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The fundamental role of reactive iron-to-sulfate ratio in determining $\delta^{34}S$ values of pyrite and organic matter in sedimentary rocks.

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Microbial sulfate reduction (MSR) occurs in oxygen-depleted environments and is one of the most effective processes shaping the sulfur cycle. The sulfur isotopic fingerprint associated with MSR is recorded in pyrite and organic matter, making their isotopic values ($\delta^{34}S_{py}$ and $\delta^{34}S_{org}$, respectively) and their isotopic offset ($\Delta^{34}S_{org\text{-}py}$) widely used to reconstruct ancient redox conditions on Earth's surface.

In this study, we analyze, and compile published data on a broad range of $\delta^{34}S_{py}$ (110‰) and $\delta^{34}S_{org}$ (93‰) values from rock samples. The samples originate from marine and lacustrine environments, spanning geological periods from the Mesoproterozoic (1.6 Ga) to the Paleogene (23 Ma). Our findings reveal a fundamental pattern of linear relationships between $\delta^{34}S_{py}$ and $\Delta^{34}S_{org\text{-}py}$ (R^2 ranging from 0.43 to 0.96) across different depositional settings. Through comprehensive iron, carbon, and sulfur analyses of various rock formations, combined with a kinetic model simulating $\delta^{34}S$ evolution under varying environmental conditions, we suggest that fluctuations in $\delta^{34}S_{py}$ and $\delta^{34}S_{org}$ values throughout Earth's history were primarily driven by variations in the ratio of reactive iron to sulfate in the depositional environment. In contrast, changes in seawater sulfate $\delta^{34}S$ values and the isotopic fractionation associated with MSR played a secondary, less significant role in shaping the $\delta^{34}S_{org}$ and $\delta^{34}S_{py}$ records.

Moreover, we identify a strong relationship between $\Delta^{34}S_{org\text{-}py}$ and Tmax-S across various rock types, ages and locations. Tmax-S is a proxy for the distribution of intermolecular sulfur cross-linkages relative to intramolecular organic sulfur bonds. As such, Tmax-S indictes the molecular pathway by which sulfur was incorporated into sedimentary organic molecules (abiotic sulfurization). While sulfur cross-linkage bonds stabilize organic matter by forming larger macromolecular structures, intramolecular sulfurization forms cyclic organic sulfur compounds that contribute less to organic matter preservation. Therefore, the $\Delta^{34}S_{org\text{-}py}$ and Tmax-S relationship suggests that the reactive iron-to-sulfate ratio plays a critical role in controlling the contribution of sulfurization to organic matter preservation.