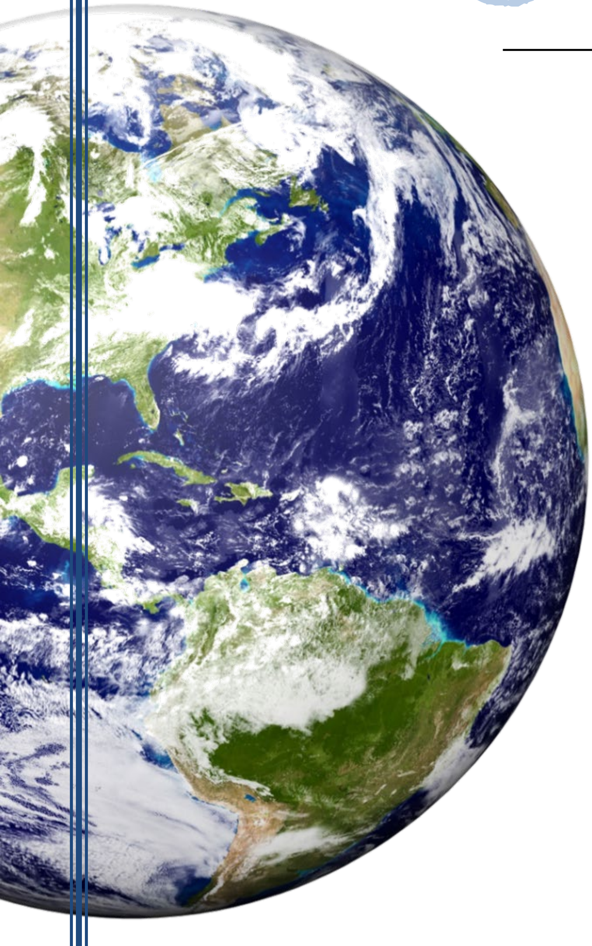
EARTH & PLANETARY SCIENCES

AT HARVARD UNIVERSITY



2021 Senior Thesis Presentations

Madison Goldberg

Elida Kocharian

Ethan Manninen

Friday, April 30th, 2021, 12:00-1:00 pm ET

https://harvard.zoom.us/j/99500771109?pwd=djBseVM5dkRTTUg5YlVyUWkxRVNSQT09

Please join us for a virtual reception following the thesis presentations.
Details and a link will be provided.

WELCOME

Message from the co-Head Tutors and Preceptors:

Thank you for joining us as we celebrate the accomplishments of our senior thesis writers who spent much of their senior year tackling an exciting range of scientific problems. The senior thesis provides an opportunity for students to gain firsthand experience in the full scope of research, from in-depth background study, to identification of core questions, design of a research plan, collection and analysis of data, and formation of rigorous conclusions. Due to the COVID-19 global pandemic, this year's students faced unprecedented challenges as they left campus during their Junior year, unsure of when they would return, just as they were preparing to begin their thesis research. They adapted their academic and social lives to the realities of remote learning and exhibited incredible flexibility and perseverance as they navigated strict requirements to be on campus, limited hours to complete their research in laboratories, and wrote their theses without the traditional in-person support network. These theses and today's presentations reflect the academic excellence and dedication of these students.

Their efforts would not be possible without the support of faculty advisors, graduate students, post docs, fellow undergraduate students, and family. We thank these mentors and friends and congratulate our seniors on their achievement.

Roger Fu and Zhiming Kuang
Co-Head Tutors

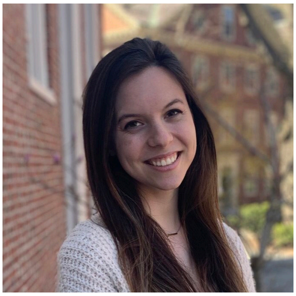
Esther James and Annika Quick
EPS Preceptors

Roger Fu, Stein Jacobsen, Zhiming Kuang, Marianna Linz
Undergraduate Curriculum Committee

Campbell Halligan
Academic Program Manager

Madison Goldberg

Concentration: Earth and Planetary Sciences



Pyrite Oxidation in Acid Mine Drainage Systems: Oxygen Isotope Systematics of Intermediate Sulfoxyanions in Sociopolitical Context

Advisors: **Dave Johnston**, Professor of Earth and Planetary Sciences, Harvard University
Andy Knoll, Fisher Professor of Natural History and Professor of Earth and Planetary Sciences, Harvard University
Jordon Hemingway, Postdoctoral Fellow, Earth and Planetary Sciences, Harvard University

Acid mine drainage (AMD) is a widespread and persistent environmental threat in the United States, affecting ecosystems at all trophic levels and endangering human health. Produced by the oxidation of sulfide minerals exposed to the atmosphere during mining and construction projects, AMD is characterized by acidic runoff containing high concentrations of dissolved sulfate and heavy metals. Although AMD impacts watersheds from coast to coast, its effects are not evenly distributed and tend to mirror socioeconomic and racial inequities.

This thesis attempts to investigate both the sociopolitical and scientific dimensions of this issue. The preface considers the ways in which AMD affects Indigenous communities, focusing specifically on the Navajo Nation; primary- and secondary-source research, as well as interviews with stakeholders, indicate that the prevalence of AMD in these communities reflects a long history of structural inequities faced by Indigenous peoples in the U.S. Against that backdrop, the majority of the thesis investigates an unresolved dimension of the mechanism by which pyrite – the most abundant metal sulfide in the Earth's crust and the primary contributor to AMD – oxidizes. Specifically, the precise roles of the aqueous intermediate sulfoxyanions sulfite (SO_3^{2-}) and thiosulfate ($S_2O_3^{2-}$) remain a subject of debate. This work aims to constrain the prevalence and isotope systematics of these species and apply those results to a mining-influenced environment.

It is found that sulfite and thiosulfate make up a notable proportion of the aqueous sulfoxyanion pool at circumneutral or high pH, particularly under oxic conditions. The equilibrium oxygen isotope fractionation factor $^{18}\varepsilon_{\mathrm{SO3\text{-}H2O}}$ of the sulfite-water system at 22°C is determined to range from 9.76‰ at pH 2 to 7.64‰ at pH 10, with a clear dependence on speciation within the sulfite system. The equilibrium oxygen isotope fractionation factor $^{18}\varepsilon_{\mathrm{S2O3\text{-}H2O}}$ for the thiosulfate-water system is also reported at 22°C (ranging from 22.11‰ at pH 2 to 14.67‰ at pH 10), as well as at 4°C (23.93‰ at pH 2 to 14.74‰ at pH 10) and at 93°C (13.02‰ at pH 7 and 14.25‰ at pH 10; thiosulfate appeared to have decomposed at 93°C and pH 2). Measured $^{18}\varepsilon_{\mathrm{S2O3\text{-}H2O}}$ at pH 2 (22°C and 4°C) was in good agreement with theoretical predictions presented by

Hemingway et al. (in preparation). Based on those predictions, the thiosulfate-water system appeared not to have reached oxygen isotopic equilibrium at higher pH values, suggesting that the rate of oxygen isotope exchange between these two species is pH-dependent. Given that interpretation, the reliability of the $^{18}\varepsilon_{S2O3\text{-}H2O}$ values calculated for pH 7 and 10 at all temperatures is considered to be limited.

The isotope systematics constrained by these experiments are ultimately applied to samples from a natural environment affected by a former gold mine, in order to constrain the specific pathways by which sulfate has formed via pyrite oxidation. The oxygen isotopic composition of these environmental samples ranges widely, and comparison with the isotopic equilibrium data suggests that multiple pathways involving both H_2O and O_2 as donors of a fourth oxygen atom are involved in the production of sulfate at these sites. The combined results of this work, therefore, suggest that AMD prevention strategies should target multiple sulfate formation pathways if they are to be effective.

Elida Kocharian

Concentrations: Earth and Planetary Sciences and Environmental Science and Engineering

Amine-mediated CO_2 hydration as a potential carbonic anhydrase alternative in marine Thaumarchaeota

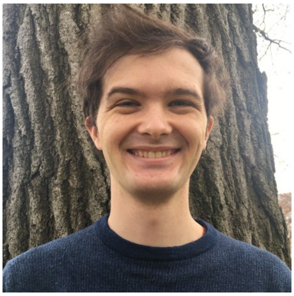
Advisor: **Ann Pearson**, Murray and Martha Ross Professor of Environmental Sciences, Harvard College Professor, and Department Chair, Earth and Planetary Sciences, Harvard University

Marine Thaumarchaeota are ammonia-oxidizing archaea that make up the predominant group of nitrifiers in the global N cycle and fix bicarbonate (HCO_3^-) autotrophically via the highly efficient 3-HP/4-HB pathway. Most autotrophs produce intracellular bicarbonate via the ubiquitous enzyme carbonic anhydrase (CA), which catalyzes CO_2 hydration. However, the common Thaumarchaeota species *Nitrosopumilus maritimus* lacks CA, and it is unknown how this organism produces sufficient intracellular bicarbonate to satisfy its anabolic requirement without this enzyme. One hypothesis is the autocatalytic addition of water to CO_2 mediated by free intracellular amines, in the form of protein N-termini, via a carbamate intermediate at physiological pH. In order to determine the viability of this bicarbonate pathway as a potential CA alternative in *N. maritimus*, the reaction kinetics of 12 aqueous primary and secondary amine solutions buffered to pH 7.2 were measured via ^{13}C NMR spectroscopy and compared to a novel chemical kinetic model of intracellular carbon dynamics in *N. maritimus*. The experimental observations showed that amine reactivity generally increases with increasing pKa of the amine group, but is heavily influenced by the amine structure; primary and secondary amines form carbamate and bicarbonate through a two-step mechanism involving formation and decarboxylation of a carbamate zwitterion, while sterically hindered and tertiary amines form bicarbonate via a base-catalysis mechanism in which the nitrogen abstracts a proton from water to drive CO_2 hydroxylation. The measured 1st-order reaction rate constants of carbamate formation and dissociation are 1.1×10^{-2} s^{-1} and 4.88×10^{-3} s^{-1} respectively, yielding intracellular fluxes of carbamate and bicarbonate of 4.4×10^{-4} mM s^{-1} and 1.46×10^{-4} to 1.46×10^{-2} mM s^{-1}, respectively. The bicarbonate-fixing enzyme of the 3-HP/4-HB pathway, acetyl-CoA/propionyl-CoA carboxylase, has a turnover rate of 2.168×10^{-1} mM s^{-1}, and the modeled fluxes required to sustain this rate are 5.067×10^{-1} mM s^{-1} for carbamate formation and 2.153×10^{-1} mM s^{-1} for carbamate dissociation/bicarbonate formation. Thus, the flux of bicarbonate supplied by amine-mediated CO_2 hydration is insufficient to drive autotrophy in *N. maritimus*. Future work to determine the reaction kinetics of tertiary amines could shed light on the potential activity of the base-catalysis pathway of amine-mediated CO_2 hydration; however, it is suggested that the true hydration mechanism may be driven by the generation of hydroxide ions *in situ* coupled to redox potentials present in copper-containing oxidoreductase enzymes responsible for electron transfer at the cell membrane that could double as CA alternatives or antecedents.

Ethan Manninen

Concentration: Earth and Planetary Sciences

Cluster Analysis of N_2O Enhancements Observed by ATom



Advisor: **Steve Wofsy**, Abbott Lawrence Rotch Professor of Atmospheric and Environmental Science, Department of Earth and Planetary Sciences, Harvard University

In this work, we address the following questions: 1) What is the balance between global transport and regional emissions in the vertical structure of N_2O mixing ratios in the African outflow? 2) Is it possible to distinguish different combustion sources of N_2O in Africa? 3) Can we confirm or deny the possibility of a heterogeneous chemical N_2O source in air heavily polluted by urban-industrial emissions? 4) How do N2O enhancements modeled from ATom observations compare to current understanding of N_2O budgets in the region? 5) What is the total amount of N_2O flowing through the African outflow? N_2O is the third most important greenhouse gas and the most important ozone depleting gas; understanding these contributions to its African regional budget is an important piece of the climate puzzle. We analyze trace gas data gathered by the Atmospheric Tomography Mission, with a focus on N_2O in the Atlantic basin. We use a clustering technique built around the DBSCAN and t-SNE algorithms to improve understanding of different N_2O sources. Some Atlantic ATom clusters are broadly characterizable as part of the African outflow. N_2O enhancements in the ATom 2 African outflow are associated with combustion emissions. Within these emissions, we find an enhancement from anthropogenic biomass burning, a possible enhancement from heterogeneous chemistry, and an important transport contribution from Europe. The urban biomass burning source we identified is associated with discrepancies between ATom N_2O modeled enhancements and a recent landmark N_2O budget. We evaluate N_2O enhancements outside of the African outflow and find that aged pollution is an important driver of N_2O. We also develop a technique to estimate the atmospheric N_2O background using atmospheric transport models and global ATom N_2O data. This method also shows that advection is a crucial process in the arrangement of N_2O in the African outflow. We use this more region specific model of N_2O enhancements to find 0.9-1.1 Tg N yr^{-1} of N_2O flowing through the African outflow. We also use a more global N_2O background to find 1.9-2.1 Tg N yr^{-1} of N_2O flowing through the African outflow. Emissions from burning wood and urban-industrial emissions with high sulfur content, along with transport processes, are the key to our understanding of N_2O in the African outflow.