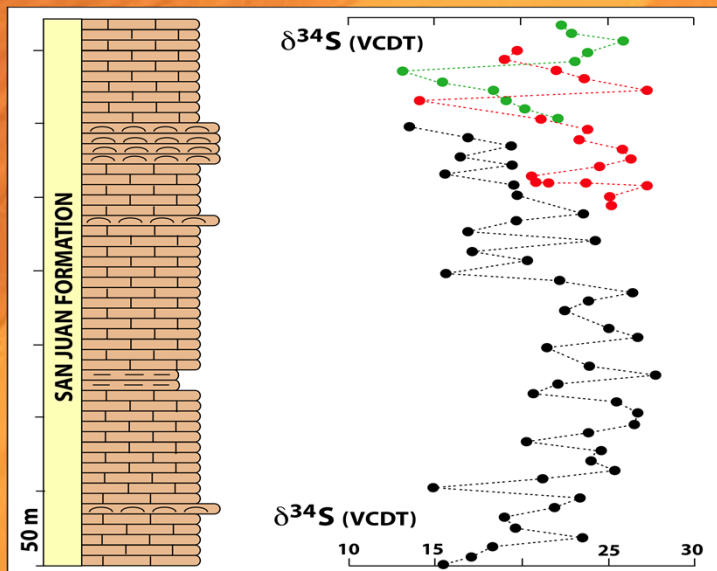


Ocean Circulation, Nutrient Cycling, and the S-isotope Composition of Earth Paleozoic Marine Systems

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Evolution of the marine sulfur cycle and its linkage to oceanic carbon cycling is a critical link in understanding depositional environments and time-temperature pathways experienced during hydrocarbon maturation. Many of these depositional and diagenetic models, however, are based on assumptions of marine sulfate concentrations similar to that of today, despite growing evidence that marine sulfate concentrations may have been much lower than present for much of Earth history. For instance, lower sulfate concentrations in the Early Paleozoic would have been influenced by even small changes in marine oxygenation and redox cycling, potentially driven by changing oceanic circulation patterns. Redox cycling, in turn would result in substantially more variable isotopic compositions, and may even contribute, ultimately, to organic carbon availability.



Currently, geologic systems are modeled only with a single reservoir model that considers marine sulfate. A two-box model better fits marine CAS and pyrite data. In this model, observed large and abrupt changes in CAS composition reflect rapid oxidation of a portion of the sulfide reservoir and delivery of this isotopically light material to the relatively small sulfate reservoir); longer-term change in the isotopic composition of marine pyrite reflect slower response of the sulfide reservoir to changes in isotopic composition because of its relatively larger size; and (3) isotopic inversion of sulfide and sulfate isotopic values reflect isotopic fractionation associated with oxidation of a reactive sulfide reservoir that can lead to isotopically heavy sulfide. The existence of two distinct reactive reservoirs effectively decouples marine hydrogen sulfide and pyrite formation from the parent marine sulfate reservoir.