

Sulfur isotopic constraints on the evolution of Earth's surface environments

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Sulfur occurs in a variety of redox states from the most reduced form sulfide to the most oxidized sulfate, and cycles through environmental and biological reservoirs. Since this versatile element has four stable isotopes, measurements of sulfur isotopic ratios are one of the most powerful tools to study the contemporary sulfur cycle. More importantly, sulfur isotope signatures can persist for a long time in geologic materials; trace sulfate incorporates into marine carbonate rocks, and sulfide precipitates as pyrite. Changes in the global sulfur cycle, recorded in these sedimentary archives, are inherently linked those of other essential elements such as carbon, oxygen, and iron. For example, one of the most convincing evidence for extremely low oxygen levels in the early atmosphere is the mass-independent sulfur isotope anomalies reported from the sedimentary records older than 2.5Ga.

This presentation will focus on the recent advances in our understanding of the bio- and geochemical controls on the sedimentary sulfur isotope records. Throughout the long-term evolution of Earth's biogeochemical cycles, sulfur isotope fractionations between sedimentary sulfate and sulfide have increased to reach the modern values at the beginning of the Phanerozoic. Since microbial sulfate reduction is primarily responsible for this isotope fractionation, small isotopic offsets in the Archean sediments have been conventionally interpreted to represent muted biological fractionation with low environmental sulfate concentrations as the root cause. However, a growing body of evidence shows that organic substrates may have been more available to sulfate reducing microorganisms in the Archean ocean, leading to smaller fractionations. Recently, we estimated the sulfur isotope effect by the key enzyme involved in microbial sulfate reduction, providing quantitative support for these qualitative arguments. In shorter terms, high resolution sulfur isotope records help to understand the global environmental disturbances such as mass extinction events. Patterns of isotopic variability have been linked to the size of seawater sulfate pool, and multiple sulfur isotope analyses can constrain the relative timing and location of pyrite formation. Here, I will present paired sulfur isotope records during the Late Devonian and demonstrate that a larger seawater sulfate reservoir may have promoted the development of sulfidic bottom waters during the ocean anoxic events, increasing physiological stress and potentially contributing to the Devonian mass extinction.