



Multiple sulfur isotope constraints on the modern sulfur cycle



Rosalie Tostevin^{a,*}, Alexandra V. Turchyn^b, James Farquhar^c, David T. Johnston^d, Daniel L. Eldridge^c, James K.B. Bishop^e, Matthew Mcllvain^f

^a Department of Earth Sciences, University College London, Gower Street, London, WC1E 6BT, UK

^b Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, UK

^c Department of Geology and Earth Systems Science Interdisciplinary Center, University of Maryland, College Park, MD 20742, USA

^d Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, USA

^e Department of Earth and Planetary Science, University of California, Berkeley, Berkeley, CA 94720-4767, USA

^f Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

ARTICLE INFO

Article history:

Received 7 September 2013

Received in revised form 26 March 2014

Accepted 27 March 2014

Available online 16 April 2014

Editor: G.M. Henderson

Keywords:

sulfur isotopes
multiple sulfur isotopes
pyrite flux
sulfur cycle
sulfate reduction
biogeochemical cycles

ABSTRACT

We present 28 multiple sulfur isotope measurements of seawater sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$ and $\Delta^{33}\text{S}_{\text{SO}_4}$) from the modern ocean over a range of water depths and sites along the eastern margin of the Pacific Ocean. The average measured $\delta^{34}\text{S}_{\text{SO}_4}$ is 21.24‰ ($\pm 0.88\text{‰}$, 2σ) with a calculated $\Delta^{33}\text{S}_{\text{SO}_4}$ of +0.050‰ ($\pm 0.014\text{‰}$, 2σ). With these values, we use a box-model to place constraints on the gross fraction of pyrite burial in modern sediments. This model presents an improvement on previous estimates of the global pyrite burial flux because it does not rely on the assumed value of $\delta^{34}\text{S}_{\text{pyrite}}$, which is poorly constrained, but instead uses new information about the relationship between $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ in global marine sulfate. Our calculations indicate that the pyrite burial flux from the modern ocean is between 10% and 45% of the total sulfur lost from the oceans, with a more probable range between 20% and 35%.

© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/3.0/>).

1. Introduction

Sulfate is the second most abundant anion in the oceans and has a residence time of 10–20 million years, which far exceeds the mixing time of the ocean (Paytan et al., 2004). As a result, the concentration of sulfate, 28 mM, and its sulfur isotope composition should not vary among or within ocean basins. Sulfate is supplied to the ocean through rivers and removed during pyrite and evaporite mineral deposition and during hydrothermal alteration of the ocean crust (Kaplan, 1983; Krouse, 1980). Sulfate is respired during dissimilatory sulfate reduction by sulfate reducing microbes in anoxic sediments (Jørgensen, 1982). The sulfide produced during this sulfate reduction can either be buried as pyrite and enter the geologic record or be returned to the marine sulfate pool via abiotic or biotic sulfide oxidation.

The $\delta^{34}\text{S}$ of modern ocean sulfate is spatially homogeneous, and its value reflects the sources and sinks of sulfate to the ocean; the $\delta^{34}\text{S}$ of marine sulfate is particularly sensitive to the $\delta^{34}\text{S}$ of river input, the $\delta^{34}\text{S}$ associated with pyrite burial, and the flux of the buried pyrite sink (Berner and Canfield, 1989;

Garrels and Lerman, 1981, 1984). The $\delta^{34}\text{S}$ of river input reflects the minerals being weathered, and is typically thought to be between 5 and 15‰ (Canfield, 2004, 2013; Holser et al., 1988; Kurtz et al., 2003). The traditional accepted value for the $\delta^{34}\text{S}$ of marine sulfate is 20.3‰, with a typical uncertainty of $\pm 0.8\text{‰}$ (2σ) (from the reproducibility of the international marine sulfate standard, IAEA NBS127). Rees (1978) later demonstrated that there is a slight bias towards lower $\delta^{34}\text{S}$ values when sulfur isotopes are measured via combustion to sulfur dioxide and redefined the seawater value closer to 20.6‰. This $\delta^{34}\text{S}$ of marine sulfate is elevated over the $\delta^{34}\text{S}$ of the global river input because of the preferential burial of ^{32}S rich pyrite in marine sediments.

The sulfur isotopic composition of pyrite is controlled by sulfate reducing microorganisms as well as organisms that metabolize sulfur compounds at oxidation states intermediate between sulfide and sulfate. A wide phylogenetic range of microorganisms have been studied both *in situ* and in the laboratory setting to assess their sulfur isotope partitioning (Canfield et al., 2010; Chambers and Trudinger, 1979; Johnston et al., 2005, 2007; Kaplan and Rittenberg, 1964; Leavitt et al., 2013; Sim et al., 2011; Zerkle et al., 2009). These studies have shown that the sulfur isotope fractionation varies as a function of the metabolic make-up of the microbial community and the growth conditions (e.g. pressure, temperature, organic carbon availability, sulfate concentrations and

* Corresponding author. Tel.: +44 (0)7884308239.

E-mail address: rosalie.tostevin.11@ucl.ac.uk (R. Tostevin).

type of electron donors). A wide range of sulfur isotope fractionation can result from microbial sulfate reduction by even a single species of bacteria (Leavitt et al., 2013; Sim et al., 2011), and large sulfur isotope fractionations have also been recorded in natural populations of sulfate reducers (Canfield et al., 2010). When a range of metabolisms cohabitate in natural environments, the result is a mix of $\delta^{34}\text{S}$ signatures that often offset one another. As a result, pyrite grains can display large local variability in $\delta^{34}\text{S}$, with a range of up to 35‰ reported from pyrite grains within a single sediment sample (Kohn et al., 1998). It is therefore difficult to define a global average value for $\delta^{34}\text{S}_{\text{pyr}}$ from direct measurements. The $\delta^{34}\text{S}$ of marine pyrite is often taken to be between 15‰ and –50‰ (Strauss, 1997).

The other primary control on the $\delta^{34}\text{S}$ of marine sulfate is the flux of pyrite burial, which is often considered as the proportion of the total sulfur flux from the oceans (Garrels and Lerman, 1981; Halevy et al., 2012; Holser et al., 1988). This proportional pyrite burial flux varies with the availability of suitable environments for sulfate reduction, favored by anoxia either in the water column or in shallow organic-rich sediments, and the rate of active iron delivery (to precipitate the sulfide as pyrite). Assuming a $\delta^{34}\text{S}$ of river input and average $\delta^{34}\text{S}$ of pyrite buried, the $\delta^{34}\text{S}$ of marine sulfate has been used to place constraints on this proportional pyrite burial flux over time. Canfield (2004) argued that nearly all sulfur was buried as pyrite in the Precambrian and that the proportional fraction of pyrite burial dropped significantly during the Palaeozoic to around 30% today. A number of other studies have also suggested that the present-day proportional pyrite burial flux is close to 30–40% of the total sulfur lost from the oceans (Bernier, 1989, 1987; Canfield, 2004; Kampschulte and Strauss, 2004; Kump and Garrels, 1986; Ono et al., 2006), with the rest of the sulfur leaving the oceans as evaporite minerals or in hydrothermal systems. Recently, Halevy et al. (2012) suggested that the net evaporite burial flux is lower than the estimates used in some of these models, and arrived at significantly higher Phanerozoic proportional net pyrite burial fluxes (70–90%). These authors suggested that the $\delta^{34}\text{S}$ of modern river input is elevated in its $\delta^{34}\text{S}$ due to contributions from rapidly recycled evaporites, and that when this ‘gross flux’ of evaporites is removed, the $\delta^{34}\text{S}$ of river input is lower and thus the proportional net pyrite burial flux must be much higher. Canfield (2013) has since shown that the $\delta^{34}\text{S}$ of Phanerozoic coal can be used to constrain the $\delta^{34}\text{S}$ of riverine input, and suggests that river input remained elevated throughout the Phanerozoic, indicating that the effect of these rapidly recycled evaporites has been present over the last 500 million years. The $\delta^{34}\text{S}$ of marine sulfate reflects the integrated riverine flux from both the rapidly recycled evaporites as well as the longer tectonically controlled weathering of ancient evaporites, pyrite and magmatic sulfide.

Inclusion of minor sulfur isotope ratios (e.g. $^{33}\text{S}/^{32}\text{S}$) may place additional constraints on the fraction of sulfur buried as pyrite (Ono et al., 2006) and also on biological reactions that partition, or separate, isotopes as a function of their mass (Johnston et al., 2005, 2006, 2008; Leavitt et al., 2013; C. Li et al., 2010; X. Li et al., 2010; Sim et al., 2011; Wu et al., 2010; Zerkle et al., 2009). If all sulfur isotope fractionation followed the same mass law, then the amount of ^{33}S in the modern ocean could be directly calculated from the relative amount of ^{34}S versus ^{32}S , and so no new information would be gained by measuring the less abundant sulfur isotopes. However, there are unique mass laws that control different mass dependent processes, and these can be identified using high-precision measurements of both major and minor sulfur isotopes. Deviations from expected mass dependence are reported using $\Delta^{33}\text{S}$ (Farquhar et al., 2000; Hulston and Thode, 1965; Ono et al., 2006), which is defined as:

$$\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \left[\left(1 + \frac{\delta^{34}\text{S}}{1000} \right)^{0.515} - 1 \right] \quad (1)$$

where the reference mass dependence law has been assigned an exponent of 0.515. Small shifts from the theoretical equilibrium value of 0.515 occur in different metabolic pathways, and can generate small non-zero $\Delta^{33}\text{S}$ values on the order of a few tenths of a permil during purely mass-dependent biological processes. These deviations result from intracellular branching reactions with back-and-forth exchange of sulfur between multiple reservoirs (Farquhar et al., 2003, 2007; Johnston et al., 2005; Ono et al., 2006). These small variations in the exponent of Eq. (1) that are provided by the analysis of both $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ can be used to trace microbial processes in the sulfur cycle. Although the $\delta^{34}\text{S}$ of modern marine sulfate is well constrained, $\delta^{33}\text{S}$ has seldom been measured alongside $\delta^{34}\text{S}$. Some $\delta^{33}\text{S}$ data has been reported for standard materials that derive from seawater sulfate, IAEA-S2 and NBS-127 (Ono et al., 2006; Peters et al., 2010; Wu et al., 2010), as well as for several seawater samples from sites close to both Bermuda and Hawaii (Ono et al., 2012).

Sulfate reducing bacteria, sulfur disproportionating bacteria and sulfide oxidizing bacteria have all been assessed for their associated multiple sulfur isotope fractionations (Farquhar et al., 2003; Johnston et al., 2005, 2007; Zerkle et al., 2009). The minor isotope relationship describing the metabolism-specific effects or mass law is often expressed as $^{33}\lambda$. This term defines the slope of a line in $\delta^{34}\text{S}$ – $\delta^{33}\text{S}$ space and is defined as:

$$^{33}\lambda_{\text{pyr-SW}} = \frac{\left[\ln \left(1 + \frac{\delta^{33}\text{S}_{\text{pyr}}}{1000} \right) - \ln \left(1 + \frac{\delta^{33}\text{S}_{\text{SW}}}{1000} \right) \right]}{\left[\ln \left(1 + \frac{\delta^{34}\text{S}_{\text{pyr}}}{1000} \right) - \ln \left(1 + \frac{\delta^{34}\text{S}_{\text{SW}}}{1000} \right) \right]} \quad (2)$$

The $^{33}\lambda$ values measured for modern microbial communities range from 0.508 to 0.514 for sulfate reduction, with higher values describing oxidative metabolisms. Much work is needed to define the full range of fractionations and $^{33}\lambda$ that are possible during sulfur transformations, such as thermochemical sulfate reduction and inorganic sulfur oxidation. However, the values for sulfate reduction capture the geological average for all published sulfide data, suggesting that sulfate reducers are the primary sulfur isotope fractionation mechanism within the sulfur cycle (Johnston, 2011).

In this study we have measured both $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ in sulfate in modern seawater from sites at various locations and depths on the eastern margin of the Pacific Ocean, which we use to calculate the $\Delta^{33}\text{S}$ of marine sulfate. We use the average $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ of sulfate to build a box model to explore the range of possible $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ values associated with pyrite burial in modern marine sediments and then compare these with published pyrite sulfur isotope data. This is a methodologically different approach than has been taken previously. Constraints on $^{33}\lambda$ and the multiple sulfur isotope composition of riverine sulfur input are used to quantify the proportional flux of buried pyrite in modern ocean sediments.

2. Methods

Seawater samples were collected during two separate cruises to the eastern margin of the Pacific Ocean (Fig. 1). Samples from off the coast of Peru were collected in October–November 2005 through the Woods Hole Oceanographic Institute. These samples were collected between 0 and 3000 m depth, using Niskin bottles and then transferred into 60 mL HDPE bottles. The bottles were rinsed three times with sample prior to filling and stored frozen at –20 °C until analysis. Samples from off the coast of southern California were collected in June 2007. These samples were collected between 0 and 1000 m water depth using rosette mounted 10 L PVC Niskin Bottles in the San Clemente Basin. All samples were syringe filtered and stored without acid prior to isotope analyses.

Download English Version:

<https://daneshyari.com/en/article/6429526>

Download Persian Version:

<https://daneshyari.com/article/6429526>

[Daneshyari.com](https://daneshyari.com)