Modeling the signature of sulfur mass-independent fractionation produced in the Archean atmosphere

Mark W. Claire [a,b,c,*], James F. Kasting [b,d], Shawn D. Domagal-Goldman [b,c,e], Eva E. Stüeken [b,f], Roger Buick [b,f], Victoria S. Meadows [b,g]

[a] Department of Earth and Environmental Sciences, University of St Andrews, Irvine Building, St Andrews, Fife KY16 9AL, UK
[b] NASA Astrobiology Institute – Virtual Planetary Laboratory, University of Washington, Seattle, WA 98195, USA
[c] Blue Marble Space Institute of Science, 1200 Westlake Ave N Suite 1006, Seattle, WA 98109, USA
[d] Department of Geosciences, Pennsylvania State University, 443 Deike Building, University Park, PA 16802, USA
[e] Planetary Environments Laboratory, NASA Goddard Space Flight Center, 8800 Greenbelt Road, Greenbelt, MD 20771, USA
[f] Department of Earth and Space Sciences, University of Washington, 335 Johnson Hall, Seattle, WA 98195, USA
[g] Department of Astronomy, University of Washington, Box 351580, Seattle, WA 98195, USA

Abstract

Minor sulfur isotope anomalies indicate the absence of O_2 from the Archean atmosphere. A rich dataset showing large variations in magnitude and sign of $\Delta^{33}S$ and $\Delta^{36}S$, preserved in both sulfates and sulfides, suggests that further constraints on Archean atmospheric chemistry are possible. We review previous quantitative constraints on atmospheric $\Delta^{33}S$ production, and suggest that a new approach is needed. We added sulfur species containing ^{33}S and ^{34}S to a 1-D photochemical model and describe the numerical methodology needed to ensure accurate prediction of the magnitude and sign of $\Delta^{33}S$ produced by and deposited from the Archean atmosphere. This methodology can test multiple MIF-S formation mechanisms subject to a variety of proposed atmospheric compositions, yielding $\Delta^{33}S$ predictions that can be compared to the rock record. We systematically test SO_2 isotopologue absorption effects in SO_2 photolysis (Danielache et al., 2008), one of the primary proposed mechanisms for $\Delta^{33}S$ formation. We find that differential absorption through the Danielache et al. (2008) cross sections is capable of altering predicted $\Delta^{33}S$ as a function of multiple atmospheric variables, including trace O_2 concentration, total sulfur flux, CO_2 content, and the presence of hydrocarbons, but find a limited role for OCS and H_2S. Under all realistic conditions, the Danielache et al. (2008) cross sections yield $\Delta^{33}S$ predictions at odds with the geologic record, implying that additional pathways for sulfur MIF formation exist and/or the cross sections have significant errors. The methodology presented here will allow for quantitative constraints on the Archean atmosphere beyond the absence of O_2, as soon as additional experimental measurements of MIF-S producing processes become available.

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* Corresponding author at: Department of Earth and Environmental Sciences, University of St Andrews, Irvine Building, St Andrews, Fife KY16 9AL, UK. Tel.: +44 (0)1334 463688.

E-mail address: mc229@st-andrews.ac.uk (M.W. Claire).

1. INTRODUCTION AND BACKGROUND

The presence of mass-independent fractionation in sulfur isotopes (MIF-S or $\Delta^{33/36}S$[1]) is a distinctive feature of sedimentary rocks older than 2.45 Gyr, and constrains paleoatmospheric composition. Both formation and preservation of MIF-S require reducing atmospheric conditions (Farquhar et al., 2000a, 2001; Pavlov and Kasting, 2002; Ono et al., 2003; Zahnle et al., 2006), so the existence of the MIF-S data indicates the near absence of O_2, and the presence of a reducing gas (likely CH_4 and/or H_2). The geologic record preserves time-varying magnitudes and signs of MIF-S in both sulfides and sulfates, along with correlations between $\Delta^{33}S$ and $\Delta^{36}S$. These additional parameters might allow us to infer the concentrations of other gases in the ancient atmosphere, if we can correctly model MIF-S formation, deposition, and preservation (Lyons, 2009; Farquhar et al., 2013; Halevy, 2013). Here, we focus on the methodology to model atmospheric formation and deposition of $\Delta^{33}S$.

The only two mechanisms experimentally shown to produce the coincident large absolute values of $\Delta^{33}S$ and $\Delta^{36}S$ seen in the Archean geologic record involve gas phase SO_2. These are the photolytic destruction of SO_2 (Farquhar et al., 2000a, 2001), an atmospheric reaction $SO_2 + hv \rightarrow SO + O$ triggered by absorption of photons (hv) between 180 and 220 nm (the SO_2 "photolysis band"), and the SO_2 "photoexcitation band" between 250 and 350 nm (Danielache et al., 2012; Whitehill and Ono, 2012; Whitehill et al., 2013), where the absorbed energy is not enough to break the SO_2 bond ($SO_2 + hv \rightarrow SO_2^* \rightarrow SO_2$). In the modern atmosphere, O_2 and O_3 absorb UV radiation at wavelengths between 180 and 300 nm, preventing significant tropospheric SO_2 photolysis and MIF-S generation. By contrast, in the absence of O_2/O_3, 180–220 nm photons reach the lower atmosphere, enabling formation of large MIF-S by SO_2 photolysis. More critically, nearly all sulfur input into the modern atmosphere is removed in a single redox state (SO_4^{2-}). The preservation potential of MIF-S is significantly enhanced in reducing atmospheres as these conditions allow sulfur to leave the atmosphere via multiple "exit channels" (sulfate, S_8 aerosol, and/or SO_2), enabling transfer of any generated isotopic heterogeneity to the surface environment (Pavlov and Kasting, 2002; Ono et al., 2003; Halevy et al., 2010; Zerkle et al., 2012). Preservation potential is further enhanced in anoxic oceans, which enable burial of discrete redox phases before isotopic homogenization (Farquhar et al., 2013; Halevy, 2013).

While the presence of large Archean $\Delta^{33}S$ and $\Delta^{36}S$ is widely accepted as indicating a reducing atmosphere (Farquhar et al., 2007; Johnston, 2011), the magnitude and sign of MIF-S is less understood. The Archean data (Fig. 1) show positive and negative $\Delta^{33}S$ values in both sulfides and sulfates. A puzzling asymmetry exists: negative $\Delta^{33}S$ magnitudes rarely extend below $-2‰$, while positive $\Delta^{33}S$ signals range as high as $+12‰$. There are multiple
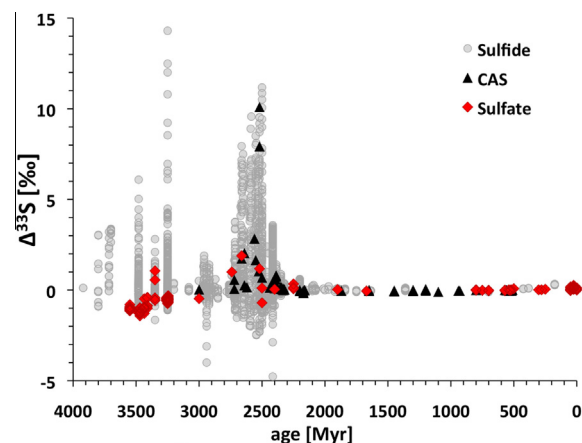

Fig. 1. A compilation of $\Delta^{33}S$ in sedimentary sulfides (grey circles), sulfates (red diamonds), and carbonate associated sulfate (black triangles), updated from the compilation in Stüeken et al. (2012) and references therein, and supplemented with additional data (Fabre et al., 2011; Bontognali et al., 2012; Bühn et al., 2012; Guy et al., 2012; McLoughlin et al., 2012; Philippot et al., 2012; Roerdink et al., 2012, 2013; Grosch and McLoughlin, 2013; Johnson et al., 2013; Kurzweil et al., 2013; Thomazo et al., 2013). Detrital, igneous and hydrothermal sulfides were excluded, as were diamond inclusions and ice-core sulfate data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

possible explanations for the asymmetry, including dilution by biogeochemical processes prior to sedimentation (Halevy et al., 2010), sampling bias, or preservational bias due to scarcity of Archean deep-sea sediments, soils (Maynard et al., 2013) or carbonate-associated sulfate (CAS) data. Preservational bias may be important if the mantle is a long-term reservoir for negative $\Delta^{33}S$ (Farquhar et al., 2002, 2010; Cabral et al., 2013). Alternatively, the asymmetry could result from atmospheric mass balance, whereby a single MIF-S formation mechanism partitions into a dominant reservoir with small magnitude negative $\Delta^{33}S$ and a minor (by mass) exit channel with a correspondingly larger positive $\Delta^{33}S$ signal (Zerkle et al., 2012). This latter interpretation is exemplified by oxygen MIF in the modern atmosphere, which arises during O_3 formation (Thiemens and Heidenreich, 1983). Large positive $\Delta^{17}O$ are seen in quantitatively small exit channels such as nitrate, sulfates, and perchlorates (e.g., Bao and Gu, 2004; Michalski et al., 2004), while the very small negative $\Delta^{17}O$ remains in the much larger reservoir of atmospheric O_2 (Luz et al., 1999).

A widely adopted interpretation of the sign of geologic $\Delta^{33}S$ is that it reflects a single, primary atmospheric source mechanism which partitions into a positive $\Delta^{33}S$ elemental sulfur exit channel and a negative $\Delta^{33}S$ sulfate exit channel (Farquhar et al., 2001; Pavlov and Kasting, 2002; Ono et al., 2003, 2006b, 2009a). This "conventional interpretation" therefore requires that most observed sedimentary sulfides are derived directly from reduced atmospheric species (H_2S or S_8) carrying positive $\Delta^{33}S$, and that most sulfates are derived directly from more oxidized species

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[1] $\delta^{3x}S = 1000[(^{3x}S/^{32}S_{model})/(^{3x}S/^{32}S_{standard}) - 1]$, with a standard value of 1 adopted in these calculations. $\Delta^{33}S$ is calculated as $\delta^{33}S - 0.515 \delta^{34}S$.