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Project Title: New Approaches to Reconstructing the Timing of Diagenesis and Porosity Evolution in Sedimentary Carbonate Strata using Coupled X-Ray Spectromicroscopy and Secondary Ion Mass Spectrometry (SIMS)

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The precipitation of carbonate cements during early and late diagenesis is a critical control on the evolution of porosity and permeability in sedimentary strata. This work seeks to develop a system to characterize the micron-scale chemical environments in which both early (e.g., zone of sulfate reduction vs. methanogenesis) and late diagenetic (meteoric fluids; basinal brines) cements formed in order to better understand and predict porosity evolution in sedimentary strata. We are specifically focused on using micron-scale observations of the sulfur constituents in carbonate strata to answer these questions.

In YR 1, we have focused particularly on the abundance and chemical speciation of S phases within a suite of Paleozoic carbonate strata from a range of different lithofacies and depositional environments. The rationale behind this focus lies in the fact that within sediments, microbial sulfate reduction draws down concentrations of ambient sulfate (at the same time increasing its $\delta^{34}\text{S}$ isotopic compositions). This results in a progressive decrease in the abundance of sulfate found within carbonates as CAS (carbonate-associated sulfate) going from the water column to shallow marine sediments and into deeper sediments. Here, we seek to demonstrate the potential of 2D micron-scale mapping of the abundance of sulfate to provide geochemical insights into conditions during deposition and the timing, nature, and extent of subsequent diagenetic alteration. CAS incorporation reflects the pool of aqueous sulfate from which the carbonate precipitated. As such, sulfate abundance can be used to distinguish marine, meteoric, and basinal brine fluids. Further, early diagenetic microbial processes, particularly sulfate reduction and sulfide oxidation, have diagnostic impacts on pore-water sulfate within sediments. High-resolution (micron-scale) maps of CAS abundance and isotopic composition, obtained from thin sections within a known petrographic context, have enabled new insights into the formation of diagenetic carbonate cements, particularly as it relates to the modification and occlusion of sedimentary porosity and permeability with implications for both reservoir formation and hydrocarbon migration. As part of this work, we analyzed a suite of carbonate samples at the synchrotron facilities at Argonne National Laboratory (GSE-CARS, beamline 13-ID-E) and Stanford Synchrotron Radiation Lightsource (SSRL, beamline 14-3) to identify and distinguish between the various sulfur-bearing components of carbonates (e.g., Figure 1). Focusing on the sulfate component, we can map and quantify the variations in sulfate content across a range of carbonate constituents (fossils, abiotic grains, micrite, and various stages of cements). Combining the results with petrographic observations (e.g., drusy vs equant vs late-stage spar cements) allows us to uniquely reconstruct the environment of cementation and improve our understanding of the evolution of these samples following deposition. This allows us to generate a paragenetic sequence of the evolution of our samples based on their sulfur characteristics.

Graduate student Jocelyn Richardson has spearheaded this work, which has become the main thrust of her PhD. During YR 1, she has presented this work at a range of international meetings (e.g., 2018 Geobiology Gordon Research Conference (Galveston, TX) and the 2018 Carbonate Sediments as Archives of Earth Evolution Meeting (Tallinn, Estonia) as well as at the

2018 Midwest Geobiology Symposium (Northwestern University) and during presentations to the Department of Earth & Planetary Sciences at Washington University. This has work has resulted in two publications that currently are under review in *Geology* (Rose et al., 2018) and *Geochimica et Cosmochimica Acta* (Richardson et al., 2018) – and in the process provided Jocelyn with invaluable training opportunities as she begins to consider her career after graduate school.

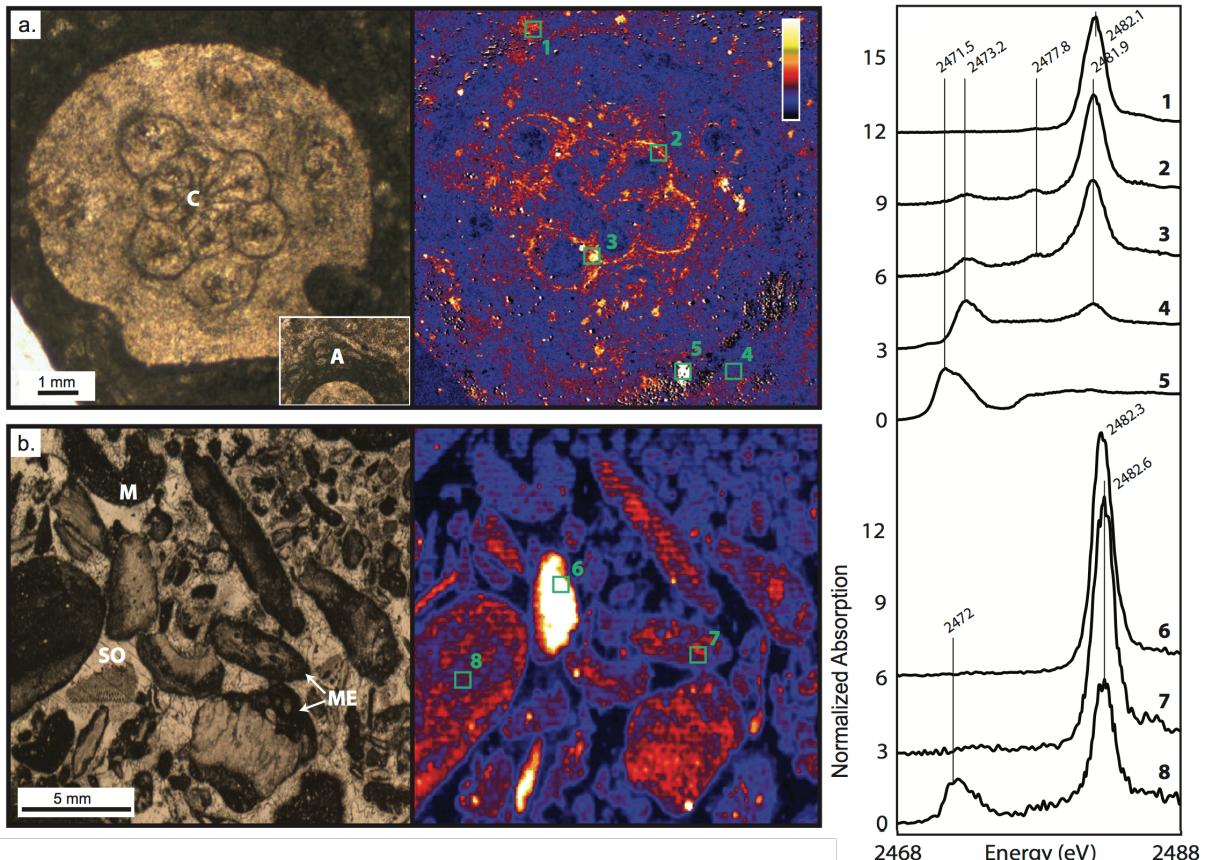


Fig. 1 – Petrographic thin section images showing a variety of fossils, fossil fragments and grains with corresponding sulfate energy map on the right. A = *Allonema*, C = *Coenites* sp., M = micrite infilling, ME = micrite envelope, SO = syntaxial overgrowth. Map colors correspond to abundance where black is minimum and white is maximum abundance (applies to all maps a.) *Coenites* sp., with *Allonema* (inset) from a coral grainstone from the Upper Visby Formation, Gotland b.) Fossiliferous grainstone from an oncolite platform, Lousy Cove Member, Anticosti Island. At the right, XANES of locations numbered in a-b with important peak energies annotated, highlighting sulfate (~2428.3 eV), pyrite (~2471.5 eV), and intermediate valence organic S components (2473.2 eV and 2477.8 eV).

References

- Fike, D.A., Bradley, A.S., Rose, C.V., 2015. Rethinking the Ancient Sulfur Cycle. *Annual Review of Earth & Planetary Sciences*, 43: 20.1 - 20.30.
- Richardson, J.A., Newville, M., Lanzilliotti, A., Webb, S.M., Rose, C.V., Catalano, J.G., Fike, D.A., 2018. Depositional and Diagenetic Constraints on the Abundance and Spatial Variability of Carbonate-Associated Sulfate. *Geochimica et Cosmochimica Acta*, in review.
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