

EARTH HISTORY: Sulfate Clues for the Early History of Atmospheric Oxygen

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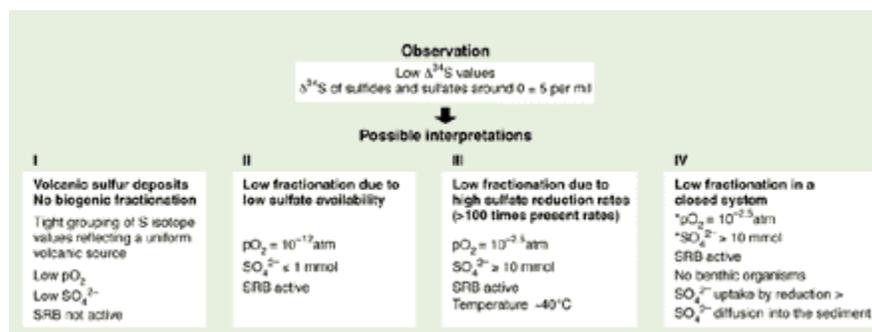
Earth's atmosphere and its composition played a key role in the origin and evolution of life and the development of Earth's surface environment (1). Prebiotic chemical evolution, which culminated in the origin of life, would have been impossible in an atmosphere containing much free oxygen (2). On the other hand, without some molecular oxygen, life could have not evolved to its present-day level of complexity. Sedimentary deposits reveal that there was a change in the oxidation state of the atmosphere during the Early Proterozoic [\sim 2300 million years ago (Ma)] (1, 3, 4), but the details remain elusive. Estimates for the timing of accumulation of appreciable concentrations of free oxygen in the Archean atmosphere range from as early as 3500 Ma (5, 6) to 2000 Ma (7). Although biologically mediated isotope distributions in the geological record could potentially constrain the time of evolution of the underlying biochemical processes and environmental conditions, in fact this source of information has proved frustrating: Rock sequences of Archean age are rare, of limited extent, poorly preserved, and mostly highly metamorphic. The geochemical remnants of ancient biologic signatures in such sequences are chemically complex and highly altered, and the information they originally contained has been all but obliterated.

In their attempts to elucidate the history and evolution of atmospheric oxygen, many researchers have turned to the isotopic composition of sulfur-bearing minerals such as marine sulfates and sedimentary pyrite (3, 8). Local depositional effects and/or postdepositional modifications frequently affect the sulfur isotopic composition of these minerals (9). Nevertheless, the $\delta^{34}\text{S}$ values of Archean sulfur deposits turn out to be fairly consistent between different sites, indicating that global patterns are captured in the record (10). A study by Canfield *et al.* on page 658 of this issue (11) sheds light on how the sulfur isotopic signature may be interpreted to reveal the characteristics of the Archean atmosphere.

How can sulfur-containing minerals assist in timing the evolution of atmospheric oxygen? Sulfate (SO_4^{2-}) is likely to have established itself as a mobile and ubiquitous constituent of the upper ocean at the time when oxygen became a prominent constituent of the atmosphere (12, 13). It is likely that this abundant sulfate was accompanied by the proliferation of sulfate-reducing bacteria (SRB). The question of when Earth's atmosphere began to accumulate free oxygen could then be answered by determining when the oceans became sulfate-rich and SRB became active.

The answer may lie in the isotopic composition of sedimentary (biogenic) pyrite, which reflects chemical conditions during its formation through bacterial sulfate reduction. The $\delta^{34}\text{S}$ values of Archean sulfides and sulfates differ from those of younger sediments. They are characterized by a tight grouping of S isotope values, with both sulfates and sulfides falling mostly within a narrow range of 0 ± 5 per mil (10). The small isotopic

difference between Archean sulfates and sulfides and the scarcity of sulfates in Archean sediments have often been interpreted as indicative of a magmatic sulfur source. Sedimentary sulfides were considered to be of hydrothermal rather than biogenic origin; thermochemical redox conditions could have caused the observed small isotopic fractionation (14). The scarce sulfate minerals would, in this view, have formed through H₂S oxidation by anaerobic sulfide-oxidizing bacteria. The above interpretation implies that Archean seawater was H₂S-rich and SO₄²⁻-poor and that the partial pressure of atmospheric oxygen was low. But comparative biochemical evidence suggests that sulfate reduction may have arisen in the earliest stages of biological evolution, probably at about 3500 Ma (15). Other explanations for the small isotopic difference between sulfate and sulfide minerals in the Archean are thus required (see the figure).



Possible scenarios for explaining the Archean sulfur isotope record. Present-day partial pressure of oxygen (pO₂) = 10^{-0.7} atm. Δ³⁴S is the difference in the δ³⁴S value between contemporary sulfates and sulfides. SRB is sulfate-reducing bacteria. Values marked with an asterisk were suggested by Ohmoto (5), but Δ³⁴S in such systems would only depend on the relative rates of sulfate uptake by SRB and sulfate diffusion to the sediment (see text).

It has been argued that the generally small ³⁴S depletion in Archean sulfides relative to sulfates is a result of rapid sulfate reduction in oceans with moderate concentrations of sulfate (thus, less isotopic discrimination) (13, 16), sulfide formation in a closed system of poorly mixed sediments (13, 17), or sulfide formation in sulfate-poor oceans (6, 18). In all these scenarios, SRB were able to reduce available sulfate to sulfur efficiently, resulting in limited isotopic fractionation between sulfide and sulfate. But the environmental implications of these scenarios differ widely. A small fractionation caused by low oceanic sulfate concentrations would indicate low partial pressures of atmospheric oxygen, whereas a reduced fractionation effect due to rapid reduction rates at high temperatures would imply moderate to high sulfate and oxygen concentrations. Reduced fractionation in closed system sedimentary environments only indicates that the sulfate reduction rates in the sediment were higher than the diffusion rate of sulfate into the sediments. Such conditions can occur over a large range of seawater sulfate concentrations and are not diagnostic of Archean oxygen concentrations.

Comparison of sulfur isotope fractionation by SRB and the isotopic record of sulfide and sulfate minerals (6, 13, 18, 19) could help assess the validity of the arguments made in

support of the different interpretations. The kinetic isotope fractionation associated with bacterial sulfate reduction depends on parameters such as reduction pathways and rates, type and concentration of electron donors, and temperature. If we know how the isotopic fractionation is influenced by these and other parameters, this would help us understand the environmental conditions in the Archean. Canfield *et al.* (11) study natural bacteria populations and observe relatively large S isotope fractionation (and presumably high reduction rates) during sulfate reduction at elevated temperatures. Other systems, with different organisms or settings, indicate reduced fractionation under conditions of high reduction rates (20). If in the Archean, SRB were similar to the present-day natural assemblages studied by Canfield *et al.* (11), then arguments attributing low fractionation to high reduction rates at high temperatures would have to be discounted. Unfortunately, extensive data on organism-specific fractionation effects and their dependence on environmental parameters are still lacking. As more data such as that presented by Canfield *et al.* (11) become available, the formulation of a theoretical framework for the interpretation of environmental conditions at this important time of Earth's history should become possible.

Such new and innovative studies impose constraints on interpretations of the Archean S isotope record, but firm conclusions concerning the environmental evolution of the Archean Earth cannot yet be reached. To do so, we need a more reliable record of the chemistry of the atmosphere and/or oceans. As yet, data are limited, and the biological origin of many S-bearing minerals of Archean age remains questionable. Independent indicators--such as trace element concentrations and oxygen, strontium, and iron isotopes--may enable us to distinguish between sulfate and sulfide deposits of biogenic and magmatic origins and possibly between minerals that precipitated from sulfate-poor versus sulfate-rich solutions. Likewise, independent proxies for atmospheric oxygen or seawater sulfate concentrations in the Archean are needed. Sulfate concentrations in other marine minerals (such as carbonates) or distribution of redox-sensitive elements may also prove useful.

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