

Organic matter and Fe competition on reduced S during deposition of Senonian organic-rich chalk in Israel

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The Senonian organic-rich chalk in Israel and other areas along the southern paleo Tethyan margins is characterized by high S in different organic and inorganic phases. In order to understand the paleo environmental history associated with the deposition of these organic-rich chalk we studied the S content and $\delta^{34}\text{S}$ of different bulk S phases extracted from these rocks, the Fe content and speciation in organic and inorganic phases, and the compound-specific S isotope composition of the organic S. We analyzed nine cores that were taken from the Aderet borehole (Israel), representing the thickest and most complete Senonian organic-rich sequence in Israel.

The organic S and organic matter contents show an inverse relation with the pyritic S content. These inverse relations, as well as the uniform degree of pyritization ($\sim 40\%$), suggest a Fe-limited system and competition between organic S and pyrite formation. The kerogen S and pyritic S are both ^{34}S depleted relative to the source marine sulphate at that period ($\delta^{34}\text{S} \sim -17$ - 20%). Kerogen S was consistently and unusually ^{34}S enriched relative to coexisting pyrite by up to about 41% . The $\delta^{34}\text{S}$ values of specific organic S compounds, namely polyprenoid sulphides, show an inverse relation with those of pyrite. This is also consistent with competition between organic S and pyrite formation.

A numerical model suggests large S isotope fractionation (~ 60 - 70%) during microbial sulphate reduction (MSR), which appears to be necessary to reproduce the fractionation observed between pyrite and sulphate at some intervals. We explain smaller observed pyrite-sulphate fractionations in organic-rich parts of the core by Fe limitation that was caused by reaction (e.g., complexation) of organic compounds with Fe. The lower consequent Fe concentrations, coupled with the high concentrations of organic matter, resulted in competition for reduced S, such that sulfurization of organic matter outcompeted pyrite formation, captured the isotopically lightest S, and led to formation of isotopically heavier pyrite. Thus, the Senonian organic-rich chalk in Israel cover a range of organic matter content over which either reaction with Fe or with organic matter is the leading diagenetic sink of sulphide produced by MSR.