Chain formation as a mechanism for mass-independent fractionation of sulfur isotopes in the Archean atmosphere

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ABSTRACT

The anomalous abundances of sulfur isotopes in ancient sediments provide the strongest evidence for an anoxic atmosphere prior to ~2.45 Ga, but the mechanism for producing this 'mass-independent' fractionation pattern remains in question. The prevailing hypothesis has been that it is created by differences in the UV photolysis rates of different SO_2 isotopologues. We investigate here a recently proposed additional source of fractionation during gas-phase formation of elemental sulfur (S_4 and S_8). Because two minor S isotopes rarely occur in the same chain, the longer S_4 and S_8 chains should be strongly, and roughly equally, depleted in all minor isotopes. This gives rise to *negative* $\Delta^{33}S$ values and *positive* $\Delta^{36}S$ values in elemental sulfur—just the opposite of (and much larger than) what is predicted from SO_2 photolysis itself. Back-reactions during chain formation, specifically photolysis of S_2 and S_3, pass sulfur having the opposite fractionation back to atomic S, and thence to other sulfur species, causing H_2S, SO_2, sulfate, and short-chain elemental sulfur to have positive $\Delta^{33}S$ and negative $\Delta^{36}S$. Positive $\Delta^{33}S$ values in elemental sulfur produced in laboratory SO_2 photolysis experiments could be caused by the initial fractionation during photolysis, combined with rapid condensation of short-chain sulfur species on the walls of the reaction chamber, along with a scarcity of back-reactions. The simulated fractionations produced by the chain formation mechanism do not directly match fractionations from the rock record. The mismatch might be explained if the isotopic signals leaving the atmosphere were significantly modulated by life, by uncertainties in the rates of reactions of both major and minor isotopic sulfur species, or by the relatively large potential range of atmospheric parameters. Further work is needed to better constrain these uncertainties, but this novel mechanism suggests new avenues to explore in our search for a explanation for the S-MIF record.

1. Introduction

In the late 1960's and early 1970's, Cloud (1972) proposed that Earth's atmosphere experienced a dramatic rise in O_2 sometime around 2 Ga, building off earlier work by MacGregor (1927). The case for a 'Great Oxidation Event' in the Paleoproterozoic was further elaborated by Holland (Holland, 1984; Rye and Holland, 1998).

The arguments were based on several lines of geological evidence, including the replacement of graybeds with redbeds, the disappearance of detrital pyrite and uraninite, and the retention of iron in paleosols. However, some researchers continued to question this hypothesis (Towe, 1990; Ohmoto, 1996).

In 2000, Farquhar and colleagues strengthened the case for an anoxic Archean atmosphere by showing that sulfur isotopes in sediments were fractionated in an anomalous manner prior to ~2.45 Ga, but not since then (Fig. 1) (Farquhar et al., 2000a). Sulfur has four stable isotopes: ^{32}S (~95%), ^{33}S (~0.75%), ^{34}S (~4.25%), and ^{36}S (~0.01%). To measure fractionation, $\delta^x S$ is defined as the deviation in parts permil (‰, parts per thousand) of the ratio
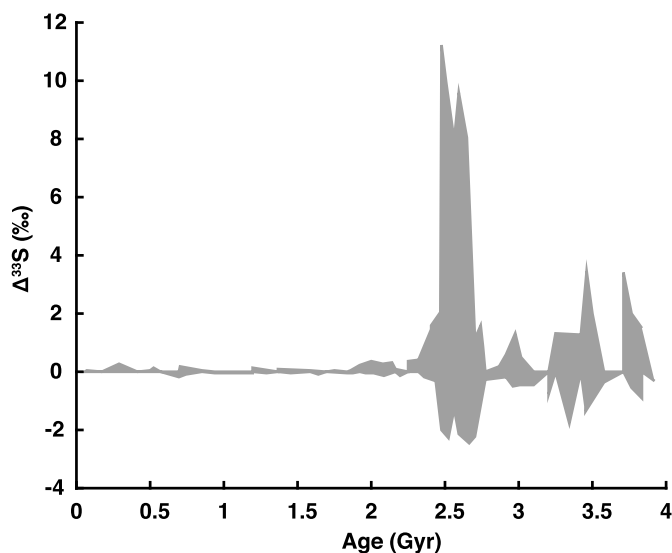
Fig. 1. The Δ^{33}S data from sulfides in the geologic record are plotted with respect to time. Adapted from Johnston (2011) and references therein.
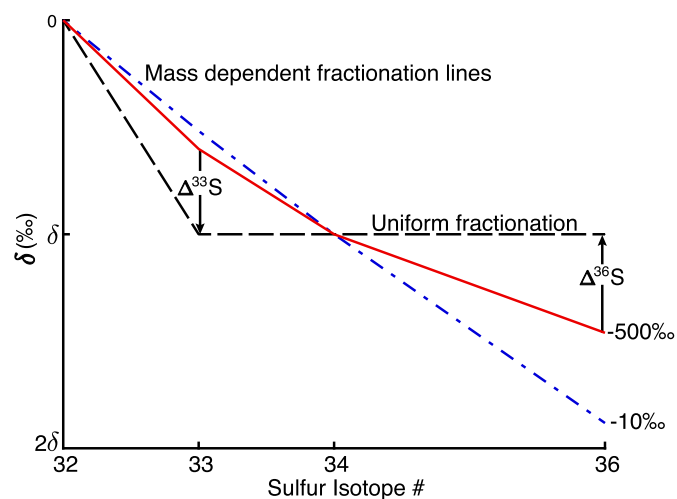
Fig. 2. Mass-dependent fractionation lines, or curves, for two different values of δ: $-10‰$ (blue curve) and $-500‰$ (red curve). Values for the red solid (large fractionation) curve are calculated using eq. S17. The blue dot–dash (small fractionation) curve is from eq. S18. For the mass-independent mechanism proposed here, δ should be approximately the same for all minor isotopes (shown as the horizontal dashed line). Δ^xS is then the distance between the dashed line and the colored lines (as noted on the plot), and will be proportionally smaller as the magnitude of the fractionation increases.

^{x}S/^{32}S from an isotopic standard, where ^{x}S represents any of the minor S isotopes (^{33}S, ^{34}S, and ^{36}S). The anomalous fractionation seen by Farquhar et al., often called 'mass independent' fractionation (MIF), results when S isotopes do not fractionate in proportion to the difference in their masses. For processes that result in small mass-*dependent* fractionations, δ^{33}S $\cong 0.51\delta^{34}$S, and δ^{36}S $\cong 1.89\delta^{34}$S (see Supplemental Materials). Deviations from these predicted values, representing any MIF signal, are expressed as Δ^{33}S and Δ^{36}S, respectively (Fig. 2).

In a subsequent paper, Farquhar et al. (2001) demonstrated that MIF could be induced by photolysis of SO$_2$ at specific UV wavelengths. They argued that sulfur MIF required a low-O$_2$/low-O$_3$ atmosphere so that the SO$_2$ 190–220 nm photolysis band would not be shielded from solar UV. In a modeling study, Pavlov and Kasting (2002) refined this argument by pointing out that MIF could only be preserved if sulfur exited the atmosphere in more than one oxidation state. Today, nearly all sulfur is oxidized in the atmosphere

and joins the large dissolved sulfate reservoir in the ocean, erasing any photochemical MIF signature. The upper limit on Archean pO$_2$ derived from this modeling study was 10^{-5} PAL (times the Present Atmospheric Level).

It should be noted that the MIF signal tracked in the Pavlov and Kasting model was arbitrary in both sign and magnitude. It was assumed to be produced during SO$_2$ photolysis and to have been unaffected by subsequent photochemical reactions in the atmosphere. We argue in Section 2.1 that neither of these assumptions is correct; nevertheless, the upper limit on pO$_2$ derived by these authors remains valid because it relies on the gas-phase speciation, and not on the specific fractionation mechanism.

Other authors built on the work of Pavlov and Kasting (2002). Zahnle et al. (2006) further refined the atmospheric conditions necessary to produce atmospheric elemental sulfur (e.g., O$_2$ and CH$_4$ concentrations and total sulfur outgassing rates), as well as the consequences of the rise of oxygen to both climate and the S-MIF signal. Kurzweil et al. (2013) noted a transition in the relationship between Δ^{36}S and Δ^{33}S around 2.7 Ga, as well as an observed asymmetry in the Δ^{33}S record prior to $\sim$2.5 Ga (Fig. 1), with more and higher positive Δ^{33}S values than low ones. The asymmetry can be explained if the dominant sulfur species left the atmosphere with negative Δ^{33}S, driving the remaining sulfur species strongly positive. In their hypothesis, an influx of photosynthetic O$_2$ in the Late Archean increased the formation and preservation of oxidized sulfur species like SO$_2$, making them dominant, and decreased the formation rate of S$_8$. S$_8$ was assumed to carry a positive Δ^{33}S signal, based on laboratory SO$_2$ photolysis experiments (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013; Whitehill et al., 2013), while sulfate and SO$_2$ were both negative. (We will return to the laboratory experiments later, where we will argue that they have been misleading.)

Danielache et al. (2008) measured isotope-specific cross sections for ^{32}SO$_2$, ^{33}SO$_2$, and ^{34}SO$_2$, but these results were shown to be inaccurate (Lyons, 2009). Claire et al. (2014) used a much finer wavelength grid than Pavlov and Kasting (2002) to calculate photolysis rates using the Danielache et al. (2008) cross sections. Their calculation predicted that the signals would be just the opposite from the canonical model: S$_8$ should have *negative* Δ^{33}S, while sulfate and SO$_2$ Δ^{33}S should be *positive*. Revised cross sections for various SO$_2$ isotopologues (Endo et al., 2015) enabled new calculations (Izon et al., 2017) which predicted that S$_8$ should have *positive* Δ^{33}S, while sulfate and SO$_2$ Δ^{33}S should be *negative*. However, this model failed to reproduce either the magnitude of the S-MIF signal or the Δ^{36}S/Δ^{33}S slopes seen in geologic record (Izon et al., 2017), suggesting that other mechanisms might be at work. We argue below that 1) the S-MIF signal is influenced by a novel mechanism, namely, chain formation, 2) that elemental sulfur formed photochemically in the Archean atmosphere initially had negative Δ^{33}S, and 3) that the strongly positive Δ^{33}S values preserved in pyrite could result either from biological reduction of sulfate or (to a lesser extent) sulfite, or from incorporation of atmospheric sulfide. This last inference is speculative, as the processing of atmospheric sulfur products through the marine biosphere is complex, and so other mechanisms for generating pyrite with positive Δ^{33}S values are possible.

2. Sulfur chain formation

2.1. Forward reactions and comparisons with Pavlov and Kasting

One of the sulfur compounds formed photochemically in a reducing atmosphere is elemental sulfur. At room temperature, the thermodynamically stable sulfur allotrope is solid S$_8$. Pavlov and Kasting modeled sulfur formation by the sequence of reactions