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Sulfur Isotope Composition of Pyrite and Organic Matter from the Monterey Formation: Implications for δ34S as a Paleoenvironmental Proxy

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Abstract

The isotopic composition of organic sulfur (δ34Sorg) is a potential recorder of past biogeochemical conditions that has, thus far, received relatively little attention in comparison to the pyrite sulfur isotope record (δ34Spyr). This study presents continuous organic and pyrite δ34S records from three basins of the organic-rich Miocene Monterey Formation, deposited over a similar time interval of c.14.5-6 Ma but under varying depositional conditions. In the San Joaquin basin, δ34Sorg and δ34Spyr average 0constant pyrite-organic sulfur isotopic offset of c. 5Basin exhibits δ34Sorg values that are >10coeval San Joaquin basin intervals, with average δ34Sorg of c. 24the upper siliceous member the highest yet reported for marine organic sulfur and roughly 2-3consistently c. 12lower phosphatic member of the Santa Maria Basin, but an abrupt enrichment in both δ34Spyr and δ34Sorg coincident with a sharp lithostratigraphic transition at c. 11 Ma reduces this offset to <4Basin shows a sulfur isotope record intermediate between the San Joaquin and Santa Maria Basins, with average δ34Spyr and δ34Sorg of 3respectively, and relatively consistent c. 10offset. Records for all three basins demonstrate a close correlation between coeval δ34Spyr and δ34Sorg values which we attribute to derivation from an equivalent, or at least similar, source of sedimentary or water column sulfide. However, marked offset in the isotopic composition of coexisting pyrite and organic sulfur, of variable magnitude within and between basins, implies some contrast in the diagenetic processes underlying sulfur incorporation into the two phases. We argue that the prominent δ34Spyr and δ34Sorg isotopic differences between broadly coeval basin sections are largely the result of differences in sedimentation regime and the associated balance of iron and sulfide supply during diagenesis. A likely factor of additional importance to this iron-sulfide balance is basin-specific sedimentary and water column redox. These findings illustrate the importance of determining independent constraints on the nature of a sedimentary system before conclusions are made relating the sulfur isotope composition of sedimentary species to paleoenvironmental conditions. Additionally, we suggest that records of δ34Spyr have a strong dependence on interaction with organic sulfur during formation, and thus that existing δ34Spyr records are more effectively interpreted in combination with δ34Sorg records.

Sulfur Isotope Composition of Pyrite and Organic Matter from the Monterey Formation: Implications for $\delta^{34}S$ as a Paleoenvironmental Proxy

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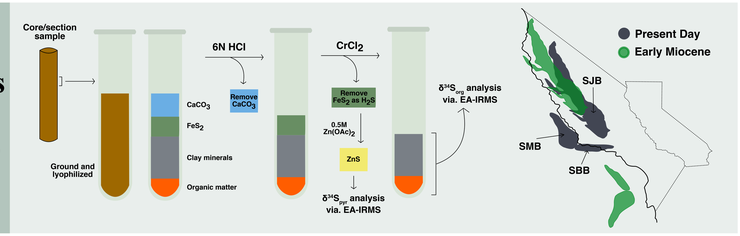
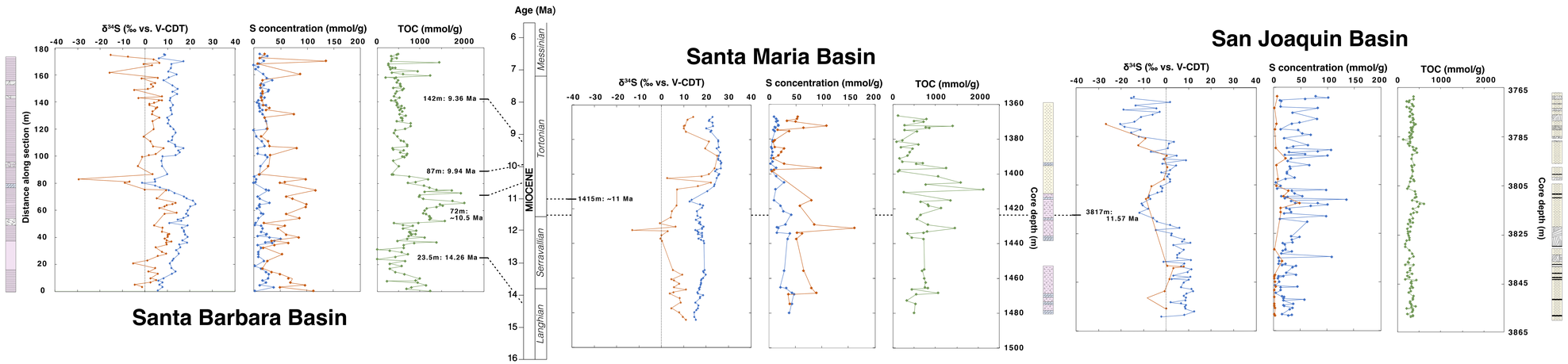
Introduction

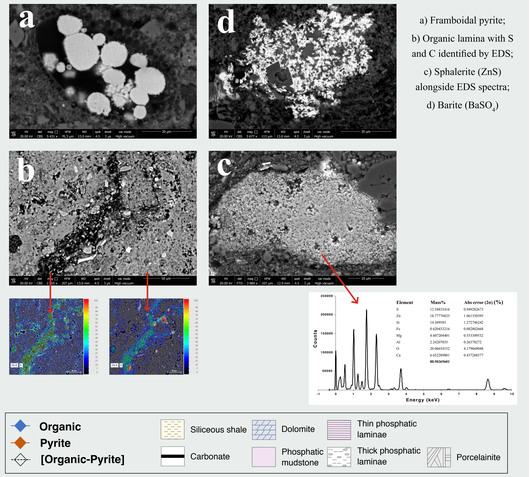
The isotopic composition of organic sulfur ($\delta^{34}S_{org}$) is a potential recorder of past biogeochemical conditions that has, thus far, received relatively little attention in comparison to the pyrite sulfur isotope record ($\delta^{34}S_{pyr}$). This study presents continuous $\delta^{34}S_{pyr}$ and $\delta^{34}S_{org}$ records from three basins of the Miocene Monterey Formation. We suggest that strongly contrasting isotopic records between coeval basin sections result from differences in sedimentation regime and the associated balance of iron and sulfide supply during diagenesis, as well as differences in the locus of sedimentary or water column sulfate reduction. Intervals of marine $\delta^{34}S_{org}$ significantly in excess of Miocene seawater sulfate $\delta^{34}S$[10] may reflect episodic deposition and deviation from 'steady state' diagenesis. Our results illustrate the importance of determining independent constraints on the nature of a sedimentary system before conclusions are made relating the sulfur isotope composition of sedimentary species to paleoenvironmental conditions. Additionally, we suggest that records of $\delta^{34}S_{pyr}$ have a strong dependence on interaction with organic sulfur during formation, and thus that existing $\delta^{34}S_{pyr}$ records are more effectively interpreted in combination with $\delta^{34}S_{org}$ records.

Materials and Methods



Results





a) Framboidal pyrite; b) Organic lamina with S and C identified by EDS; c) Sphalerite (ZnS) alongside EDS spectra; d) Barite ($BaSO_4$)

Discussion - what determines $\delta^{34}S_{org}$, $\delta^{34}S_{pyr}$ and $\Delta\delta^{34}S$?

(I) Sedimentation Rate

Hypothesis: Elevated sedimentation rates are associated with enrichments in $\delta^{34}S_{org}$ and $\delta^{34}S_{pyr}$[2]

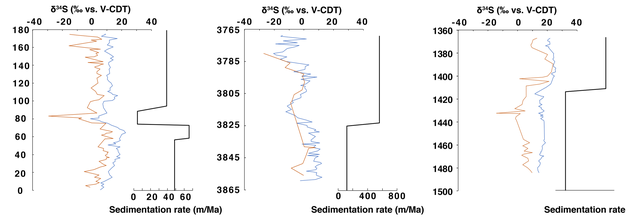
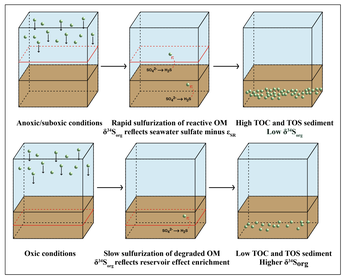


Figure 5. Isotopic record of each basin alongside estimation of sedimentation rates[3,4]. No quantitative sedimentation rates are known for the SMB UL51-18 core but rates are suggested to be comparable to SBB.

SBB: hypothesis ✓ SJB: hypothesis ✗ SMB: hypothesis ✓

(II) Locus of Microbial Sulfate Reduction (MSR)

Hypothesis: Expansion of euxinia is associated with reduction in $\delta^{34}S_{org}$ and $\delta^{34}S_{pyr}$



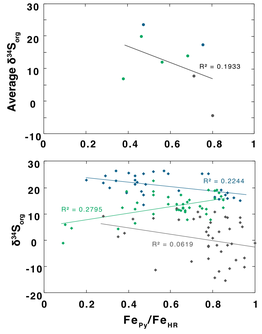


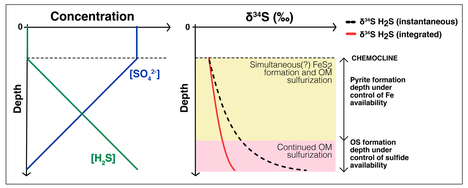
Figure 6 (above). A possible mechanism producing change in $\delta^{34}S$.[5]

Figure 7 (top L). Average Fe_{Py}/Fe_{HR} against average $\delta^{34}S_{org}$. Averages over intervals of constant sedimentation rate (fig. 5).

Figure 8 (bottom L). Fe_{Py}/Fe_{HR} against $\delta^{34}S_{org}$ for individual depth intervals within each basin. (SJB: grey; SMB: blue; SBB: green).

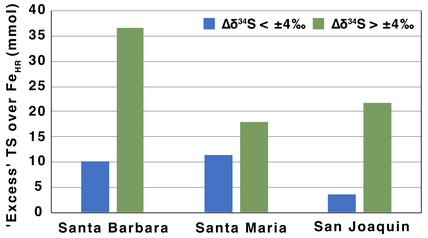
Between basins: hypothesis ≈ ✓
SMB: hypothesis ≈ ✓
SJB: hypothesis ✗
SBB: hypothesis ✗

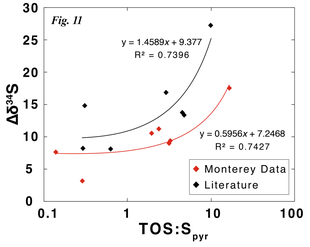
(III) Iron Limitation



Hypothesis: Excess of total sulfur (TS) over highly reactive iron (Fe_{HR}) wrt. pyrite stoichiometry is associated with larger $\Delta\delta^{34}S$

Figure 9 (L). A mechanism by which the balance of iron and sulfide availability may determine $\Delta\delta^{34}S$.[1,11]. *Figure 10 (below L).* 'Excess' sedimentary TS over Fe_{HR} (average of [TS - (FeHR x 2)]) against $\Delta\delta^{34}S$ < or > 4‰. *Figure 11 (below R).* Average sedimentary TOS:S_{pyr} vs. $\Delta\delta^{34}S$ for the Monterey Fm. (green) and literature data[1,6,7,8,9] (black). Monterey Fm. values are averages over intervals of constant sedimentation rate. Note log scale.





Between basins: hypothesis ✓ SBB: hypothesis ✓ SJB: hypothesis ✓ SMB: hypothesis ✓

(IV) MSR Rate

Hypothesis: Increased MSR rate leads to enriched $\delta^{34}S_{org}$ and $\delta^{34}S_{pyr}$ and is associated with elevated TOC

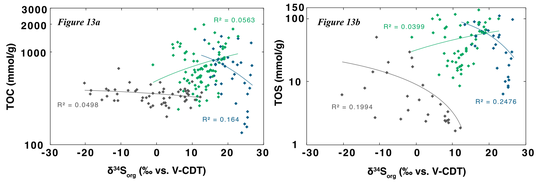


Figure 13a and 13b. $\delta^{34}S_{org}$ vs. TOC and TOS for SJB: grey; SMB: blue; SBB: green.

Between basins: hypothesis ≈ ✓ SBB: hypothesis ≈ ✓ SJB: hypothesis ✗ SMB: hypothesis ✗

(V) Non-steady state effects

Hypothesis: Episodic deposition can generate significantly enriched isotopic products during diagenesis[11].

Hypothesis: ?

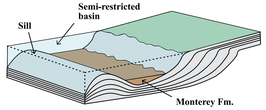


Figure 12. The depositional environment of the Monterey Fm. is generally interpreted as low-gradient, semi-restricted continental margin slopes[12]. The Monterey was characterised by episodic event-deposition within an intermittently erosional regime[13].

Conclusions

1. We present the first continuous organic sulfur isotope records for any interval of the Cenozoic using three basins of the Monterey Fm. They are the first to show $\delta^{34}S_{org}$ and $\delta^{34}S_{pyr}$ as significantly covariant in stratigraphic section, and also record the highest known marine $\delta^{34}S_{org}$.
2. We identify basin-specific depositional effects, such as sedimentation and local redox conditions, as most significant in determining $\delta^{34}S_{org}$, $\delta^{34}S_{pyr}$, and $\Delta\delta^{34}S$.
3. If these findings are more widely applicable, they may place strong limitation on the extent to which sulfur isotope records can be used to interpret global perturbation to the sulfur cycle in the absence of independent constraints on the nature of their associated depositional systems.
4. Additionally, we propose that $\delta^{34}S_{org}$ is a potential new proxy for depositional and environmental conditions, although details of what it records are yet to be fully understood.

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