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The Formation of Salt Dome Cap Rock Calcites and Relationships with Sulfate Reduction
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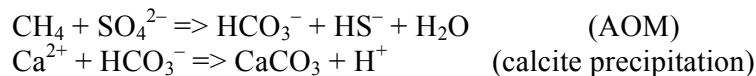
Introduction

Salt domes represent significant liquid petroleum and natural gas traps. Locally trapped hydrocarbons can experience degradation through microbially mediated processes largely supported by reactants sourced from the salt itself. As this hydrocarbon is degraded, authigenic carbonate minerals and elemental sulfur can form, representing a hallmark “geobiologic” system. Supported by PRF, my lab uses geochemical techniques to more specifically identify the microbial processes involved in mineral formation.

Results, Implications and Ongoing Study

It is well established that hydrocarbon degradation occurs in proximity to salt domes in the Gulf Coast. Although speculated in the literature, the specific mechanisms facilitating degradation are poorly understood. Upon degradation, hydrocarbon is oxidized by sulfate to produce dissolved inorganic carbon (DIC) and sulfide species in pore waters near salt domes. DIC reacts with dissolved calcium to produce calcium carbonate minerals and aqueous sulfides are oxidized to form extensive accumulations of elemental sulfur. Geochemical analyses of carbonates, sulfides and elemental sulfur provide insight into 1) the hydrocarbon degradation mechanisms and 2) the nature of the locally trapped hydrocarbon.

In order to address these issues, my lab has been conducting integrated carbon and sulfur geochemical analyses on samples derived from six Gulf Coast salt domes. Carbonate carbon isotope compositions ($\delta^{13}\text{C}_{\text{carb}}$) range from ~ -55 permil (VPDB) to near neutral, with most samples plotting below the liquid hydrocarbon (oil) end member. These $\delta^{13}\text{C}_{\text{carb}}$ values suggest that carbonates received a significant amount of carbon from the degradation of methane. Whereas these data provide insight into carbon sources (addressing #2 above), they do not reveal methane (or hydrocarbon in general) degradation mechanisms. Complimentary sulfur isotope analysis of trace sulfate incorporated into the carbonate lattice (so called carbonate-associated sulfate, CAS) allows the determination of sulfur-related degradation mechanisms and in particular sulfate reduction and/or sulfide oxidation processes. We find CAS sulfur isotope compositions ($\delta^{34}\text{S}_{\text{CAS}}$) that range from $\sim +10$ to $\sim +70$ permil (VCDT). These values exceed the $\delta^{34}\text{S}$ values of local, salt-hosted anhydrite and gypsum that are thought to represent the original source of dissolved sulfate in these systems. Such high $\delta^{34}\text{S}$ values primarily result from closed-system sulfate reduction facilitated by microbes. When considered together, the carbon and sulfur isotope compositions suggest that the anaerobic oxidation of methane (AOM) acts to degrade methane, reduce sulfate and ultimately promote the precipitation of carbonates (and sulfur minerals) through the following reactions:



However, the anaerobic oxidation of methane coupled with sulfate reduction can occur in both biological (microbial) and abiotic settings. Abiotic reactions require relatively high temperatures (>100 degrees Celsius) in order to overcome kinetic barriers (barriers that are overcome at lower temperatures due to biological processes). Therefore it is possible to discern between these two possibilities through temperature determination.

We have now collected clumped isotope compositions (reported as Δ_{47} values) from all six salt domes. Resultant Δ_{47} values indicate carbonate precipitation temperatures ranging from ~15 to ~80 degrees Celsius (Figure 1), consistent with microbial (rather than thermal abiotic) reaction pathways for carbonate formation.

The discovery of AOM in salt dome systems is very intriguing, primarily as it is most widely reported from seafloor sediments associated with methane seeps, far removed from the subsurface depths at which salt domes occur. In addition, salt dome AOM appears to be a microbial process, implying that salt domes host similar communities that live in the so-called “deep-biosphere”.

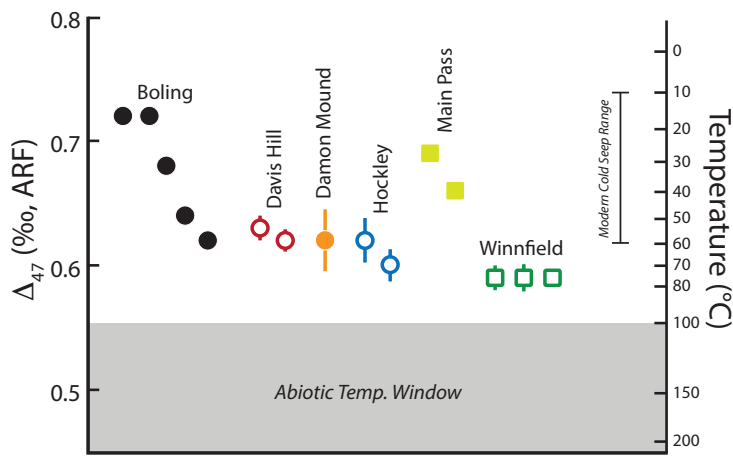


Figure 1: Clumped isotope derived temperatures from salt dome carbonates. Notice that temperatures fall below the abiotic window.

Student Involvement

This research has funded eight undergraduates and two graduate students working toward theses. The undergraduate students include Yasmeen de la Cruz, Andres Bustos, Celeste Flores, Kaelin Andelin, Connor Frederickson, Lucas Lu, Shawn Colby and Bayne Westrick-Snapp and five of these students have completed their undergraduate thesis. Masters student Kylie Caesar has completed her thesis and is first author of a manuscript in revision at Nature Communications. Masters student John Hill is nearly finished with his thesis exploring elemental sulfur formation mechanisms in salt dome cap rocks using multiple sulfur isotope techniques. All students have presented their research at meetings (total of 20 abstracts). Kylie was awarded an oral presentation at the 2016 Southern California Geobiology Symposium at Caltech, a particularly important achievement, as oral presentations are highly competitive at this venue. John Hill was awarded best graduate proposal at the Calstate Fullerton, Geology Research Day Symposium 2017.

Advancement of the PIs Career

This funding has provided an excellent platform onto which I have and will continue to build a promising and exciting research directive. As a young faculty member, I intend to use this directive as a cornerstone to reach tenure. Aside from new discovery and the opportunity to work with students, this research has promoted external collaboration. This work has allowed continued collaboration with long time colleagues (Dr. Tim Lyons, UCR and Aradhna Tripathi, UCLA) and development of new collaborations (Dr. Rick Kyle, UT Austin and Dr. James Farquhar, UMD). I look forward to expanding this research (including beyond the PRF funding window), involving more students and collaborators, and to publishing results for dissemination to the broader scientific community.