabs and pillars of varying depth, (3) instruments deployed on building rooftops of varying foundation quality, and (4) instruments that are braced in sediments at varying depths. These instruments are either setup as stations that are left in the field to continuously measure positions (continuous sites), or as campaign sites where you have to periodically return to the site to collect data. The region of study spans longitudes 22° to 56° and latitudes -52° to 20°. For the stations analyzed at this stage in the project, we have found that there are 7 continuous sites braced in sediments. Continuous GPS stations set on bedrock are largely clustered in the northern areas of the study area, whereas stations on buildings and rooftops are clustered more centrally. Continuous GPS stations positioned in concrete are more evenly dispersed. In the next steps of this research, we will visualize the vectors collected from the instruments for each group of monumentation style in order to determine if there are statistical differences among the datasets, or obvious outliers due to errors in data collection due to station monumentation.

Advisor: Dr. S. Stamps

SYNTHESIS AND CHARACTERIZATION OF MIXED IRON AND ALUMINUM NANOMINERAL COATINGS ON CALCITE

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Exposure of mine tailings containing pyrite (FeS_2) and other metal sulfide minerals to water and oxygen initiates a series of acid-producing chemical reactions. The resulting low-pH (<4) waters, known as acid mine drainage (AMD) often contain high concentrations of iron, aluminum, and sulfur, as well as various environmental contaminants. Passive remediation systems consisting of drainage ditches lined with crushed carbonate minerals (e.g., limestone) are commonly used to neutralize AMD due to relative low cost and ease of construction. Unfortunately, the efficiency of these systems decreases with time due to mineral coatings that develop on the limestone surface and slow carbonate dissolution. This research aims to understand how the initial solution chemistry, mainly Fe:Al ratio and concentration, impacts the growth and physical and chemical characteristics of the coatings.

The experiments used a 3D-printed mixed flow reactor (MFR) to mix a simulated AMD feed solution with crushed calcite (0.8-1.0 mm). The feed solution was a 1:1 mixture of ferric sulfate and aluminum sulfate (5 mM) with pH 2.91. The solution was fed through the MFR continuously via peristaltic pump (1 mL/min) to allow the AMD mixture to react with the calcite surface. The pH of the effluent solution was monitored and recorded continuously using a custom 3D-printed in-line flow cell. The effluent was collected in 9-minute intervals for subsequent chemical analysis via inductively coupled plasma optical emission spectroscopy (ICP-OES). The calcite coatings were removed and characterized by powder x-ray diffraction (pXRD) and small-angle x-ray scattering (SAXS).

We observe a rapid spike in the pH of the effluent solution during the first minute of the experiment, which we attribute to the dissolution of highly reactive surface sites on calcite. This is followed by a period of slow and sustained pH decrease over time that is coincident with the formation of fluffy orange-colored coatings on the calcite surfaces. Powder XRD shows that the precipitates consist of schwertmannite-like material having particle sizes of ~1 nm based on SAXS analysis. Chemical analysis by ICP-OES shows that the solids contain some aluminum, although the Al:Fe ratio is <<1 suggesting that most Al remained in solution at these pH conditions. Future experiments will assess the effect of initial pH on the composition and mineralogy of the coatings. The results will help to inform the design of future passive treatment systems in AMD systems that are enriched in both Fe and Al.

INFLUENCE OF TECTONIC DEFORMATION ON ACTIVE VOLCANISM AND SEISMIC ACTIVITY IN CENTRAL AMERICA

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This study involves testing the influence of tectonic deformation on active volcanism and seismic activity in Central America with a particular focus on the Middle America Trench and the Pacaya volcano in Guatemala. The approach is to calculate the seismic potential in areas with active volcanoes using the Seismic Hazards Inferred from Tectonics (SHIFT) hypothesis and the Global Strain Rate Model (GSRM). We can then compare the seismic potential calculated before, during, and after periods of volcanic activity to predict possible patterns for future volcanic activity. To study the influence of tectonic deformation on seismic activity in Central America, we study different ranges of magnitudes of historic shallow earthquakes. We then compare this data with the calculated seismic potential to determine how the earthquakes may be affected.

EVALUATING REACTION AND COMPOSITIONAL HISTORY OF THE ALLALIN GABBRO: AN INVESTIGATION ON ELEMENT MOBILITY DURING SUBDUCTION

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Subduction zone metamorphism fundamentally controls tectonic processes such as arc magmatism, seismicity, and global geochemical cycling, and provides the “slab pull” driving force for subduction. However, recent research suggests that at least portions of subducting slabs may remain dry and metastable without the presence of fluids necessary to catalyze the metamorphic reactions that transform ocean crust into denser blueschist and eclogite. The consequences of a dry, metastable slab on subduction zone processes are not well understood and little is known about the length scales at which elements mobilize during hydration reactions that occur far from equilibrium. Here, we use a combination of petrographic and electron beam methods to determine the sequence and progress of metamorphic reactions and the mobility of elements during hydration of the Allalin Gabbro. The Allalin gabbro is a slice of oceanic crust that was subducted to eclogite facies *P-T* conditions (~80 km in depth) during Eocene age Alpine subduction. Despite being subducted to great depth, the Allalin gabbro is interpreted to have persisted as metastable gabbro (olivine + plagioclase + pyroxene) until the addition of fluids near peak depth.

Petrographic analysis reveals that the Allalin gabbro does not display the characteristic mineral assemblage and textures of “normal” eclogite, which we interpret to be due to rapid fluid-induced metamorphism far from equilibrium. Microdomainal textures such as garnet coronae and pseudomorphs of former igneous plagioclase and olivine suggest limited element mobility, which are likely controlled by diffusion. Ongoing work includes SEM-EDS semi-quantitative analysis and element mapping of microdomains to describe mineral compositions and elemental distributions, which will be paired with petrographic observations to determine the redistribution of elements between phases during metamorphism. Preliminary results suggest that the Allalin gabbro underwent at least three different stages of hydration and dehydration during subduction, as evident by the presence of mineral replacement textures and pseudomorphism. Future work will focus on determining the length-scales of element mobility during these hydration and dehydration stages, and the consequences for element cycling on the entire subduction zone spatial scale.

MONITORING TZVOLCANO GNSS DATA WITH GRAFANA DASHBOARDS AND KAPACITOR VIA THE EARTHCUBE CYBERINFRASTRUCTURE CHORDS

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Visualizing societally relevant data in easy to comprehend formats is necessary for making informed decisions by non-scientist stakeholders. Despite scientists' efforts to inform the public, there continues to be a disconnect in information between stakeholders and scientists. Closing the gap in knowledge requires increased communication between the two groups facilitated by models and data visualizations. In this work we use real-time streaming data from TZVOLCANO, a network of GNSS/GPS sensors that monitor the active volcano Ol Doinyo Lengai in Tanzania, as a test-case for visualizing societally relevant data. Real-time data from TZVOLCANO is streamed into the US NSF Geodesy Facility UNAVCO archive (www.unavco.org) from which data are made available through the EarthCube cyberinfrastructure CHORDS (Cloud-Hosted Real-Time Data Services for the Geosciences). CHORDS uses InfluxDB to make streaming data accessible in Grafana, an open source software that specializes in the display of time-series analysis. Creating user-friendly visualizations ("dashboards") for the TZVOLCANO GNSS/GPS data in Tanzania can help scientists and stakeholders communicate effectively so informed decisions can be made about volcanic hazards during a time-sensitive crisis. To extend capabilities of data analysis, this work explores the use of the Kapacitor software to apply threshold-defined email alerts for stakeholders. Our use of the open-source software for our specific case-study provides an example for other geoscientists to develop analogous visualizations with the objectives of increasing the knowledge for the general public and facilitating a more informed decision-making process.

INVESTIGATING THE DEVELOPMENT OF ANOXIA WITHIN THE EUROPEAN EPICONTINENTAL SEAWAY DURING THE TOARCIAN OCEANIC ANOXIC EVENT (T-OAE)

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The loss of oxygen from portions of the oceans today due to climatic warming is a growing environmental concern. We can look to the geologic record for past episodes with similar environmental changes to better understand the present and future impact of decline in marine oxygen levels. One such time was a portion of the Early Jurassic Period (a time known as the Toarcian Oceanic Anoxic Event or T-OAE: ~183 million years ago). The sedimentary record shows that there was a large influx of carbon dioxide from volcanic activity that had cascading effects on the environment including a warmer and wetter climate, mass extinctions, and potentially large-scale oxygen loss from the oceans resulting in portions of the oceans becoming anoxic and euxinic (anoxic water columns with free hydrogen sulfide). However, the geographic and temporal extent of deoxygenation during the T-OAE is still not well defined.

In order to better understand the history of deoxygenation during the T-OAE, we investigated the record of local redox conditions across this event as recorded within three basins of the European epicontinental seaway: the Cleveland Basin (United Kingdom), the Paris Basin (Luxembourg), and the Southern German Basin (Germany and Switzerland). Specifically, we utilized the iron speciation proxy and sulfur isotope composition of sedimentary pyrite to reconstruct the water column redox conditions at each site. These data show that the first intervals of local anoxia occurred in the late Pliensbachian and near the Pliensbachian-Toarcian boundary in the Southern German and Cleveland Basin, respectively. Both anoxic and euxinic conditions are more persistent and most common in the interval attributed to T-OAE, but in all three basins evidence for anoxia persists well after this interval. This importantly demonstrates a greater temporal extent of anoxic conditions and suggests a greater sensitivity of marine oxygen levels to climatic change than previously considered for this event. More broadly, these records provide a timeline of marine deoxygenation in response to an episode of rapid climatic warming in Earth's history.

CHARACTERIZING NANOSCALE SURFACE PROPERTIES OF NATURAL IRIDESCENT MINERALS

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A variety of natural and synthetic materials exhibit beautiful and intense coloration known as iridescence. In contrast to color from pigmentation, iridescence involves the interference of visible light from diffraction by multi-layer thin films or modulated microstructures. The latter type, which has been studied intensely for biological materials such as insect exoskeletons and bird feathers, is known as structural coloration. A unique characteristic of structural coloration is that it is largely angle-independent (i.e., color does not change with viewing angle). This has made the mechanisms of structural color of interest for developing new photonic materials for applications such as optical filters and colorimetric sensors. We are studying natural ferric oxide/hydroxide minerals that exhibit vibrant, rainbow-like bands of color that change reversibly when exposed to warm, moist air.

Iridescent samples of botryoidal goethite/hematite (a.k.a., turgite) from Graves Mountain, Georgia were obtained and characterized by high-resolution digital microscopic imaging and scanning electron microscopy (SEM) methods. Digital imaging shows colors ranging from vibrant red and deep violet. ImageJ software was used to quantify the contributions of red, green and blue to regions of the sample at room temperature and with high relative humidity. Botryoidal surface features are evident from the millimeter to the sub-micrometer scale. High-resolution SEM imaging showed that the surfaces are covered by amorphous arrays of pseudo-spherical particles around 50 nm in diameter.

Previous research reported that iridescence in hematite samples from Brazil is caused by diffraction from periodic arrays of 200-300 nm nanorods. However, our samples of iridescent hematite from Graves Mountain, Georgia were absent of these nanorods and still possessed bright, iridescent surfaces. We propose that the nanoscale botryoidal surface features of our samples are responsible for their iridescent behavior, an idea that has not been presented previously for minerals. We are also interested in understanding the unique behavior of our samples when exposed to heat and high relative humidity, which causes a dramatic and reversible color change. The exact mechanism of this behavior also remains unknown. We are hypothesizing it is caused by rapid condensation of a thin film of water on the surface that results in a temporary phase shift. The ultimate goal of this research is to develop a model to explain the property-behavior relationships of these exceptional iridescent minerals.

CHANGES IN METAL CONCENTRATIONS IN A LOCAL DRINKING WATER RESERVOIR DUE TO OXYGENATION

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The presence of soluble iron (Fe) and manganese (Mn) in water bodies is important to monitor, as these metals cause aesthetic problems (i.e., color and taste) and Mn, in particular, can cause detrimental health issues when consumed. Under oxic (dissolved oxygen (DO) > 2 mg/L) conditions, Fe and Mn naturally occur in sediments in their oxidized, insoluble form. However, when DO is depleted, bacteria can reduce Fe and Mn to their soluble forms, which are then released into the water column. Many drinking water reservoirs, including Falling Creek Reservoir (FCR), in Vinton VA, have installed oxygenation systems to provide in situ treatment of metals.

The purpose of this project was to record the changes in concentrations of Fe and Mn due to changes of water column DO resulting from the oxygenation system in FCR. In 2017, the system was run continuously, while in 2018 the system ran from May – July but shut off from August – October. Total and soluble (filtered, 0.45 micron) samples for Fe and Mn were collected weekly from FCR during the summers of 2017 and 2018. Concentrations of metals and DO from FCR in oxygenated and non-oxygenated conditions were compared using heat maps (displaying variables such as depth, concentration, and time) created using RStudio. In 2017, when the reservoir was continuously oxygenated, the average total Fe concentration was 0.673 mg/L. While in 2018, when FCR was only oxygenated for part of the summer, average total Fe concentration was 3.88 mg/L. Similar patterns were observed with total Mn concentrations. When the oxygenation system shut off in August of 2018, there was a significant increase in soluble Fe and Mn. In 2017, the average concentrations of soluble Fe and Mn were 0.085 mg/L and 0.297 mg/L, respectively, while in 2018, the average concentrations of soluble Fe and Mn increased to 0.602 mg/L and 2.864 mg/L, respectively.

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