



Sulfur isotopes in rivers: Insights into global weathering budgets, pyrite oxidation, and the modern sulfur cycle

Andrea Burke^{a,b,*}, Theodore M. Present^b, Guillaume Paris^{b,c}, Emily C.M. Rae^a,
Brodie H. Sandilands^a, Jérôme Gaillardet^{d,e}, Bernhard Peucker-Ehrenbrink^f,
Woodward W. Fischer^b, James W. McClelland^g, Robert G.M. Spencer^h, Britta M. Voss^f,
Jess F. Adkins^b

^a University of St Andrews, St Andrews, UK

^b California Institute of Technology, Pasadena, CA, USA

^c CRPG – CNRS, Vandoeuvre-lès-Nancy, France

^d Institut de Physique du Globe de Paris (IPGP), Sorbonne Paris Cité, University Paris Diderot, CNRS, Paris, France

^e Institut Universitaire de France, France

^f Woods Hole Oceanographic Institution, Woods Hole, MA, USA

^g University of Texas at Austin, Austin, TX, USA

^h Florida State University, Tallahassee, FL, USA

ARTICLE INFO

Article history:

Received 6 November 2017

Received in revised form 13 May 2018

Accepted 14 May 2018

Available online xxxx

Editor: D. Vance

Keywords:

sulfur
rivers
weathering
pyrite

ABSTRACT

The biogeochemical sulfur cycle is intimately linked to the cycles of carbon, iron, and oxygen, and plays an important role in global climate via weathering reactions and aerosols. However, many aspects of the modern budget of the global sulfur cycle are not fully understood. We present new $\delta^{34}\text{S}$ measurements on sulfate from more than 160 river samples from different geographical and climatic regions—more than 46% of the world's freshwater flux to the ocean is accounted for in this estimate of the global riverine sulfur isotope budget. These measurements include major rivers and their tributaries, as well as time series, and are combined with previously published data to estimate the modern flux-weighted global riverine $\delta^{34}\text{S}$ as $4.4 \pm 4.5\%$ (V-CDT), and $4.8 \pm 4.9\%$ when the most polluted rivers are excluded. The sulfur isotope data, when combined with major anion and cation concentrations, allow us to tease apart the relative contributions of different processes to the modern riverine sulfur budget, resulting in new estimates of the flux of riverine sulfate due to the oxidative weathering of pyrites ($1.3 \pm 0.2 \text{ Tmol S/y}$) and the weathering of sedimentary sulfate minerals ($1.5 \pm 0.2 \text{ Tmol S/y}$). These data indicate that previous estimates of the global oxidative weathering of pyrite have been too low by a factor of two. As pyrite oxidation coupled to carbonate weathering can act as a source of CO_2 to the atmosphere, this global pyrite weathering budget implies that the global CO_2 weathering sink is overestimated. Furthermore, the large range of sulfur isotope ratios in modern rivers indicates that secular changes in the lithologies exposed to weathering through time could play a major role in driving past variations in the $\delta^{34}\text{S}$ value of seawater.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

The biogeochemical sulfur cycle is intimately linked to the cycles of carbon and oxygen (e.g. Berner and Raiswell, 1983). Reconstructing the sources and sinks of sulfur to the marine environment in the past is thus important for understanding long-term changes in climate and the redox processes operating in Earth's surface environments. The sulfur isotope compositions of

these sources and sinks provide a sensitive tracer of the processes that drive the sulfur cycle because there are large isotope fractionations that occur associated with cycling sulfur between oxidized and reduced phases (e.g. Garrels and Lerman, 1984). Microbial sulfate reduction, for instance, imparts a large sulfur isotope fractionation ($\varepsilon \approx 0$ to -70% (e.g. Habicht and Canfield, 2001; Sim et al., 2011)), leaving, on average, pyrite and other sulfide-bearing minerals with lower sulfur isotope ratios than seawater and sedimentary sulfate.

Reconstructions of sulfur isotope ratios through geologic time from marine sedimentary rocks have typically been used to infer

* Corresponding author.

E-mail address: ab276@st-andrews.ac.uk (A. Burke).

past changes in the burial flux of reduced sulfur (pyrite) relative to the removal of oxidized sulfur in the form of sulfate (evaporite deposits) (Kump and Garrels, 1986). In a simple isotope box model of the marine sulfur reservoir, variations in the isotopic composition of marine sulfate are interpreted as being driven by relative changes in these outputs, while typically assuming that the input of sulfur to the ocean has remained constant through time. Recent work (Halevy et al., 2012), however, has highlighted the need to consider changes in the flux and the isotopic composition of sulfur to the ocean. Riverine sulfur is the major source of sulfate to the ocean, supplying approximately 4.7 Tmol/y today (including 1.3 Tmol/y from anthropogenic sources (Meybeck, 2003)). Thus in order to fully understand the secular changes in the $\delta^{34}\text{S}$ value of seawater, we need to better constrain both the modern values for, and controls on, the isotopic composition of riverine sulfate.

The modern riverine sulfur isotopic composition can also inform estimates of chemical weathering fluxes, with important implications for the carbon cycle. Sulfur isotopes in rivers can provide insight into how much riverine sulfate is sourced from dissolution of sedimentary sulfate minerals versus oxidative weathering of pyrite (OWP) (Calmels et al., 2007). OWP produces sulfuric acid, which is a source of acidity for chemical weathering and which, when it interacts with carbonate minerals, can lead to a net release of CO_2 , in contrast to the sink of CO_2 associated with silicate weathering (e.g. Calmels et al., 2007; Torres et al., 2015, 2016). Previous estimates of global OWP fluxes range from 0.5 to 0.65 Tmol/y (Francois and Walker, 1992; Berner and Berner, 1996; Lerman et al., 2007). However, recent studies that use sulfur isotopes (and sulfate-oxygen isotopes) from individual catchments indicate that estimates of global OWP flux are potentially much too low. The sum of OWP fluxes (0.15 Tmol/y) from just three river basins (Mackenzie (Calmels et al., 2007), Kaoping (Das et al., 2012), and Jialing (Li et al., 2011)) can account for a third of previous global OWP flux estimates, despite covering less than 2% of global land area (Das et al., 2012). Underestimating global OWP by this magnitude may result in substantial overestimates of the modern-day sink of CO_2 associated with chemical weathering.

1.1. Previous estimates of $\delta^{34}\text{S}$ of river water

Previous estimates of the global sulfur isotopic composition of rivers come from either measurements of river water from a single geographical region (Ivanov et al., 1983) or back-of-the-envelope calculations based on simple geochemical assumptions (Berner and Berner, 1996). The previous data-based study that included the largest amount of river data was limited to the Eurasian continent, and reported an average riverine $\delta^{34}\text{S}$ of 9.2‰ (Ivanov et al., 1983). The rivers sampled represent only 7% of the total global riverine discharge and have a total sulfate flux of 0.4 Tmol/y, accounting for only 9% of the total riverine sulfate flux. The limited geographic extent of this estimate raises the question of how representative the value of 9.2‰ is for the global riverine $\delta^{34}\text{S}$ input to the oceans, especially given that many of the rivers sampled are weathering large evaporitic deposits of Cambrian/Ordovician age that are exposed across the Siberian Platform (Ivanov et al., 1983; Huh et al., 1998b). These deposits might bias the riverine $\delta^{34}\text{S}$ to high values, since evaporites have $\delta^{34}\text{S}$ values reflecting the seawater $\delta^{34}\text{S}$ during the time of deposition, and range from between 10‰ to 30‰ (e.g. Kampschulte and Strauss, 2004).

Geochemical calculations tend to form the basis of the most commonly cited sulfur isotope compositions for modern riverine sulfate. Isotope mass balance models of the sulfur cycle have typically employed a riverine $\delta^{34}\text{S}$ value of around 7–8‰ (e.g. Garrels and Lerman, 1984; Kump and Garrels, 1986; Kurtz et al., 2003; Halevy et al., 2012). These values can be traced back to assumptions about the relative contributions of sulfide and sulfate weathering to the riverine sulfate budget.

Specifically, it was assumed that the abundance of sedimentary sulfate minerals is equal to the abundance of sedimentary sulfide minerals and that gypsum weathers twice as fast as pyrite (Berner and Berner, 1996). These two assumptions imply that sulfate mineral weathering should contribute twice as much sulfate to rivers as pyrite weathering. Thus, if a $\delta^{34}\text{S}$ value of 17‰ is assumed for sulfate in evaporite minerals and a $\delta^{34}\text{S}$ value of –12‰ is assumed for pyrite, then a simple river isotope mass balance predicts an average riverine $\delta^{34}\text{S}$ of between 7 to 8‰ (ignoring anthropogenic and other minor sources of sulfate to rivers). It is important to note that because these calculations assumed a fixed ratio of riverine sulfur from sulfide weathering to sulfate weathering, this isotopic composition cannot then be used to calculate the relative proportion of sulfide weathering.

Given the large uncertainties in these estimates of the relative fluxes in the modern biogeochemical sulfur cycle, and the resulting implications for weathering and the modern carbon cycle, the aims of this paper are to: (1) re-evaluate the modern global sulfur isotopic composition of riverine sulfate, and (2) estimate the modern flux of pyrite-derived sulfate supplied to the ocean from rivers using two different and complementary methods: a weathering end-member decomposition and a simple sulfur isotope mass balance.

2. Methods

2.1. Measurement of river water sulfate and $\delta^{34}\text{S}$

River waters were sampled either opportunistically or as part of a number of field campaigns between years 1993–2013. Details of all rivers measured in this study for sulfur isotopes can be found in Supplementary Table 1. Previously published sulfur isotope data from main stems of rivers were compiled from the literature, and can be found in Supplementary Table 2, along with the new main stem data from this study. The locations of the main stems of rivers included in this study can be seen in Fig. 1.

The concentration of sulfate in river waters was determined by ion chromatography with a Dionex ICS-2000, using an AS-19 column and 20 mM KOH eluent at the Environmental Analysis Center at Caltech. River samples were then dried down and re-dissolved in 0.01 M HCl. The sulfate was purified from its matrix with an anion exchange column as described in Paris et al. (2014).

New measurements of sulfur isotopes in rivers were made by MC-ICP-MS on a Neptune Plus at Caltech (Paris et al., 2013). Measurement by MC-ICP-MS reduces sample size requirements by three orders of magnitude over traditional gas source mass spectrometric methods, and thus only 20 nmol of sulfate were needed for each sample. Typical rivers have micromolar concentrations of sulfate, thus sample sizes were in the range of 100 μL to a few mL of river water depending on concentration. An in-house sodium sulfate solution was used as a bracketing standard on the MC-ICP-MS to correct for instrumental mass bias. Consistency in chemical preparation and isotope measurement was monitored with multiple full replicates of a seawater standard ($21.04 \pm 0.17\text{‰}$ V-CDT 2 s.d.; $n = 20$) and an in-house consistency standard from a filtered river water sample collected from the headwaters of the Arroyo Seco in Angeles National Forest, California near Switzer Falls ($4.11 \pm 0.24\text{‰}$ V-CDT 2 s.d.; $n = 10$).

Complete chemistry blanks were monitored along with every set of 10 samples, and contained an average of 0.1 nmol of sulfate. As the smallest samples measured had 20 nmol of sulfate, the blank contamination contributes at most 0.5% of the total sulfate measured, and typically contributes closer to 0.1%, as most samples were analyzed with at least 100 nmol of sulfate. The $\delta^{34}\text{S}$ value of the blank is typically close to zero, with a long-term average for

Download English Version:

<https://daneshyari.com/en/article/8906780>

Download Persian Version:

<https://daneshyari.com/article/8906780>

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