Metabolic rates and sulfur cycling in the geologic record

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In PNAS, Leavitt et al. (1) describe the shared dependence of cell-specific sulfate reduction rate and sulfur isotope fractionations on the availability of a single electron donor for the model sulfate reducer, *Desulfovibrio vulgaris* Hildenborough. These authors then use their findings in a unique way to calibrate past sedimentary sulfate reduction rates (SedSRR) using sulfur isotope data from sedimentary pyrite and sulfate. This approach reveals evidence for changes in SedSRR over the past 200 million years that played a critical role in determining sulfur isotope fractionations in marine sediments.

Sedimentary sulfides and sulfates preserve a record of changes in ocean chemistry and ecology that has been used to understand how the Earth's surface environments have evolved over the past 500 million years. The sulfur isotopic composition of oceanic sulfate reflects a combination of processes related to the supply of sulfate to the oceans, the proportion of sulfur that is buried as pyrite (FeS_2) and as organic compounds, and the isotope fractionation associated with microbial sulfate reduction (2, 3). Sulfur isotope fractionations during microbial sulfate reduction are influenced by ecological factors, such as: (*i*) sulfate levels in marine sediments, (*ii*) the temperature of sulfate reduction, and (*iii*) the availability and type of organic electron donor (cf. refs 4 and 5). These three factors tune the balance between uptake and efficiency of enzymatic transformations of sulfate and sulfur-intermediate isotopologues (6–9).

The Leavitt et al. (1) treatment is premised on how the metabolism of sulfate reducers determines the isotopic fractionation between sulfate and sulfide. Isotopic models of the sulfate reduction metabolism consist of pathways that describe the transfer of sulfur between various metabolic intermediates, the reactants, and ultimately the metabolic products. Discrimination of isotopes can occur either as a result of transport of compounds from one location to another (for example, transport of sulfate into the cytoplasm from outside the cell), or as a result of chemical transformations that occur within the cell or in contact with the cell wall. This isotopic discrimination produces variations in both the $^{34}S/^{32}S$ ($\varepsilon_{sulfate\text{-}sulfide}$) and the exponent describing the relationship between $^{34}S/^{32}S$ and $^{33}S/^{32}S$ ($\lambda_{sulfate\text{-}sulfide}$). The many metabolic intermediates and pathways of the sulfate reduction metabolism makes it possible for sulfate reducers to produce a variety of relationships for $\varepsilon_{sulfate\text{-}sulfide}$ and $\lambda_{sulfate\text{-}sulfide}$. The Leavitt et al. (1) experiments reveal a dependence of $\varepsilon_{sulfate\text{-}sulfide}$ and $\lambda_{sulfate\text{-}sulfide}$ for the microbial sulfate reduction metabolism of *Desulfovibrio vulgaris* Hildenborough on the availability of the organic electron donor lactate and on sulfate reduction rates. The data for $\varepsilon_{sulfate\text{-}sulfide}$ and $\lambda_{sulfate\text{-}sulfide}$ scatter about linear arrays of constant internal fractionation (Fig. 1). This correlation between $\varepsilon_{sulfate\text{-}sulfide}$ and $\lambda_{sulfate\text{-}sulfide}$ suggests a first-order dependence of fractionation on the competition between the metabolic reduction of sulfate taken up by the cell and leakage of sulfate out of the cell (Fig. 1). A similar relationship, but shifted to slightly higher fractionations, is seen in data for natural populations of sulfate reducers studied by Canfield et al. (10), suggesting a similar first-order control. Second-order effects arising from variations in the parts of the metabolism downstream of sulfate in the cell are evidenced by scatter above and below the arrays. The existence of a first-order control that yields a relationship between sulfate reduction rates and isotopic composition is the basis for the extension to natural systems and interpretation of sulfur isotope records of oceanic sulfate and sedimentary pyrite.

A number of studies (2, 3, 11–13) have used the sulfur isotope records of oceanic sulfate and sedimentary pyrite to evaluate the way that the sulfur cycle has evolved during the Phanerozoic. Although these studies recognized the possibility that this fractionation may have changed over the course of the Phanerozoic, independent tests of this possibility were available only a few years ago (14), when the $^{34}S/^{32}S$ fractionation (ε_{GEO}) between oceanic sulfate and buried pyrite was analyzed using an independent approach rooted in the rare sulfur isotopes and geochemical models. This analysis suggests evolution of ε_{GEO} from values on the order of 30‰ to values on the order of 43‰ during an interval that started about 300 million years ago. It also appears that the three-isotope relationship between sulfate and buried pyrite (described by the exponenent λ_{GEO}) changed from values of 0.513–0.514 over the same time interval. Leavitt et al. (1) have advanced the interpretation of this record considerably by using their calibrated relationship between sulfate reduction rate, ε_{GEO} and λ_{GEO}, to estimate net SedSRR over time. Their analysis reveals a relatively well-behaved relationship between these new proxies for SedSRR and shelf area for the past 200 million years, and identifies possible connections between the delivery of organic carbon to marine sediments and to sedimentation rate.

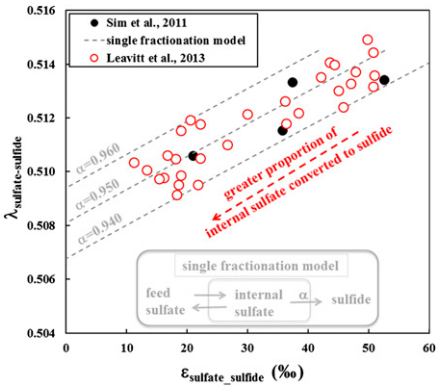

Fig. 1. Plot of $\lambda_{sulfate\text{-}sulfide}$ vs. $\varepsilon_{sulfate\text{-}sulfide}$ for pure culture chemostat experiments with contours supporting a first-order uptake control on metabolic fractionations. This first-order control provides justification for a unique approach that uses ε and λ from the geological record to place constraints on sulfate reduction rates in Earth's ancient oceans. $\lambda_{model} = 0.5145$ used for model calculation. Filled circles represent Sim et al. (15), open circles, Leavitt et al. (1).

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The relationship between ε_{GEO} and λ_{GEO} diverges from the relationship between ε and λ derived from the experiments for the earlier parts of the Phanerozoic, suggesting additional factors, such as changes in the location of the chemocline, a change in the community structure of the oceanic sulfur ecology, or a change in the proportion of sulfide reoxidized, distinguish the early and late parts of the Phanerozoic. Interestingly, Wu et al. (14) also called on processes like these to explain the change, but argued for a smaller—rather than greater—proportion of sulfide oxidation early in the record.

The logic underlying Leavitt et al.'s (1) argument that the coupled ε_{GEO} and λ_{GEO} relationships in marine sediments reflect those observed in culture experements is sound, and the conceptual leap to use coupled ε_{GEO}-λ_{GEO} relationships to calibrate a first-order control on the isotopic variations, such as SedSRR, provides a fresh way to evaluate the evolution of the sulfur cycle and to understand the connections between the sulfur isotope records and environmental parameters, such as the areal extent of shallow seafloor environments. Future work that focuses on developing better calibrations of ε_{GEO} and λ_{GEO}, as well as of the relationship between SRR and ε and λ for microbial sulfate reducers, will further refine this unique approach.

What is next? Leavitt et al. (1) point out that the isotope fractionation associated with pyrite burial is not equivalent to the fractionation produced by the microbial communities that are reducing sulfate. This difference depends upon what proportion of sulfide is reoxidized, the fractionations associated with sulfide reoxidation, and possibly sulfur disproportionation. The same effects are also seen for λ associated with pyrite burial when sulfur is cycled from sulfide back to sulfate. Development of the next generation of sulfur-cycle models that integrate ε and λ from geological samples with these and other calibration experiments, therefore, has great potential to reveal even more about the evolution and structure of the oceanic sulfur cycle. A better understanding of connections between the evolution of sulfate concentration and global sulfate reduction rates, such as is revealed for the past 100 million y (1), also has the potential to generate a more complete understanding and to provide new directions related to sulfur-cycle evolution research.

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