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The five stable isotope compositions of Fig Tree barites: Implications on sulfur cycle in ca. 3.2 Ga oceans

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Abstract

The discovery of ^{33}S anomalies in Archean sedimentary rocks has established that the early Earth before ~2.2 Ga (billion years ago) had a very different sulfur cycle than today. The origin of the anomalies and the nature of early sulfur cycle are, however, poorly known and debated. In this study, we analyzed the total sulfur and oxygen isotope compositions, the δ^{18}O, Δ^{17}O, δ^{34}S, Δ^{33}S, and Δ^{36}S, for the >3.2 Ga Fig Tree barite deposits from the Barberton Greenstone Belt, South Africa. The goal is to address two questions: (1) was Archean barite sulfate a mixture of ^{33}S-anomalous sulfate of photolysis origin and ^{33}S-normal sulfate of other origins? (2) did the underlying photochemical reactions that generated the observed ^{33}S anomalies for sulfide and sulfate also generate ^{17}O anomalies for sulfate?

We developed a new method in which pure barite sulfate is extracted for oxygen and sulfur isotope measurements from a mixture of barite sands, cherts, and other oxygen-bearing silicates. The isotope data reveal that (1) there is no distinct ^{17}O anomaly for Fig Tree barite, with an average Δ^{17}O value the same as that of the bulk Earth (-0.02 ± 0.07‰, $N = 49$); and (2) the average δ^{18}O value is $+10.6 \pm 1.1$‰, close to that of the modern seawater sulfate value (+9.3‰). Evidence from petrography and from the δ^{18}O of barites and co-existing cherts suggest minimum overprinting of later metamorphism on the sulfate's oxygen isotope composition. Assuming no other processes (e.g., biological) independently induced oxygen isotope exchange between sulfate and water, the lack of reasonable correlation between the δ^{18}O and Δ^{33}S or between the δ^{34}S and Δ^{33}S suggests two mutually exclusive scenarios: (1) An overwhelming majority of the sulfate in the Archean ocean was of photolysis origin, or (2) The early Archean sulfate was a mixture of ^{33}S-normal sulfates and a small portion (<5%?) of ^{33}S-anomalous sulfate of photolysis origin from the atmosphere. Scenario 1 requires that sulfate of photolysis origin must have had only small ^{33}S or ^{36}S anomalies and no ^{17}O anomaly. Scenario 2 requires that the photolysis sulfate have had highly negative δ^{34}S and Δ^{33}S values, recommending future theoretical and experimental work to look into photochemical processes that generate sulfate in Quadrant I and sulfide in Quadrant III in a δ^{34}S (X)–Δ^{33}S (Y) Cartesian plane. A total sulfur and oxygen isotope analysis has provided constraints on the underlying chemical reactions that produced the observed sulfate isotope signature as well as the accompanying atmospheric, oceanic, and biological conditions.

1. INTRODUCTION

The timing and driving mechanisms of the irreversible oxygenation of Earth's surface environment are among the most significant problems of Earth history (Holland, 2002; Catling and Claire, 2005; Kasting and Ono, 2006). In Earth's redox budget, sulfate is one of the most abundant electron acceptors for microbial processes. The history of sulfate is closely linked to the history of oxygen in the atmosphere (e.g., Berner and Petsch, 1998). The amount of sulfate (C) at anytime in the ocean is a function of influxes (sources) F_{in} and out-fluxes (sinks) F_{out}.

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$$dC/dt = F_{\mathrm{in}}(f_{\mathrm{ow}}, f_{\mathrm{mh}}, f_{\mathrm{ph}}, f_{\mathrm{de}}) - F_{\mathrm{out}}(f_{\mathrm{sr}}, f_{\mathrm{hr}}, f_{\mathrm{mp}}) \quad (1)$$

Influxes include oxidative weathering (f_{ow}), magmatic and hydrothermal input (f_{mh}), photochemical reactions (f_{ph}), and dissolution of old evaporites (f_{de}). Out-fluxes include microbial sulfate reduction (f_{sr}), hydrothermal reduction (f_{hr}), and sulfate mineral precipitation (f_{mp}). The dynamic changes of these fluxes in geological history are revealed in the concentration of seawater sulfate and its sulfur and oxygen isotope compositions. With information on carbon cycling plus a few reasonable assumptions, it is possible to reconstruct various sulfate fluxes for the recent past, including certain critical transition periods in geological history (e.g., Berner, 2005).

While optimistic for this effort in many Phanerozoic cases, we are poorly equipped when tackling the ocean sulfate budget on the early Earth, a time during which no simple system analogous to that of the modern era may have existed. Archean barite deposits in South Africa (Reimer, 1980; Wilson and Versfeld, 1994), Western Australia (Dunlop and Groves, 1978), and India (Deb et al., 1991) represent the earliest conspicuous sulfate deposits on Earth. Although of wide geographic occurrence, these early barite units appear to be confined within a period from ~3.5 to ~3.2 Ga. Similar barite deposits are rarely seen again in the rest of the Archean (Huston and Logan, 2004).

Recent discovery of ^{33}S anomalies in sedimentary sulfur (sulfide and sulfate) of Archean age (Farquhar et al., 2000), laboratory experiments on mechanisms for the generation of ^{33}S anomalies (Farquhar et al., 2001), and photochemical models for the production and preservation of the anomalous signals (Pavlov and Kasting, 2002) reinforced the widely held view that the Archean atmospheric O_2 concentration was lower than 10^{-5} times the present atmospheric level (PAL) and probably as low as 10^{-13} PAL. If so, the sulfate influx from oxidative weathering would have been greatly diminished if not absent in the early half of the Earth history. So, why did sulfate, a rather oxidized form of sulfur, appear in the 3.5–3.2 Ga oceans?

Another key but largely unresolved issue concerns the early history of sulfate reduction and sulfide oxidation as part of the emerging metabolic activities of evolving microorganisms. As it turns out, the deep branching history of these functions is difficult to constrain on the basis of genomics or the molecular “clock” because of the frequent and almost pervasive lateral gene transfer among prokaryotes (Martin et al., 2003). In fact, evolutionary biologists will have to rely on geologists to provide independent evidence for the temporal sequence of these important metabolic functions on the early Earth. Overall, a poorly known but probably fundamentally different sulfur cycle was in operation during the Archean.

Published multiple sulfur isotope data for >3.2 Ga barite from the Fig Tree Group, Barberton Greenstone Belt, South Africa; the Warrawoona Group, North Pole Dome, Pilbara Block of Western Australia; and the Sargur Group, the Dharwar Craton, Karnataka, India (Hoering, 1989; Farquhar et al., 2000) show non-mass dependent ^{33}S depletions. The widespread occurrence of this anomaly is consistent with the absence of O_2 and O_3 from the Archean atmosphere because the presence of O_2 and O_3 would form an ultraviolet shield and prevent either the production (Farquhar et al., 2001) or the survival of the anomalous signature (Pavlov and Kasting, 2002). Currently, however, there are at least two outstanding questions associated with the sulfate cycle at >3.2 Ga.

First, having a ^{33}S-anomalous signature does not mean that the >3.2 Ga sulfate was entirely of photolysis origin. Was early Archean barite sulfate a mixture of ^{33}S-anomalous sulfate of photolytic origin (f_{ph}) and ^{33}S-normal sulfate of other origins? If yes, what are the likely isotope compositions for the two end-member sulfates? Archean barites have shown a variation in the value of Δ^{33}S, ranging from −1.28‰ to −0.42‰ (Farquhar et al., 2000). It could be argued that these variations reflect sulfate formation under variable photochemical conditions; a claim that appears to be supported by the variable Δ^{33}S values for the product S^0 in laboratory experiments (Farquhar et al., 2001). It could also be argued, however, that the variations were due to mixing of photochemical sulfates with sulfate from other sources such as oxidative weathering (f_{ow}) or magmatic–hydrothermal inputs (f_{mh}) that did not have a ^{33}S anomaly. It should be noted that if there were no mixing with sulfate from other sources, subsequent redox changes, either inorganic or biological, and diagenetic or metamorphic processes would not alter the Δ^{33}S value. So far, the multiple sulfur isotope data cannot distinguish between the two cases, and this is largely because we do not have constraints on the isotope parameters for sulfate end-members.

If the >3.2 Ga barite sulfate was a mixture of two main sulfate fluxes, f_{ph} with a negative Δ^{33}S value and the rest (f_{ow} and/or f_{mh}) with zero Δ^{33}S value, it may be possible to test specific versions of this scenario. For example, we can reasonably suggest that if the f_{ph} sulfate formed in gas-phase reactions at certain altitudes, it ought to carry an oxygen isotope signature that was partially equilibrated with that of ambient water vapor that had a lower δ^{18}O value than the water at the surface from which f_{ow} or f_{mh} sulfate might have formed. If this is true, we should expect to find a positive correlation between the δ^{18}O and the Δ^{33}S among the various barites: i.e., the lower the δ^{18}O the more negative the Δ^{33}S will be.

This leads to a second question: did the underlying photochemical reactions that generated the observed ^{33}S anomalies for sulfide and sulfate also generate ^{17}O anomalies for sulfate? Laboratory SO_2 photolysis experiments suggest that the 193-nm radiation, not the >220-nm radiation, produced Δ^{33}S and Δ^{36}S values similar to those of Archean barites (Farquhar et al., 2001), implying a plausible reaction mechanism for generating the observed Archean data. If a 193 nm photolysis reaction was largely responsible for the observed ^{33}S anomalies, we should expect a negative correlation between δ^{34}S and Δ^{33}S in a two-component mixing scenario: i.e., photolytic sulfate f_{ph} with highly negative Δ^{33}S but highly positive δ^{34}S value was mixing with sulfate that had no ^{33}S anomaly but slightly positive δ^{34}S. If an expected negative correlation between δ^{34}S and Δ^{33}S is not seen, however, the observational data may be used to constrain underlying photochemical reactions.