Unraveling microbial paleorates and burial history of methane-derived carbonates using novel approaches

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Methane cycling and its role in climatic variation throughout Earth's history have been studied extensively, but a complete understanding of methane's closely coupled relationship to the sulfur cycle is still largely unresolved. Modern and ancient methane seeps are ideal natural labs for studying these coupled cycles and their geochemical fingerprints. This study focuses on ancient methane cycling and its relationship to sulfur metabolic pathways by tracing sulfur, carbon, and oxygen isotopes in a Cretaceous seep system. This system is marked by a complex fabric paragenesis as captured by petrographic relationships of the carbonate phases. Carbon and oxygen isotopic variation and trace metal abundance measured in these complex phases aid in unraveling the complex diagenetic processes and burial history. Sulfur isotopes in pyrite have been considered in previous studies of seeps, but pyrite formation is ultimately limited by the availability of reactive iron and therefore only captures the earliest diagenetic processes. A better way to track sulfur cycling is by following the pathways of dissolved sulfate, using carbonate-associated sulfate or CAS. Though commonly used to track evolving seawater composition, CAS can also constrain conditions of diagenetic carbonate precipitation. CAS concentrations and isotopic compositions were measured using both traditional and novel micro-CAS methods. Preliminary data suggest paired isotopic and concentration measurements of CAS may provide insight into sulfate reduction rates and thus potential sulfide availability in these systems. Rates of sulfate reduction are highly variable both spatially and temporally in seep environments, and play a major role in the redox landscapes at these sites, where sulfate reduction and sulfide oxidation may be the dominant metabolic processes. Furthermore, CAS isotopic relationships and inferred rates of sulfate reduction and sulfide production can be used as a backdrop for assessing thiotrophic and methanotrophic symbiosis in the macrofaunal assemblages associated with these unique settings.