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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)

PI: David A. Fike, Washington University in St. Louis

Narrative Progress Report (2017-2019)

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 research has developed an approach to characterize the micron-scale chemical environments in which both early marine and late diagenetic (meteoric fluids; basinal brines) cements formed so that we can better understand, reconstruct, and predict porosity evolution in sedimentary strata. We have focused specifically on using micron-scale observations, particularly synchrotron-based X-ray analyses of the sulfur constituents in carbonate strata to answer these questions.

Work on this grant focused 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 motivation for this approach is grounded 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. Over the past two years, we have demonstrated the utility 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 (Rose et al., 2019). CAS incorporation reflects the pool of aqueous sulfate from which the carbonate precipitated. As such, sulfate abundance can be used to distinguish between early (e.g., in connection with seawater) and late (chemically evolved porewaters) marine cements (Richardson et al., 2019), as well as between meteoric and basinal brine fluids.

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.

This work has provided invaluable training opportunities for three graduate students. Graduate student Jocelyn Richardson spearheaded this work, which formed the main thrust of her PhD. In addition to 4 papers (2 published, 2 in review) from her thesis, she has presented this work

at a range of international meetings (e.g., 2018 Geobiology Gordon Research Conference (Galeveston, TX) and the 2018 Carbonate Sediments as Archives of Earth Evolution Meeting (Tallinn, Estonia). She is currently a DOE-funded postdoc at SSRL working with a range of users to apply the techniques developed as part of her thesis to a broad range of petroleum-relevant questions. In the final year of the project, two additional graduate students became involved in this research. Seth Wood (2nd year) plans to continue to combine synchrotron and SIMS approaches to understand combined carbonate-sulfate systems and we expect his first paper on the SIMS results to be submitted later this fall. Jake Bernstein (1st year) is focused on the lateral geochemical heterogeneity (along and between facies) that is recorded in these carbonates. We hope to submit his first paper in spring 2020.

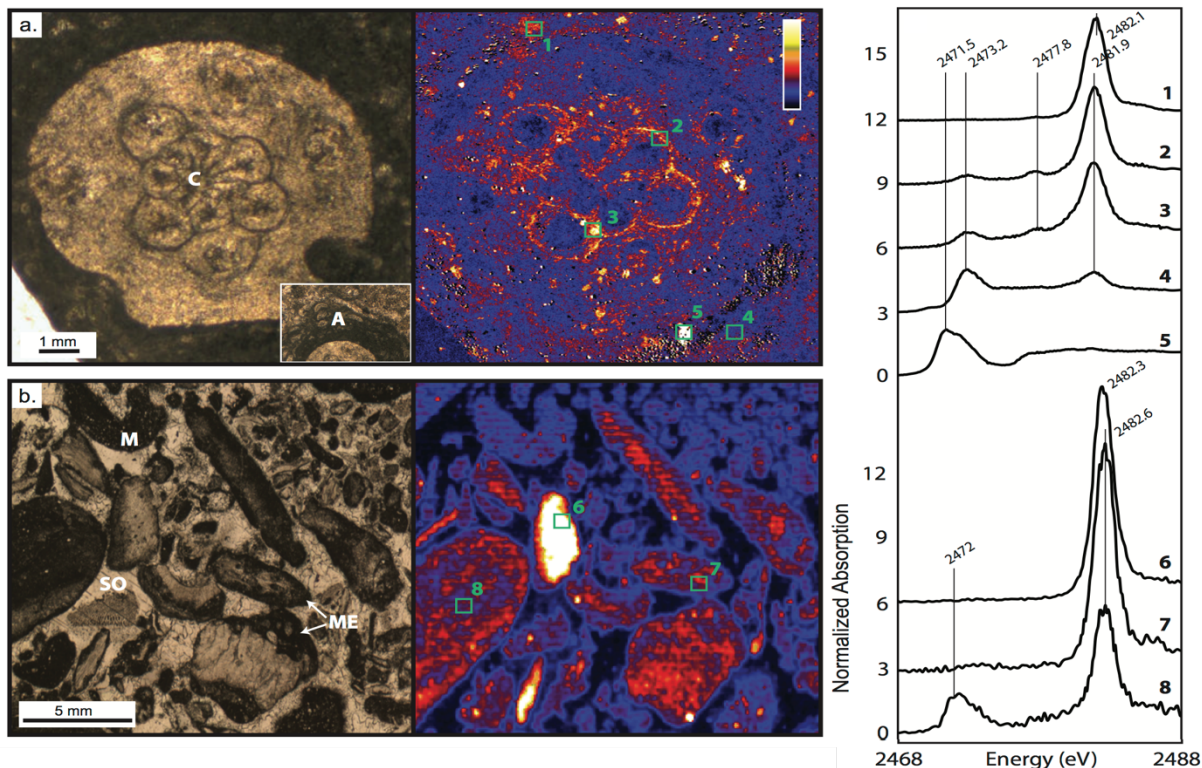


Fig. 1 – Petrographic thin section images showing a variety of fossils, fossil fragments and grains with corresponding sulfate energy map on the right. A = *Allonema*, C = *Coenites sp.*, M = micrite infilling, ME = micrite envelope, SO = syntaxial overgrowth. Map colors correspond to abundance where 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 (~2482.3 eV), pyrite (~2471.5 eV), and intermediate valence organic S components (2473.2 eV, 2477.8 eV). Figure from Richardson et al. 2019.

References

- Richardson, J.A., Newville, M., Lanzirotti, A., Webb, S.M., Rose, C.V., Catalano, J.G., Fike, D.A., 2019. Depositional and Diagenetic Constrains on the Abundance and Spatial Variability of Carbonate-Associated Sulfate. *Chemical Geology*, 523: 59 - 72.
- Rose, C.V., Webb, S.M., Newville, M., Lanzirotti, A., Richardson, J., Tosca, N.J., Catalano, J.G., Bradley, A.S., Fike, D.A., 2019. Insights into past ocean proxies from micron-scale mapping of sulfur species in carbonates. *Geology*, 47(9): 833 - 837.