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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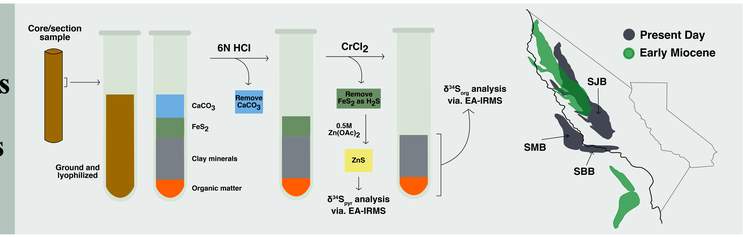
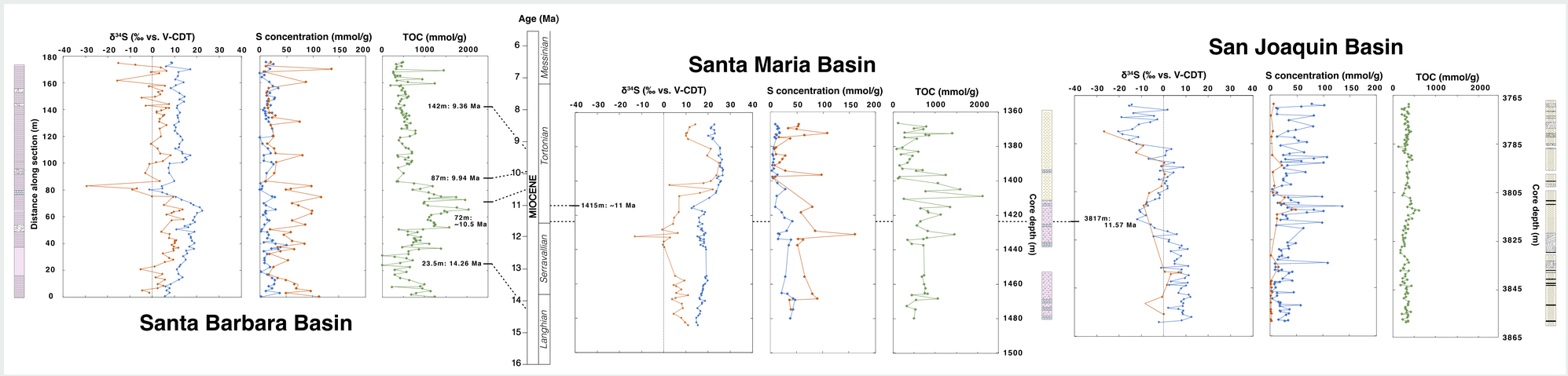
Introduction

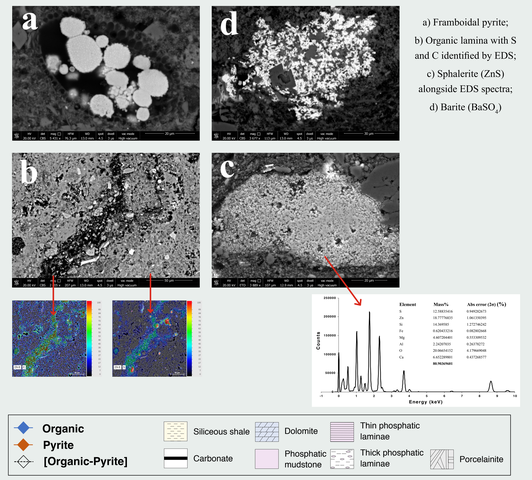
The isotopic composition of organic sulfur ($\delta^{34}S_{org}$) is a potential recorder of past biogeochemical conditions that has, thus far, received relatively little attention in comparison to the pyrite sulfur isotope record ($\delta^{34}S_{pyr}$). This study presents continuous $\delta^{34}S_{pyr}$ 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]

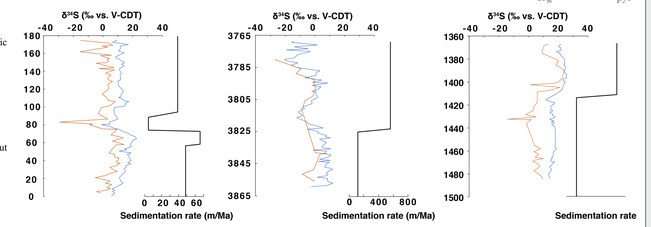
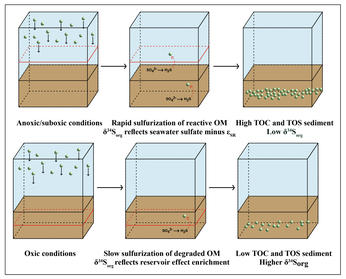


Figure 5. Isotopic record of each basin alongside estimation of sedimentation rates[3,4]. No quantitative sedimentation rates are known for the SMB UL51-18 core but rates are suggested to be comparable to SBB.

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 $\delta^{34}S_{pyr}$



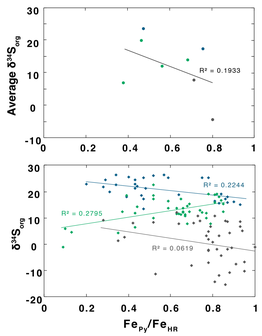


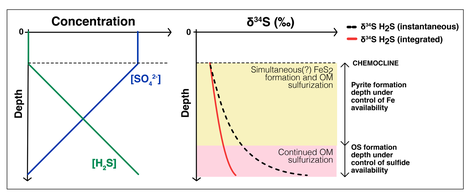
Figure 6 (above). A possible mechanism producing change in $\delta^{34}S$.[1]

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).

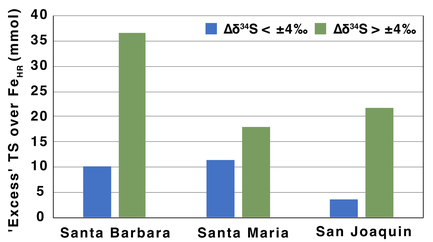
Between basins: hypothesis ≈ ✓
SMB: hypothesis ≈ ✓
SJB: hypothesis ✗
SBB: hypothesis ✗

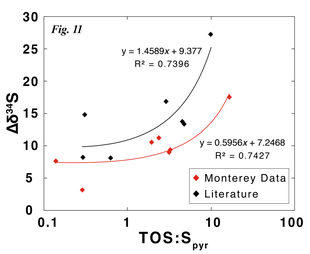
(III) Iron Limitation



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

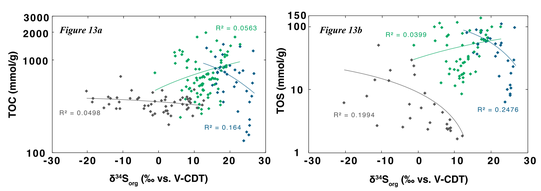


Figure 13a and 13b. $\delta^{34}S_{org}$ vs. TOC and TOS for SJB: grey; SMB: blue; SBB: green.

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: ?

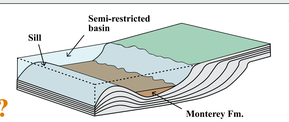


Figure 12. The depositional environment of the Monterey Fm. is generally interpreted as low-gradient, semi-restricted continental margin slopes[12]. The Monterey was characterised by episodic event-deposition within an intermittently erosional regime[13].

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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