



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

Andrea Burke, Theodore Present, Guillaume Paris, Emily C.M. Rae, Brodie Sandilands, Jérôme Gaillardet, Bernhard Peucker-Ehrenbrink, Woodward Fischer, James Mcclelland, Robert G.M. Spencer, et al.

### **► To cite this version:**

Andrea Burke, Theodore Present, Guillaume Paris, Emily C.M. Rae, Brodie Sandilands, et al.. Sulfur isotopes in rivers: Insights into global weathering budgets, pyrite oxidation, and the modern sulfur cycle. *Earth and Planetary Science Letters*, 2018, 496, pp.168-177. 10.1016/j.epsl.2018.05.022 . hal-02118784

**HAL Id: hal-02118784**

**<https://hal.science/hal-02118784>**

Submitted on 5 Dec 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Andrea Burke<sup>1,2</sup>, Theodore M. Present<sup>2</sup>, Guillaume Paris<sup>2,3</sup>, Emily C. M. Rae<sup>1</sup>,  
Brodie H. Sandilands<sup>1</sup>, Jérôme Gaillardet<sup>4</sup>, Bernhard Peucker-Ehrenbrink<sup>5</sup>,  
Woodward W. Fischer<sup>2</sup>, James W. McClelland<sup>6</sup>, Robert G.M. Spencer<sup>7</sup>, Britta M.  
Voss<sup>5</sup>, Jess F. Adkins<sup>2</sup>

<sup>1</sup> University of St Andrews, St Andrews, UK;

<sup>2</sup>California Institute of Technology, Pasadena, CA, USA

<sup>3</sup>CRPG – CNRS, Vandoeuvre-lès-Nancy, France

<sup>4</sup>Institut de Physique du Globe de Paris, Paris, France

<sup>5</sup>Woods Hole Oceanographic Institution, Woods Hole, MA, USA

<sup>6</sup>University of Texas at Austin, Austin, TX, USA

<sup>7</sup>Florida State University, Tallahassee, FL, USA

Keywords: sulfur; rivers; weathering; pyrite

## 26    **Abstract**

27            The biogeochemical sulfur cycle is intimately linked to the cycles of  
28 carbon, iron, and oxygen, and plays an important role in global climate via  
29 weathering reactions and aerosols. However, many aspects of the modern  
30 budget of the global sulfur cycle are not fully understood. We present new  $\delta^{34}\text{S}$   
31 measurements on sulfate from more than 160 river samples from different  
32 geographical and climatic regions—more than 46% of the world's freshwater  
33 flux to the ocean is accounted for in this estimate of the global riverine sulfur  
34 isotope budget. These measurements include major rivers and their tributaries,  
35 as well as time series, and are combined with previously published data to  
36 estimate the modern flux-weighted global riverine  $\delta^{34}\text{S}$  as  $4.4 \pm 4.5 \text{ ‰}$  (V-CDT),  
37 and  $4.8 \pm 4.9 \text{ ‰}$  when the most polluted rivers are excluded. Combined with  
38 major anion and cation concentrations, the sulfur isotope data allow us to tease  
39 apart the relative contributions of different processes to the modern riverine  
40 sulfur budget, resulting in new estimates of the flux of riverine sulfate due to the  
41 oxidative weathering of pyrites ( $1.3 \pm 0.2 \text{ Tmol S/y}$ ) and the weathering of  
42 sedimentary sulfate minerals ( $1.5 \pm 0.2 \text{ Tmol S/y}$ ). These data indicate that  
43 previous estimates of the global oxidative weathering of pyrite have been too  
44 low by a factor of two. As pyrite oxidation coupled to carbonate weathering can  
45 act as a source of  $\text{CO}_2$  to the atmosphere, this global pyrite weathering budget  
46 implies that the global  $\text{CO}_2$  weathering sink is overestimated. Furthermore, the  
47 large range of sulfur isotope ratios in modern rivers indicates that secular  
48 changes in the lithologies exposed to weathering through time could play a major  
49 role in driving past variations in  $\delta^{34}\text{S}$  of seawater.

50

51

## 52 **1 Introduction**

53       The biogeochemical sulfur cycle is intimately linked to the cycles of  
54 carbon and oxygen (e.g. Berner and Raiswell, 1983). Reconstructing the sources  
55 and sinks of sulfur to the marine environment in the past is thus important for  
56 understanding long-term changes in climate and the redox processes operating  
57 in Earth's surface environments. The sulfur isotope compositions of sources and  
58 sinks provide a sensitive tracer of the processes that drive the sulfur cycle  
59 because there are large isotope fractionations that occur associated with cycling  
60 sulfur between oxidized and reduced phases (e.g. Garrels and Lerman, 1984).  
61 Microbial sulfate reduction, for instance, imparts a large S isotope fractionation  
62 ( $\epsilon \approx 0$  to  $-70\text{‰}$  (e.g. Habicht and Canfield, 2001; Sim et al., 2011)), leaving—on  
63 average—pyrite and other sulfide-bearing minerals with lower sulfur isotope  
64 ratios than seawater and sedimentary sulfate.

65       Reconstructions of sulfur isotope ratios through geologic time from  
66 marine sedimentary rocks have typically been used to infer past changes in the  
67 burial flux of reduced sulfur (pyrite) relative to the removal of oxidized sulfur in  
68 the form of sulfate (evaporite deposits) (Kump and Garrels, 1986). In a simple  
69 isotope box model of the marine sulfur reservoir, variations in the isotopic  
70 composition of marine sulfate are interpreted as being driven by relative  
71 changes in these outputs, while typically assuming that the input of sulfur to the  
72 ocean has remained constant through time. Recent work (Halevy et al., 2012) ,  
73 however, has highlighted the need to consider changes in the flux and the  
74 isotopic composition of sulfur to the ocean. Riverine sulfur is the major source of  
75 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  $\delta^{34}\text{S}$  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 S 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  $\text{CO}_2$ , in contrast to the sink of  $\text{CO}_2$  associated with silicate weathering (e.g. Calmels et al., 2007; Torres et al., 2016; 2015). Previous estimates of global OWP fluxes range from 0.5 to 0.65 Tmol/y (Berner and Berner, 1996; Francois and Walker, 1992; 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  $\text{CO}_2$  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 (Huh et al., 1998b; Ivanov et al., 1983). 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 input estimates. 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; Halevy et al., 2012; Kump and Garrels, 1986; Kurtz et al., 2003). 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. Nonetheless, this approach and its origins are important and informative to the field.

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 global modern 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 Figure 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  $\mu$ L 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 chemistry and 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  $\delta^{34}\text{S}$  of the blank is typically close to zero, with a long-term average for all blanks of  $2.4 \pm 6.5\text{‰}$  (2 s.d.;  $n = 16$ ). The measured  $\delta^{34}\text{S}$  of all river samples have been blank corrected with the average of all blanks, and the uncertainty on both the amount of blank and its isotopic ratio is propagated through to the final uncertainties on the riverine  $\delta^{34}\text{S}$  values.

Global average  $\delta^{34}\text{S}$  values were calculated based on the data in Supplementary Table 2. Sulfate fluxes were calculated for these main stem rivers by multiplying sulfate concentration by discharge, and these fluxes were used to calculate the global flux-weighted average and standard deviation of  $\delta^{34}\text{S}$ .

## *2.2 End-member weathering calculation*

Previous studies have used coupled  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  in sulfate to estimate OWP fluxes in individual river catchments (Calmels et al., 2007; e.g. Karim and Veizer, 2000; Turchyn et al., 2013). These estimates do not rely on knowing the  $\delta^{34}\text{S}$  of the pyrite being weathered which can have a large range within an individual basin (e.g. Calmels et al., 2007). This is a very powerful technique, but measurement by gas source mass spectrometry requires larger sample sizes, and has only been used on a few rivers, in contrast to the numerous  $\delta^{34}\text{S}$  measurements on riverine sulfate that have been previously published. Thus, to maximize the number of rivers included in our global database, we used riverine  $\delta^{34}\text{S}$  and major anion and cation concentrations in an end-member weathering calculation following Gaillardet et al. (1999) to further constrain the global budget of sulfide weathering.

200 Rivers that were either measured or compiled for  $\delta^{34}\text{S}$  that also had Cl, Na,  
201 Mg, Ca, and Sr concentration data (42 rivers total, representing 41% of the global  
202 riverine discharge) were included in this end-member deconvolution. A  
203 correction for atmospheric deposition from rainwater was made following  
204 Gaillardet et al. (1997) based on the Cl concentration of the river. Each river was  
205 assigned a critical value of Cl (ranging from 20 to 100  $\mu\text{M}$ , Supplementary Table  
206 2) based on the evapotranspiration factor of the river basin or nearby rivers  
207 calculated from the GEMS-GLORI database (Meybeck and Ragu, 1995), and  
208 typical values of Cl concentration in rainwater (14  $\mu\text{M}$ , Moller, 1990). If the  
209 concentration of Cl in the river was less than the critical value of Cl, then all of  
210 the Cl in that river was attributed to rainwater and typical rainwater ratios of Na  
211 to Cl (1.15) were used to determine the rainwater-derived fraction of Na for that  
212 river. The remaining Na in the river was assumed to come from the weathering  
213 of silicates, carbonates, and evaporites. If the concentration of Cl in the river was  
214 greater than the critical value, it was assumed that the contribution of Cl from  
215 rainwater was equal to the critical value for that river, with the remaining Cl  
216 sourced from evaporites. Following the approach of Gaillardet et al. (1999), we  
217 then used a series of linear equations to solve for the proportions of sodium in  
218 the river that are attributed to evaporite, carbonate, and silicate weathering. The  
219 linear equations for each river were solved 10,000 times using a random  
220 sampling of weathering end-member values from a normal distribution of the  
221 values and associated uncertainties listed in Table 1. The median and standard  
222 deviation of these Monte Carlo simulations were used as the end-member  
223 fraction and uncertainty for each river (see Supplementary Information).

224 We calculated the proportion of sulfate that could be attributed to each  
 225 end-member using the S/Na in the end-members (Table 1), and the S/Na  
 226 measured in the rivers following equation 1.

227

$$228 \quad S_i = \frac{\left(\frac{S}{Na}\right)_i \alpha_i}{\left(\frac{S}{Na}\right)_{riv}} \quad \text{Equation 1}$$

229 where (S/Na) are molar ratios of sulfate to sodium, the subscript *i* refers to the  
 230 silicate, evaporite, carbonate, and rainwater end-members (Table 1), the  
 231 subscript *riv* refers to the riverine molar ratio,  $\alpha$  is the fraction of sodium  
 232 attributed to each of the end-members (*i*) from the end-member weathering  
 233 calculation, and  $S_i$  is the fraction of sulfate in the river attributed to each of the  
 234 end-members (*i*). Any sulfate that cannot be attributed to one of the four end-  
 235 members, we call “excess sulfate”. We used Monte Carlo simulations using the  
 236 end-member values and uncertainties from Table 1 as described above.

**Table 1. End-member molar ratios ( $\pm 2$  s.d.)**

Molar Ratio	Rain	Silicate	Carbonate	Evaporite
Ca/Na	0.023 $\pm$ 0.01	0.35 $\pm$ 0.25	60 $\pm$ 30	0.5 $\pm$ 0.5
Mg/Na	0.11 $\pm$ 0.01	0.25 $\pm$ 0.2	30 $\pm$ 15	0.1 $\pm$ 0.08
Sr/Na	0.0002 $\pm$ 0.0001	0.003 $\pm$ 0.001	0.04 $\pm$ 0.02	0.003 $\pm$ 0.002
Cl/Na	1.15 $\pm$ 0.1	-	-	1 $\pm$ 0.2
S/Na	0.06 $\pm$ 0.01	0.019 $\pm$ 0.005	0.06 $\pm$ 0.03	0.4 $\pm$ 0.2

237

238 Results of this calculation are sensitive to the end-member ratios selected,  
 239 especially for evaporites, which can vary widely. We use the Ca/Na, Mg/Na, and  
 240 Sr/Na end-member ratios for silicates and carbonates from Gaillardet et al.  
 241 (1999) and Negrel et al. (1993), and rainwater ratios from Berner and Berner  
 242 (1996) and Gaillardet et al. (1999). For evaporites, we calculate molar ratios  
 243 based on mineral abundances in evaporites given in Lerman et al. (2007),

assuming congruent weathering of evaporites. These evaporite based ratios are consistent with the median ratio calculated from rivers that drain evaporites (Meybeck, 1984; 1979), giving additional support for our choice of end-members<sup>1</sup>. The S/Na value for carbonates is based on the S/Ca molar ratio of 0.001 in marine carbonates (Volkov and Rozanov, 1983) and the Ca/Na value of carbonates of 60 (Negrel et al., 1993). Finally, the S/Na value of the silicate end-member is calculated from global estimates of the abundance of S and Na<sub>2</sub>O in continental igneous and metamorphic rocks (Holser and Kaplan, 1966; Rudnick and Gao, 2003). This estimate of S/Na in silicate rocks deliberately does not include sedimentary sulfides (e.g. from shales). Consequently, any sulfate derived from oxidative weathering of sedimentary pyrite would be incorporated into the excess sulfate parameter described above.

### 3 Results

The river waters analyzed in this study yield a large range of  $\delta^{34}\text{S}$  values, between -13.4‰ and 21.7‰ (Figures 1 and 2), and represent more than 46% of the global water discharge to the ocean ( $3.88 \times 10^4 \text{ km}^3/\text{y}$  (Peucker-Ehrenbrink, 2009)). This dataset includes smaller tributaries, as well as time series measurements from individual major rivers (Fraser, Lena, Ob', Yenisei, Yukon, Mackenzie, Kolyma, and Congo rivers). Within an individual river basin, there can be a large range in the  $\delta^{34}\text{S}$  of tributaries. For instance,  $\delta^{34}\text{S}$  values from the

---

<sup>1</sup> The one exception to this statement is evaporite Mg/Na. The Mg/Na ratio based on mineral abundances is 0.03, while the Mg/Na ratio from rivers draining evaporites is 0.1. However, the final results are not sensitive to the choice of this parameter, with only a 0.02 Tmol/y difference in the estimate of the global flux of sulfate from evaporites, well within the uncertainty of the calculation (0.2 Tmol/y).

Congo River and its tributaries range from 3.7 to 12.5‰ (n = 7), those from the Ganges River system range from -1 to 13.3‰ (n = 3), and those in the Amazon River basin range from 4.5 to 13.4‰ (n= 19), though most of the Amazonian tributaries have a narrow range of 4.5 to 7‰ (n=16), consistent with the findings of Longinelli and Edmond (1983).

The  $\delta^{34}\text{S}$  measured in river time series samples can also show a large range, highlighting temporal heterogeneity in the isotopic composition of riverine sulfate, that is likely driven by varying contributions from tributaries that drain different lithologies (Figure 3). For instance the  $\delta^{34}\text{S}$  of the Lena River has a range of 7‰ between May and November, the  $\delta^{34}\text{S}$  of the Mackenzie River has a range of 4.5‰ between March and September, and the  $\delta^{34}\text{S}$  of the Fraser River has a range of 5‰ over the course of a year (Supplementary Table 1; Figure 3). In contrast, time series data from the Congo, Kolyma, Ob', Yenisei, and Yukon rivers have more constant (<2‰ variation)  $\delta^{34}\text{S}$  over the course of several months to a year (Supplementary Table 1).

The flux-weighted average of the rivers gives a  $\delta^{34}\text{S}$  value of  $4.4 \pm 4.5\text{‰}$  (1 s.d.). If the polluted rivers ( $([\text{Na}] - [\text{Cl}])/[\text{Cl}] < 0.1$ ) are excluded<sup>2</sup> from this estimate, the average  $\delta^{34}\text{S}$  of riverine sulfate is  $4.8 \pm 4.9\text{‰}$ , and accounts for more than 43% of the water discharge to the ocean. The similarity between these two values suggests that the most polluted rivers do not meaningfully change the

---

<sup>2</sup> The only river with sufficient data to estimate a pre-anthropogenic, natural  $\delta^{34}\text{S}$  and flux of sulfate is the Mississippi River. Killingsworth and Bao (2015) used an isotope mixing model to estimate a pre-anthropogenic  $\delta^{34}\text{S} = -5\text{‰}$ , and a concentration of sulfate of 115  $\mu\text{M}$ . This pre-anthropogenic estimate is *lower* than the measured  $\delta^{34}\text{S} = -0.72\text{‰}$  and sulfate concentration of 462  $\mu\text{M}$  from this study (which is similar to the isotope and concentration measurements from 2009-2013 from (Killingsworth and Bao, 2015)).

estimate of the global riverine  $\delta^{34}\text{S}$  value. We therefore take the value of 4.8‰ as our best estimate of the modern pre-anthropogenic  $\delta^{34}\text{S}$  value of river water. The flux-weighted distribution of the isotopic composition of riverine sulfate (Figure 4) shows that half of the rivers have  $\delta^{34}\text{S}$  values between 1.8 and 8.2‰ (interquartile range), including the rivers with the largest flux of sulfate (Amazon and Yangtze rivers). Notable exceptions to this include the Mississippi and Lena rivers, which contribute a large flux of sulfate to the oceans, but have low (-5‰) and high  $\delta^{34}\text{S}$  (19‰) values, respectively.

We can assess how representative our subset of rivers is of global riverine discharge by comparing the flux-weighted Mg/Na and Ca/Na ratios and strontium isotopes from our dataset with global estimates of these values from previously published studies. Our flux weighted Mg/Na ratio of 0.66 and Ca/Na ratio of 1.63 are within the range of previous global estimates of these values of 0.57 to 0.70 and 1.32 to 1.67, respectively (Meybeck and Ragu, 1995; Miller et al., 2011). The same is true if we scale the river fluxes by the large scale drainage regions (Graham et al., 1999; Peucker-Ehrenbrink and Miller, 2007) following Miller et al. (2011). In this case, our subset of rivers yields a Mg/Na ratio of 0.68 and a Ca/Na ratio of 1.70, compared to previously published values of 0.55 to 0.71 and 1.27 to 1.74, respectively (Meybeck and Ragu, 1995; Miller et al., 2011). Thus, our elemental ratios support the use of this subset of rivers for global budget estimates. The flux weighted average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio from our subset of rivers with published ratios (40% of global water discharge) is 0.7115, slightly higher than estimates of global riverine  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7111 to 0.7114 (Peucker-Ehrenbrink et al., 2010; Vance et al., 2009)). The slightly more radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  value likely reflects an underrepresentation of younger, more

volcanically dominated river basins (e.g. smaller rivers on volcanic islands and along active margins) in our subset of rivers. This might bias our estimate of global riverine  $\delta^{34}\text{S}$  to higher values, but the effect is likely small given that rivers draining volcanic islands (e.g. Reunion, Iceland) have relatively low concentrations of sulfate (34-70  $\mu\text{M}$ ) and have  $\delta^{34}\text{S}$  values only slightly (1-3‰) lower than our global average (Tables 1 and 2).

### *3.1 Weathering end-member decomposition*

End-member decomposition allows us to tease apart the different sources of sulfate to rivers. A plot of  $\delta^{34}\text{S}$  of riverine sulfate versus the percentage of Na derived from silicate weathering illustrates the importance of pyrite weathering in influencing the sulfur isotopic composition of rivers (Figure 5). For rivers with no Na derived from silicate weathering, the only other two sources of Na are evaporite and carbonate minerals. As both of these lithologies reflect the sulfur isotopic composition of seawater when they were formed, they should both have high  $\delta^{34}\text{S}$  values ( $\sim 17\text{‰}$ , (Holser and Kaplan, 1966)). Similarly, for rivers that derive 100% of their Na from silicate weathering (none from evaporites or carbonates), the  $\delta^{34}\text{S}$  of river water should be similar to the silicate value of 4‰ (Holser and Kaplan, 1966). These two end-members determine the red mixing lines in Figure 5. Most data plot below these mixing lines, implying a  $^{34}\text{S}$ -depleted source of sulfate to the rivers that does not also add Na. The oxidative weathering of sedimentary pyrite could reasonably constitute such a source.

We further quantify the sources of sulfate to rivers by using the end-member values of S/Na from Table 1 and Equation 1 to convert fractional

contributions of Na from the different end-members into fractional contributions of S from the different end-members. Based on our end-member decomposition, evaporite weathering contributes  $31 \pm 6\%$  ( $1.5 \pm 0.2$  Tmol/y) to the global riverine sulfate budget. We find that the contribution of rainwater sulfate to rivers in our database is minor, contributing about 1.6% (0.07 Tmol/y) to the total riverine sulfate flux, consistent with independent estimates of the contribution of cyclic sea salts (0.09 – 0.13 Tmol/y; (Berner and Berner, 1996; Eriksson, 1963)) to riverine sulfate. The contribution of carbonate and silicate weathering is also minor with only 0.01 and 0.09 Tmol/y derived from each of those end-members, respectively.

The remaining sulfate in each river that cannot be readily attributed to carbonate, silicate, and evaporite weathering, or to rainwater (sea-salt) constitutes a parameter we call “excess sulfate”. This “excess sulfate” is a combination of the other major sources of sulfate to rivers: pollution, volcanic atmospheric deposition, biogenic emissions, and the oxidative weathering of sedimentary pyrite. This relative contribution of excess sulfate ranges from 0 to more than 97% for all rivers, with the exception of the Narmada and Tapti rivers, which have negative excess sulfate values. A negative excess sulfate value implies that the sulfate in those rivers can be more than accounted for by weathering of the three end-members and rainwater inputs, and thus could indicate an unidentified sink for sulfate along the river (e.g. in the river flood plain). For example, from sulfur isotope data it was suggested that removal of riverine sulfate might occur via sulfate reduction and sulfide precipitation in weakly developed soils in the Marsyandi River catchment in the Himalaya (Turchyn et al., 2013). However, the extent to which this process occurs in other



river systems remains to be established (Torres et al., 2016). The excess sulfate values thus represent minimum values, and for the remainder of this study we will ignore the two rivers in our compilation that have a negative excess sulfate.

The flux weighted global percentage of excess sulfate is  $65 \pm 6\%$  ( $3.1 \pm 0.2$  Tmol/y), which is dominated by pyrite weathering and pollution. The contributions to riverine sulfate from volcanoes and biogenic emissions are both relatively small (0.34 and 0.14 Tmol/y, respectively (Berner and Berner, 1996)). Using an estimate of the pollutive sulfate in rivers of 1.3 Tmol/y (Meybeck, 2003), we estimate that the global contribution of oxidative weathering of pyrite to riverine sulfate is 1.3 Tmol/y, or about 28% of the total sulfate flux from all sources to the ocean (4.7 Tmol/y), and 46% of the flux of sulfate from weathering (i.e. 2.8 Tmol/y, excluding sulfate from pollution, volcanoes, biogenic emissions, and cyclic sea salts).

## 4 Discussion

### 4.1 Controls on riverine sulfate $\delta^{34}\text{S}$

The highest  $\delta^{34}\text{S}$  values measured (14.4 to 21.7‰) come from the Lena and Yenisei rivers which drain the Siberian Platform—a region of large evaporite and carbonate platforms deposited from late Proterozoic through Paleozoic time (Huh et al., 1998b). Since these rocks are abundant in sulfate phases derived from seawater, they are characterized by relatively high  $\delta^{34}\text{S}$  values. The sulfate minerals weather readily, resulting in both high concentrations of sulfate and high  $\delta^{34}\text{S}$  values for these rivers. The lowest  $\delta^{34}\text{S}$  values (-8.5 to -13.4‰) come from tributaries of the Santa Clara River (e.g. Sespe) in Southern California, which weather sandstones, siltstones, and organic-rich shales of the Monterey

Formation and equivalent units. Sedimentary evaporites are absent from the underlying strata, and thus sulfate in these rivers is likely dominated by the oxidation of pyrite and organic sulfur molecules, which, due to the biological isotope fractionations associated with sulfate reduction in organic-rich sediments during their diagenesis and lithification, results in lower overall  $\delta^{34}\text{S}$  values. The lowest  $\delta^{34}\text{S}$  values measured in major rivers come from the Orinoco (-5.1‰) and the Kolyma (-4.2 to -5.6‰) rivers, which also drain catchments rich in sedimentary rocks, including black shales (Edmond et al., 1996; Huh et al., 1998a). These examples are consistent with the notion that local lithology plays a key role in setting the sulfur isotopic composition of rivers, and the important role of black shale weathering in the sulfur budget.

Plots of the  $\delta^{34}\text{S}$  versus inverse concentration of sulfate and versus the riverine  $\text{Na}/\text{SO}_4$  ratio (Figure 2) show a triangular pattern, indicative of at least three end-members contributing to sulfate in rivers. The most sulfate-rich rivers span a wide range of  $\delta^{34}\text{S}$  values (-13 to 21‰), whereas the rivers with the lowest sulfate concentrations cluster tightly between ~5-10 ‰. Rivers plotting in the high concentration-high  $\delta^{34}\text{S}$  region, such as the Lena River, are likely dominated by sulfate minerals weathered from evaporites. Gypsum ( $\text{CaSO}_4$ ) dissolves easily, and rivers draining evaporitic rocks usually have high concentrations of total dissolved solids, including sulfate. These rivers have  $\text{Na}/\text{S}$  values ranging between 1.7 and 5, consistent with an evaporite end-member.

Rivers plotting in the high concentration-low  $\delta^{34}\text{S}$  region could have sulfate sources dominated by the oxidative weathering of pyrite, which has low  $\delta^{34}\text{S}$  values, or by pollution, which is often cited in the literature as having low or

negative  $\delta^{34}\text{S}$  signatures (e.g. Ivanov et al., 1983). We screened for polluted rivers using ancillary anion and cation data (Fiege et al., 2009; Miller et al., 2011; Peterson et al., 2016; Voss et al., 2014). If the value of  $([\text{Na}] - [\text{Cl}])/[\text{Cl}]$  is less than 0.1, then the river is considered polluted. The main sources of Cl to rivers are sea salt aerosols, evaporites, and pollution. As both sea salt aerosols and evaporites deliver Na and Cl in roughly equal proportions, an excess of Cl relative to Na may be indicative of a polluted river. The following rivers have high Cl relative to Na: Connecticut, Danube, Indus, Doubs, Lena, Mississippi, Neman, Rhine, Seine, and St. Lawrence. These rivers are also located near large human populations or near industrial centers. The one exception to this is the Lena River, which is influenced by Cl-rich brines (Gaillardet et al., 1999). As shown in Figure 2, the polluted rivers tend to have high sulfate concentrations ( $>100\ \mu\text{M}$ , with the exception of the Doubs whose main sulfate sources are atmospheric (Calmels et al., 2014)). However, there is a large range of  $\delta^{34}\text{S}$  for these rivers; thus they do not simply populate the bottom left of the graph, as would be expected if pollution always had a low  $\delta^{34}\text{S}$  signature. Indeed, measurements of  $\delta^{34}\text{S}$  on oil, gas, coal and sulphide ores range from -25 to +30‰ (Newman et al., 1991), and  $\delta^{34}\text{S}$  of fertilizers, another anthropogenic sulfate source, can range from -6.5 to 20.7‰ (Szynkiewicz et al., 2011; Vitoria et al., 2004). Since pollution cannot be the sole reason for the high sulfate concentration and low  $\delta^{34}\text{S}$ , it follows that the oxidation of pyrite is a major source of sulfate to these rivers. This is consistent with the abundance of shales and pyrites in the catchment areas of the rivers (e.g. the Kolyma (Huh et al., 1998a), Orinoco (Edmond et al.,

1996), Buller (Robinson and Bottrell, 1997), Kaoping (Das et al., 2012), Skeena (Spence and Telmer, 2005), and Stikine rivers (Calmels et al., 2007)).

Rivers and tributaries with low concentrations of sulfate (e.g. Amazon, Congo, and Niger rivers) tend to have  $\delta^{34}\text{S}$  values of 5 - 10‰ (Figure 2). The low sulfate concentrations likely reflect the lack of any significant weathering of evaporites or pyrite-rich shales in these drainage basins. Their low concentration of sulfate could also be attributed in part to the large flow of water and the dilution of solutes, as the concentration of total dissolved solids for these rivers is low at 35-59 mg/L (Meybeck and Ragu, 1995). However, the small range of  $\delta^{34}\text{S}$  values indicates a similar source of sulfate to the rivers, leaving us to conclude that silicate weathering of igneous rock and atmospheric deposition of sulfate (sea salts) are the major sources of sulfate to these rivers and tributaries, consistent with previous studies (Negrel et al., 1993; Gaillardet et al., 1997). Rivers with a high ratio of Na/S also plot within this narrower range of  $\delta^{34}\text{S}$ , consistent with a silicate or atmospheric source.

The wide range in  $\delta^{34}\text{S}$  from tributaries from an individual river basin (e.g. Congo, Ganges, Mackenzie) highlights the spatial heterogeneity of sulfur sources to rivers, that is most likely controlled by heterogeneity of the bedrock geology—and commensurate differences in the isotopic composition of the sulfur-bearing phases—in their catchments. The differences in the temporal variability of  $\delta^{34}\text{S}$  between individual river basins indicate that some rivers (e.g. Lena, Mackenzie, and Fraser) have weathering conditions that are more heterogeneous than other river basins with more constant  $\delta^{34}\text{S}$ , and that the varied lithologies in these river catchments contribute differently to the dissolved load at distinct times throughout the year. For instance, in the case of

the Fraser River, the  $\delta^{34}\text{S}$  of sulfate over the course of a year shows a strong correlation ( $r^2 = 0.88$ ) with the dissolved  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in these waters (Voss et al., 2014). Dissolved  $^{87}\text{Sr}/^{86}\text{Sr}$  values decrease along the flow path of the Fraser River reflecting the underlying geology, as the river flows from Precambrian/Paleozoic sedimentary rocks of the Rocky Mountains, through the young, magmatic and metamorphic rocks of the Coast Range (Cameron and Hattori, 1997). The time series data indicate a greater relative contribution of the Coast Range to the dissolved ion budget during the winter. The sulfur isotope compositions imply that during the winter months, more sulfate is derived from the oxidative weathering of  $^{34}\text{S}$ -poor sulfide-bearing phases in the Coast Range, whereas during the summer a greater proportion of the sulfate derives from sulfate minerals within Paleozoic strata.

The importance of pyrite weathering in setting the  $\delta^{34}\text{S}$  value of rivers globally can be seen in Figure 6. This figure shows the relationship between the measured  $\delta^{34}\text{S}$  versus the  $\delta^{34}\text{S}$  values predicted from a sulfur isotope mass balance in each river based on the weathering end-member decomposition. This sulfur isotope mass balance uses the proportion of sulfate derived from the weathering and rain water end-members and assumes end-member  $\delta^{34}\text{S}$  values of 17‰ for evaporite and carbonate weathering, 4‰ for silicate weathering, and 20‰ for rainwater (Herut et al., 1995; Holser and Kaplan, 1966). The 1:1 line in Figure 6 indicates rivers whose measured  $\delta^{34}\text{S}$  values can be entirely accounted for by sulfur input from sources besides pyrite weathering and pollution. Most rivers plot to the left of this line indicating that the measured values of  $\delta^{34}\text{S}$  are lower than predicted. Furthermore, the rivers that plot farthest from the line have large excess sulfate proportions (calculated from the end-

member decomposition), implying that the sulfur isotopic composition of this excess sulfate has a low  $\delta^{34}\text{S}$  value, consistent with a pyrite source<sup>3</sup>.

#### 4.2 Global dissolved sulfur isotope mass balance for rivers

The riverine  $\delta^{34}\text{S}$  values reported here ( $4.4 \pm 4.5\text{‰}$  and  $4.8 \pm 4.9\text{‰}$  excluding the most polluted rivers) are lower than the previous compilation value from Eurasian rivers of  $9\text{‰}$  (Ivanov et al., 1983) and the values of 7 to  $8\text{‰}$  typically used in models of the global sulfur cycle (Halevy et al., 2012; e.g. Kump and Garrels, 1986; Kurtz et al., 2003). At face value these lower values of the  $\delta^{34}\text{S}$  of rivers implies that a greater fraction of riverine sulfate derives from reduced sources (e.g. pyrite) than previously estimated. This finding is in line with recent studies illustrating the high relative contribution of oxidative weathering of pyrite to riverine sulfate based on detailed studies of individual river basins (e.g. Mackenzie (Calmels et al., 2007), Kaoping (Das et al., 2012), Marysandi (Turchyn et al., 2013), Amazon (Torres et al., 2016) and Ganges-Brahmaputra (Galy and France-Lanord, 1999)), and we can now expand those conclusions to the global budget.

Using a simple terrestrial weathering isotope mass balance akin to that used in Kump and Garrels (1986), we can calculate the fraction of pyrite weathering contributing to riverine sulfate:

$$f_{\text{owp}} = -(\delta_{\text{evap}} - \delta_{\text{riv}})/(\delta_{\text{py}} - \delta_{\text{evap}}) \quad \text{Equation 2}$$

---

<sup>3</sup> Note that the most polluted rivers (see text) have been excluded from these calculations and figures.

where  $f_{\text{owp}}$  is the fraction of pyrite-derived sulfate,  $\delta_{\text{evap}}$  is the  $\delta^{34}\text{S}$  of evaporite (17‰ (Holser and Kaplan, 1966)),  $\delta_{\text{riv}}$  is the  $\delta^{34}\text{S}$  of riverine sulfate (4.8‰, above), and  $\delta_{\text{py}}$  is the  $\delta^{34}\text{S}$  of pyrite from sedimentary rocks (-12‰ (Holser and Kaplan, 1966)). This gives a  $f_{\text{owp}}$  in rivers of 0.42, substantially higher than the estimate of  $f_{\text{owp}}$  of 0.28 if the riverine  $\delta^{34}\text{S}$  value is taken to be 9‰ (Ivanov, 1983).

These estimates are very sensitive to the assumption of the end-member  $\delta^{34}\text{S}$  values of the oxidized (sulfate salts) and reduced (sulfide and disulfide) sedimentary reservoirs, which are difficult to constrain from a global perspective. Estimates of the global  $\delta^{34}\text{S}$  values of oxidized S in sediments range from 12.1‰ to 19‰, and of reduced sediments from -7.4‰ to -16‰ (Holser et al., 1988 and references therein). These different combinations of  $\delta_{\text{evap}}$  and  $\delta_{\text{py}}$  give a range of  $f_{\text{owp}}$  between 0.35 to 0.42 (compared to  $f_{\text{owp}} = 0.16$  to 0.29 if the river  $\delta^{34}\text{S}$  value is taken to be 9‰), with a median  $f_{\text{owp}}$  of 0.41. Despite the large uncertainties in the correct end-member isotope values, the estimate of  $f_{\text{owp}} = 0.41$  is broadly consistent with the independently derived fluxes from the weathering end-member decomposition that indicate that pyrite weathering contributes up to 46% of the sulfate flux in rivers due to weathering. The weathering end-member decomposition is based solely on major ion concentrations and not isotope values, and so is independent of the isotope mass balance calculation in Equation 2.

#### *4.3 Implications for the modern sulfur cycle and marine isotope mass balance*

Our flux estimate of riverine sulfate from evaporite weathering (1.5 Tmol/y) that we derived from weathering end-member decomposition is larger than the assumed value of 1 Tmol/y of sulfate weathering by Berner and Raiswell (1983) and Garrels and Lerman (1981), which is widely used in box models of the sulfur cycle and is smaller than the value estimated more recently by Lerman et al. (2007) (1.98 Tmol/y). Our estimate of the sulfide weathering flux from the weathering end-member decomposition (1.3 Tmol/y) is about twice as large as the commonly cited estimates of the global OWP flux (0.5-0.64 Tmol/y (Berner and Berner, 1996; Lerman et al., 2007)), and is consistent with our estimate from an isotope mass balance discussed in the previous section that is based on the revised global average riverine  $\delta^{34}\text{S}$  value of 4.8‰. Thus the isotope and river chemistry data independently imply a larger contribution of oxidative weathering of pyrite to the riverine sulfate flux than previously estimated<sup>4</sup>.

It can be informative to investigate the derivation of previous estimates of the sulfate flux from OWP in order to understand why they were significantly lower than our new value. Previous estimates of global OWP from Berner and Berner (1996) and Lerman et al. (2007) both relied on assumptions of the relative abundance of pyrite in sedimentary rocks, though they do this differently. The 0.5 Tmol/y estimate (Berner and Berner, 1996) assumed that the riverine ratio of calcium from weathering of sedimentary rocks to pyrite-derived sulfate must be the same as the ratio of calcium to pyrite sulfur in common

---

<sup>4</sup> In order to close the riverine sulfate budget, previous estimates attributed any remaining sulfate that did not derive from pyrite or evaporite weathering to pollution (e.g. Berner and Berner, 1996), rather than using an independent estimate of sulfate pollution (Meybeck, 2003) as we have done here.



551 sedimentary rocks (which was taken to be 8.5 and 0.3 weight % of calcium and  
552 pyrite-S, giving a molar pyrite-S/Ca ratio of 0.04 (Garrels and Lerman, 1984)).  
553 The molar ratios of excess sulfate/Ca from our end-member decomposition are  
554 more typically around 0.1 and can be as high as 0.6 for catchments with  
555 abundant shales (e.g. Kolyma (Huh et al., 1998a), Orinoco (Edmond et al., 1996),  
556 and Kaoping (Das et al., 2012)). Thus the assumed ratio of calcium to pyrite  
557 sulfur in common sedimentary rocks might not fully account for the presence of  
558 pyrite-rich shales. The OWP flux estimate of 0.64 Tmol/y (Lerman et al., 2007)  
559 assumes that 24% of sedimentary sulfur is in the reduced form of pyrite. This  
560 percentage is significantly lower than previous estimates, which are closer to  
561 50% (e.g. Holser et al., 1988 and references therein). Thus both of these prior  
562 estimates potentially underestimated the global abundance of pyrite S in  
563 sedimentary rocks by a factor of two, which could help to explain the  
564 underestimation of global OWP fluxes.

565 Our revised estimate of the OWP flux is similar to the estimate of global  
566 pyrite burial in ocean sediments calculated from the estimates of global organic  
567 carbon burial and the C/S value in modern sediments (1.22 Tmol/y; (Berner,  
568 1982)). It is also similar to the upper range of estimates of pyrite burial (36% of  
569 the total natural, pre-anthropogenic flux) based on marine isotope mass balance  
570 and constraints from marine  $\delta^{33}\text{S}$  (Tostevin et al., 2014). Our upward revision of  
571 global pyrite weathering brings the oceanic input and output of reduced sulfur,  
572 which previously differed by a factor of 2, into close agreement.

573 The uncertainties on these modern fluxes from the weathering end-  
574 member decomposition of river concentration data alone are still too large (0.2  
575 Tmol/y) to assess whether the modern sulfur cycle is in steady state with regard

to the relative amounts of oxidized and reduced sulfur that are weathered and buried. However, if we assume steady-state, our new riverine  $\delta^{34}\text{S}$  value can be used in a marine isotope mass balance that solves for the fraction of the sulfate removed from the ocean through pyrite burial ( $f_{\text{pyr}}$ ):

$$f_{\text{pyr}} = (\delta_{\text{riv}} - \delta_{\text{sw}}) / (\Delta^{34}\text{S}_{\text{pyrite-seawater}}) \quad \text{Equation 3}$$

where  $\delta_{\text{sw}}$  is the  $\delta^{34}\text{S}$  of seawater (21‰; (Paris et al., 2013)) and  $\Delta^{34}\text{S}_{\text{pyrite-seawater}}$  is the isotope fractionation between seawater sulfate and sedimentary pyrite in the modern ocean ( $\delta_{\text{py}} - \delta_{\text{sw}}$ ). A plot of the solutions to Equation 3 for our new value for  $\delta_{\text{riv}}$  (4.8‰) and the previous value for  $\delta_{\text{riv}}$  (9‰) is shown in Figure 7 for a range of  $\Delta^{34}\text{S}_{\text{pyrite-seawater}}$ . Our lower value of  $\delta_{\text{riv}} = 4.8‰$  implies that there is a greater fraction of pyrite burial than previously predicted based on a  $\delta_{\text{riv}} = 9‰$ . Using this model to determine a specific value for the modern fraction of pyrite burial is not currently possible because the global average value of  $\Delta^{34}\text{S}_{\text{pyrite-seawater}}$  is difficult to constrain given the large range of  $\delta^{34}\text{S}$  values measured in modern pyrites.

If, however, we assume that the fraction of pyrite burial ( $f_{\text{pyr}}$ ) is equivalent to the fraction of pyrite weathered ( $f_{\text{owp}}$ ) as calculated either by the weathering end-member decomposition from major ion chemistry (0.46) or riverine isotope mass balance (0.41), then our data suggest that  $\Delta^{34}\text{S}_{\text{pyrite-seawater}}$  should be -35‰ or -39‰, respectively. These estimates are roughly consistent with canonical assumptions of,  $\Delta^{34}\text{S}_{\text{pyrite-seawater}} = -35‰$  (e.g. Garrels and Lerman, 1981), but are much more positive than flux weighted estimates of this value based on pyrite

measurements from modern continental shelf, slope and rise sediments ( $\Delta^{34}\text{S}_{\text{pyrite-seawater}} = -48\text{‰}$  (Yu Lein et al., 1983)). Modelling studies that use constraints from  $\delta^{33}\text{S}$  also predict a greater difference between the  $\delta^{34}\text{S}$  values of seawater and bulk pyrite buried ( $\Delta^{34}\text{S}_{\text{pyrite-seawater}} = -56 \pm 5\text{‰}$ ) (Tostevin et al., 2014). These larger offsets in the isotopic composition of seawater and buried pyrite would imply that the fraction of pyrite buried is 0.29 and 0.34 for  $\Delta^{34}\text{S}_{\text{pyrite-seawater}} = -56$  and  $\Delta^{34}\text{S}_{\text{pyrite-seawater}} = -48$ , respectively (Figure 7), significantly less than our two independent estimates of the fraction of pyrite weathered. If correct, these estimates indicate that the biogeochemical sulfur cycle may not be balanced, and that more pyrite is being weathered than is being buried in modern marine sediments. This conclusion would be consistent with recent ice core evidence that shows a decrease in atmospheric  $\text{O}_2$  over the past 800,000 years (Stolper et al., 2016). The magnitude of the imbalance between weathering and burial fluxes of reduced carbon and sulfur that is required to explain the long term oxygen trend in ice cores is  $\sim 2\%$  (Stolper et al., 2016); this number is well within uncertainties of the weathering flux estimates ( $\sim 0.2 \text{ Tmol/y}$ ). However, given the large range of estimates of  $\Delta^{34}\text{S}_{\text{pyrite-seawater}}$  more work constraining global  $\Delta^{34}\text{S}_{\text{pyrite-seawater}}$  from modern sediments would help to resolve this issue.

Our increased estimate of global OWP means that the previously published OWP rates from three river basins (Mackenzie (Calmels et al., 2007), Kaoping (Das et al., 2012), and Jialing (Li et al., 2011)) only account for  $\sim 12\%$  (rather than a third) of the total global OWP flux estimate. Nonetheless, the fact that these rivers drain less than 2% of global surface area highlights the heterogeneity of pyrite weathering; simply put, some river basins will contribute disproportionately to the global pyrite weathering budget, based on their

625 tectonic and geological characteristics. The spatial heterogeneity of pyrite  
626 weathering thus has important implications for the long-term variations in the  
627  $\delta^{34}\text{S}$  of riverine input: changes in paleogeography, paleohydrology, eustasy, and  
628 the formation and uplift of sedimentary basins will change both the amounts and  
629 types of rock exposed to weathering, which in turn will likely change the value of  
630 riverine  $\delta^{34}\text{S}$  input to the oceans through time.

631 Finally, the increased estimate of the OWP flux has implications for the  
632 modern carbon cycle and carbon-weathering feedbacks. As pyrite oxidation  
633 coupled to carbonate weathering can provide a source of  $\text{CO}_2$  to the atmosphere  
634 (e.g. Calmels et al., 2007; Das et al., 2012; Lerman et al., 2007; Torres et al., 2016;  
635 2015), the greater flux of pyrite-derived sulfate indicates a more significant role  
636 for this process in the modern biogeochemical sulfur and carbon cycles. Modern  
637 weathering and carbon budgets should be reassessed on a global scale to account  
638 for an increased global contribution from OWP.

## 640 **5 Conclusion**

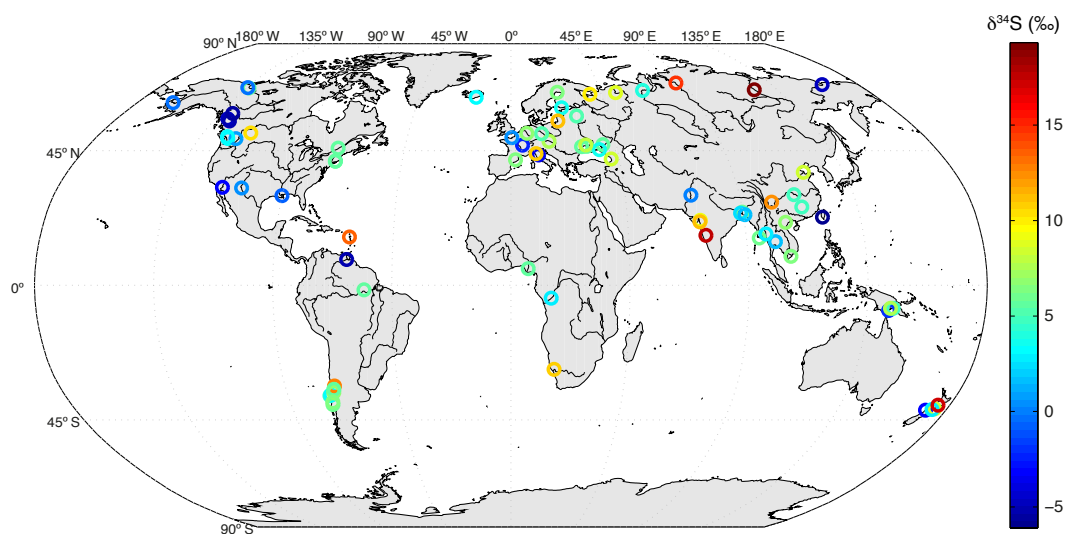
641 We determined the modern  $\delta^{34}\text{S}$  value of riverine sulfate to be  $4.4 \pm$   
642  $4.5\text{‰}$ , based on measurements of rivers that account for more than 46% of  
643 global freshwater discharge. Removing highly polluted rivers from the estimate  
644 gives a similar  $\delta^{34}\text{S}$  value of riverine sulfate of  $4.8 \pm 4.9\text{‰}$ . These  $\delta^{34}\text{S}$  values are  
645 lower than previous estimates of the isotopic composition of riverine sulfate, and  
646 imply a greater contribution of pyrite weathering to riverine sulfate than has  
647 previously been assumed. An end-member decomposition of weathering  
648 sources to these rivers indicates that the relative contributions of evaporite  
649 (sulfate) and pyrite (sulfide) weathering to riverine sulfate budgets are  $\sim 1.5$  and

1.3 Tmol S/y, respectively. This estimate of pyrite weathering is twice as high as previous estimates, and is consistent with isotope mass balance constraints on the  $\delta^{34}\text{S}$  of river water that imply that ~40% of non-anthropogenic riverine sulfate derives from weathered pyrite. Since pyrite oxidation can act as a source of  $\text{CO}_2$  to the atmosphere, this new estimate should reduce the global carbon sink attributed to chemical weathering. Basin lithology exerts a strong control on the  $\delta^{34}\text{S}$  values of riverine sulfate, questioning the validity of assuming constant  $\delta^{34}\text{S}$  of riverine input to the ocean over geological time. Stratigraphic trends observed in sulfur isotopes in ancient sedimentary rocks might therefore reflect secular changes in the isotopic composition of the riverine inputs, rather than changes in the relative burial of marine pyrite versus sulfate salt evaporites.

## 6 Acknowledgements

This research was funded by a Foster and Coco Stanback postdoctoral fellowship and a Marie Curie Career Integration Grant (CIG14-631752) to AB. JFA acknowledges the support of NSF-OCE grant 1340174 and NSF-EAR grant 1349858. WF acknowledges the support of a grant from the David and Lucile Packard Foundation.

669 **Figures**



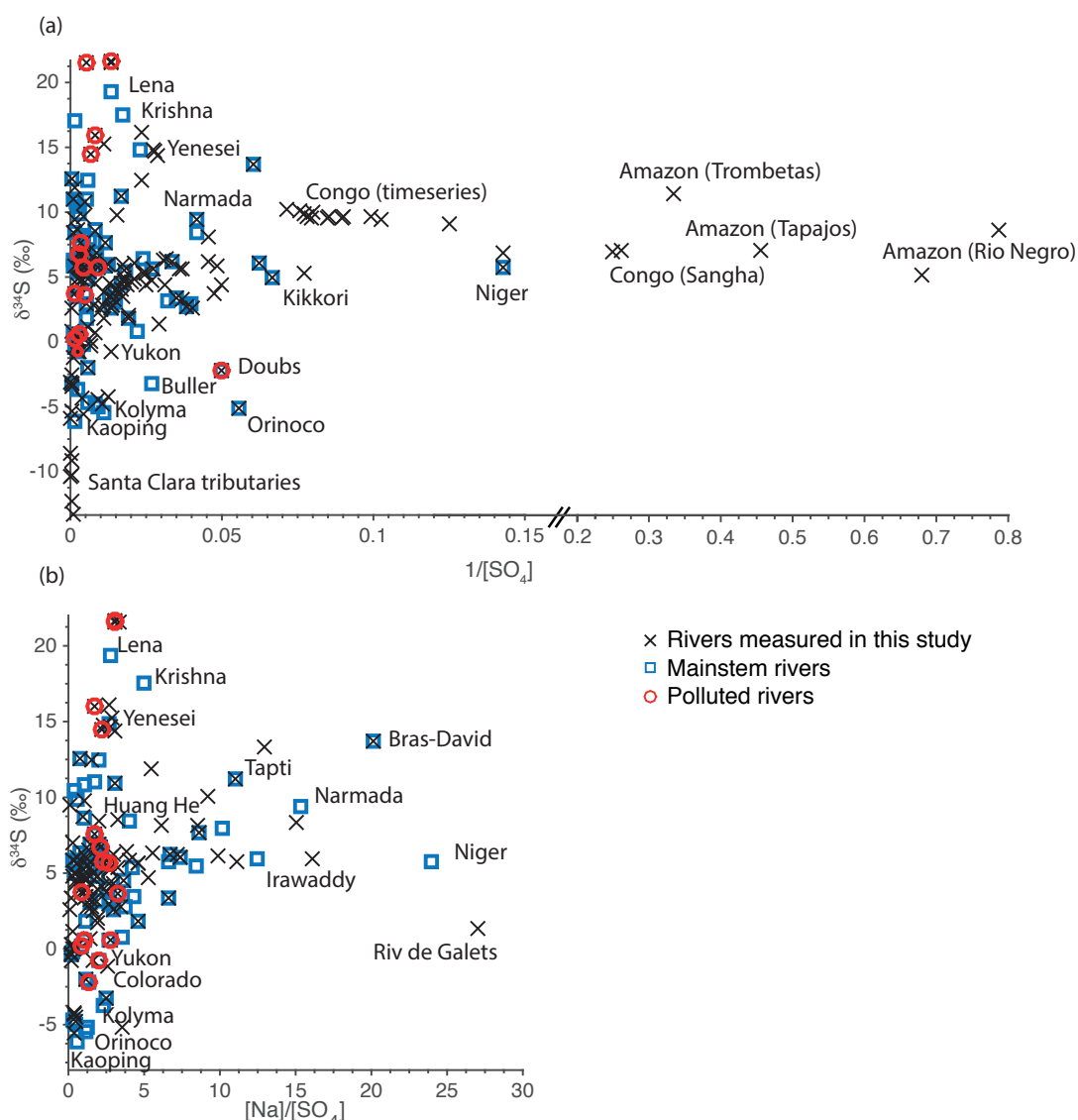
670

671 **Figure 1.** Global map of measured and compiled main stem river  $\delta^{34}\text{S}$  values

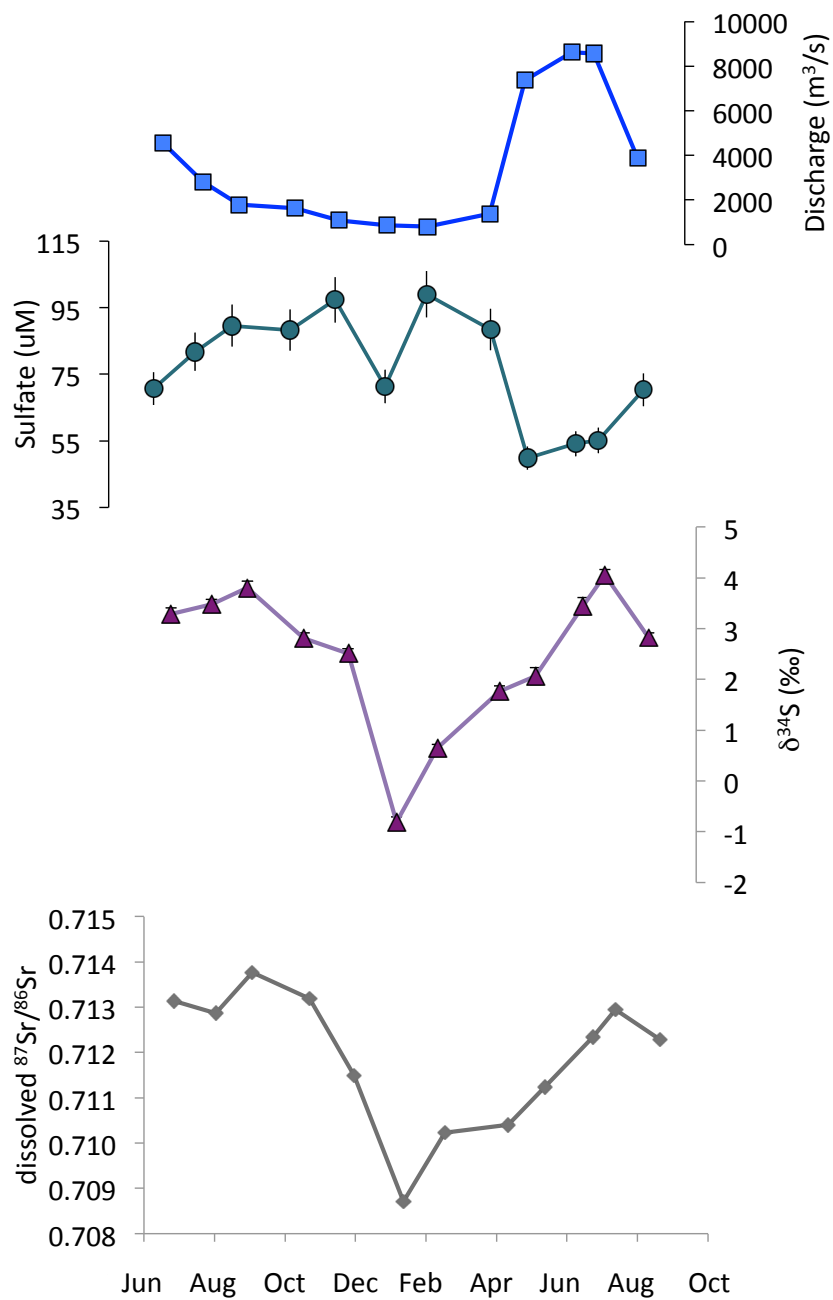
672 (‰, V-CDT) that contribute to the global flux-weighted average of 4.4‰. The

673 variation seen between these major rivers relates to differences in catchment

674 geology.

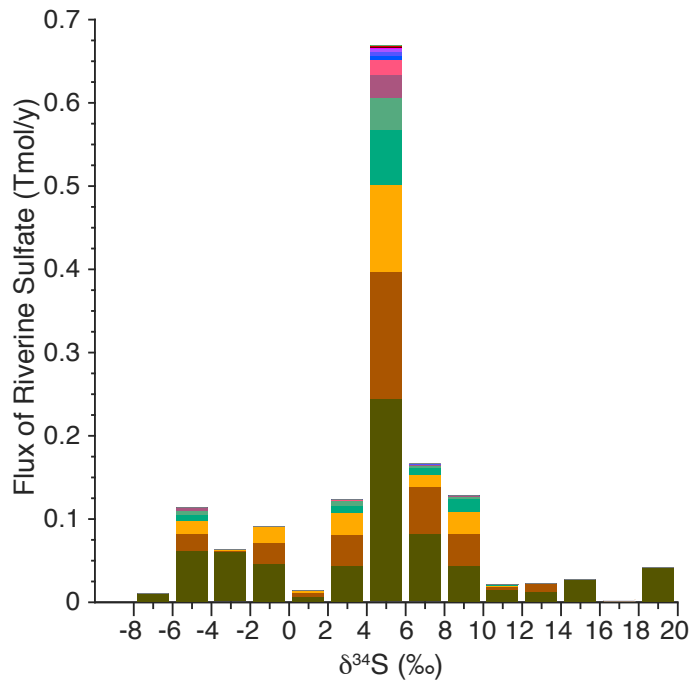


**Figure 2. (a)**  $\delta^{34}\text{S}$  values (‰, V-CDT) of all rivers measured versus the inverse concentration ( $\mu\text{M}^{-1}$ ) of sulfate (black x). Rivers designated as main stem rivers (compiled or measured) are shown as blue squares. Rivers identified as being polluted (section 4.1) are circled in red. Note the change in scale on the X-axis after the break. **(b)** Same as above but plotted against the Na/SO<sub>4</sub> molar value of the riverine dissolved load.



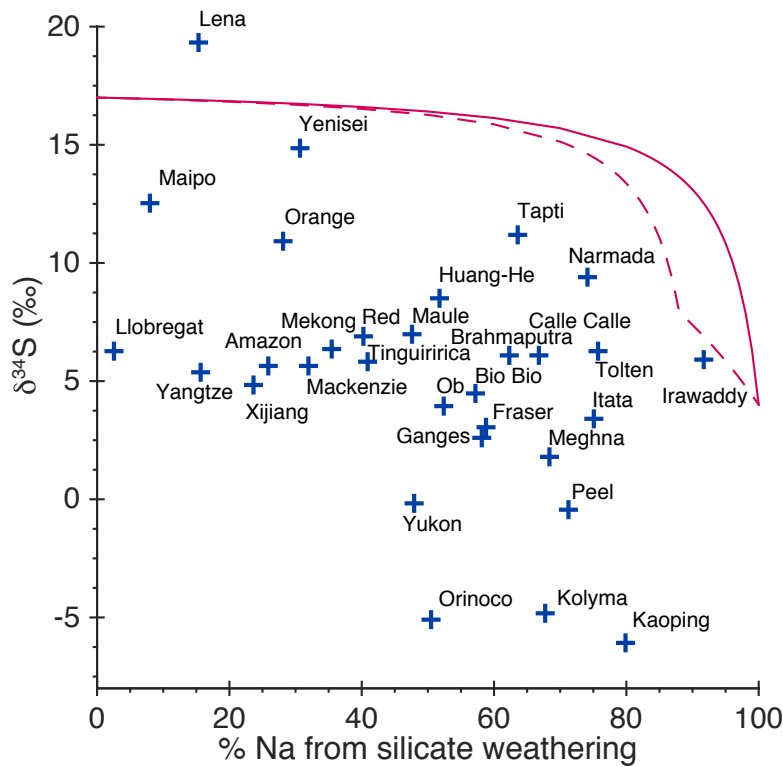
**Figure 3.** Time series data from Fraser River samples collected between June 2010 and August 2011. (a) Freshwater discharge ( $\text{m}^3/\text{s}$ ), (b) sulfate concentration ( $\mu\text{M}$ ); (c)  $\delta^{34}\text{S}$  values (‰, V-CDT), (d)  $^{87}\text{Sr}/^{86}\text{Sr}$  from (Voss et al., 2014).



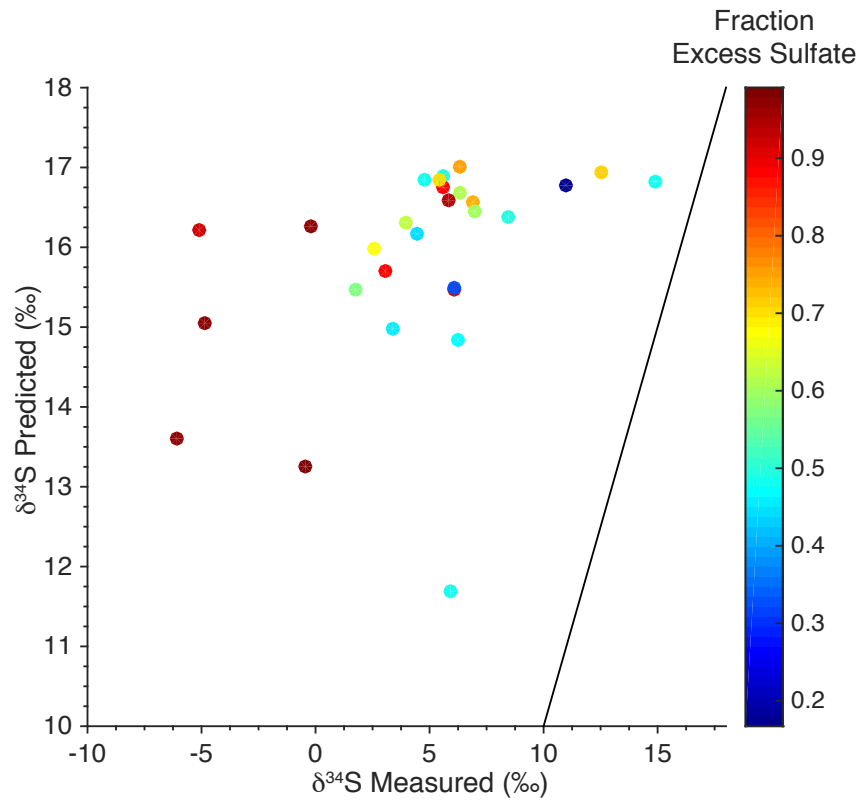


688

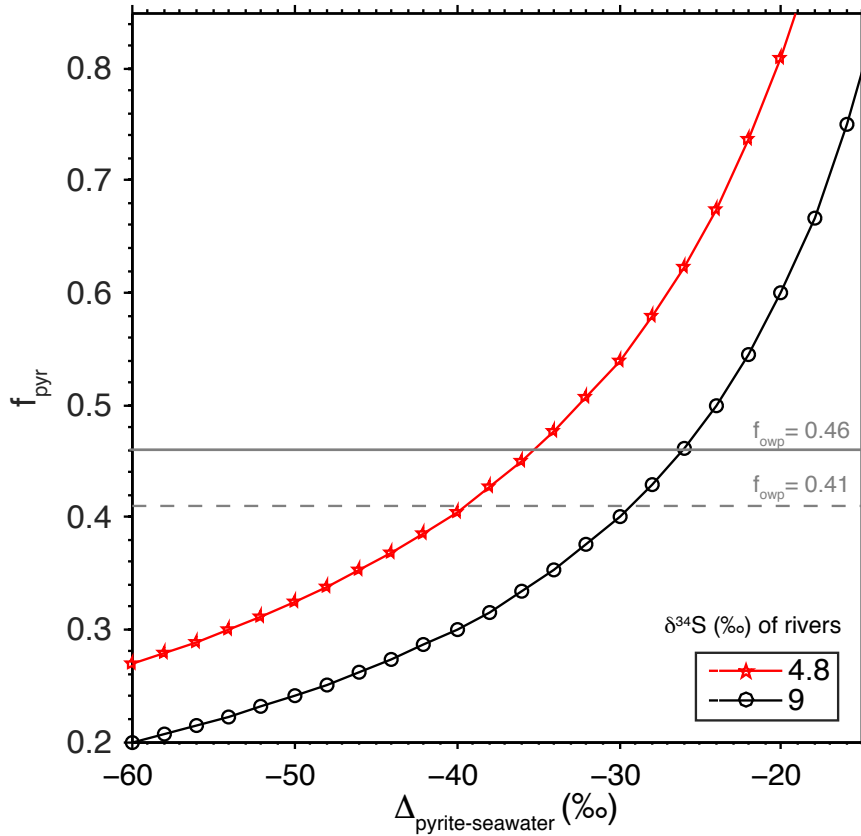
689 **Figure 4.** Stacked bar graph showing the  $\delta^{34}\text{S}$  values (‰, VCDT) and the flux of  
 690 sulfate from individual main stem rivers that contribute to the global flux-  
 691 weighted average  $\delta^{34}\text{S}$  value of 4.4‰. Each color represents a different river.



**Figure 5.** Riverine  $\delta^{34}\text{S}$  values (‰, V-CDT) of main stem rivers as a function of the percent of Na attributed to silicate weathering from the end-member decomposition. The red solid line is the predicted  $\delta^{34}\text{S}$  based on a riverine isotope mass balance, using the S/Na end-member ratios from Table 1, and assuming that the  $\delta^{34}\text{S}$  value of silicate rocks is 4‰, that the  $\delta^{34}\text{S}$  value of evaporites is 17‰, and that there is no contribution of Na from carbonates. The red dashed line is the predicted  $\delta^{34}\text{S}$  based on a riverine isotope mass balance, using the S/Na end-member ratios from Table 1, and assuming that the  $\delta^{34}\text{S}$  value of silicate rocks is 4‰, that the  $\delta^{34}\text{S}$  value of evaporites and carbonates is 17‰, and that carbonates contribute 12% of the Na (maximum contribution found for all rivers in this study), with the remainder coming from silicates and evaporites.



**Figure 6.** Plot of predicted  $\delta^{34}\text{S}$  (based on assumptions of end-members from mixing model, see section 4.1) versus measured  $\delta^{34}\text{S}$  values (‰, V-CDT). The black line is the 1:1 line. The colors indicate the fraction of excess sulfate. Rivers plotting to the left of the line have more negative  $\delta^{34}\text{S}$  values than predicted, and thus are likely influenced by oxidative weathering of pyrite.



**Figure 7.** Sensitivity of the proportion of sulfur buried marine basins as pyrite ( $f_{\text{pyr}}$ ) as a function of the fractionation ( $\Delta_{\text{pyrite-seawater}}$ , ‰) between reduced and oxidized sulfur for a given riverine sulfate  $\delta^{34}\text{S}$  value, and assuming steady state isotope mass balance in the ocean. The red line with stars represents our estimate of the modern riverine  $\delta^{34}\text{S}$  value from this study (4.8‰). Previous compilations of the riverine  $\delta^{34}\text{S}$  value were higher (~9‰, black circles; (Ivanov et al., 1983)). Estimates of the relative contribution of weathering of pyrite ( $f_{\text{owp}}$ ) to modern riverine sulfate from our two independent approaches are shown for reference ( $f_{\text{owp}} = 0.46$  (solid line, based on our weathering end-member decomposition from major ion chemistry of the rivers) and  $f_{\text{owp}} = 0.41$  (dashed line, based on riverine isotope mass balance)).

726

727 **References**

- 728 Berner, E.K., Berner, R.A., 1996. Global environment: water, air, and geochemical  
729 cycles. Prentice Hall, New York.
- 730 Berner, R.A., 1982. Burial of organic carbon and pyrite sulfur in the modern  
731 ocean; its geochemical and environmental significance. *Am J Sci* 282, 451–  
732 473. doi:10.2475/ajs.282.4.451
- 733 Berner, R.A., Raiswell, R., 1983. Burial of Organic-Carbon and Pyrite Sulfur in  
734 Sediments Over Phanerozoic Time - a New Theory. *Geochimica et*  
735 *Cosmochimica Acta* 47, 855–862.
- 736 Calmels, D., Gaillardet, J., Brenot, A., France-Lanord, C., 2007. Sustained sulfide  
737 oxidation by physical erosion processes in the Mackenzie River basin:  
738 Climatic perspectives. *Geology* 35, 1003. doi:10.1130/G24132A.1
- 739 Calmels, D., Gaillardet, J., François, L., 2014. Sensitivity of carbonate weathering  
740 to soil CO<sub>2</sub> production by biological activity along a temperate climate  
741 transect. *Chemical Geology* 390, 74–86. doi:10.1016/j.chemgeo.2014.10.010
- 742 Cameron, E.M., Hattori, K., 1997. Strontium and neodymium isotope ratios in the  
743 Fraser River, British Columbia: a riverine transect across the Cordilleran  
744 orogen. *Chemical Geology* 137, 243–253. doi:10.1016/S0009-  
745 2541(96)00168-4
- 746 Das, A., Chung, C.-H., You, C.-F., 2012. Disproportionately high rates of sulfide  
747 oxidation from mountainous river basins of Taiwan orogeny: Sulfur isotope  
748 evidence. *Geophys. Res. Lett.* 39, n/a–n/a. doi:10.1029/2012GL051549
- 749 Edmond, J.M., Palmer, M.R., Measures, C.I., Brown, E.T., Huh, Y., 1996. Fluvial  
750 geochemistry of the eastern slope of the northeastern Andes and its foredeep  
751 in the drainage of the Orinoco in Colombia and Venezuela. *Geochimica et*  
752 *Cosmochimica Acta* 60, 2949–2974. doi:10.1016/0016-7037(96)00142-1
- 753 Eriksson, E., 1963. The yearly circulation of sulfur in nature. *Journal of*  
754 *Geophysical Research* 68, 4001–4008.
- 755 Fiege, K., Miller, C.A., Robinson, L.F., Figueroa, R., Peucker-Ehrenbrink, B., 2009.  
756 *Chemical Geology*. *Chemical Geology* 268, 337–343.  
757 doi:10.1016/j.chemgeo.2009.09.013
- 758 Francois, L.M., Walker, J.C.G., 1992. Modelling the Phanerozoic carbon cycle and  
759 climate; constraints from the 87 Sr/ 86 Sr isotopic ratio of seawater. *Am J Sci*  
760 292, 81–135. doi:10.2475/ajs.292.2.81
- 761 Gaillardet, J., Dupré, B., Allegre, C.J., Negrel, P., 1997. Chemical and physical  
762 denudation in the Amazon River basin. *Chemical Geology* 142, 141–173.
- 763 Gaillardet, J., Dupré, B., Louvat, P., Allegre, C.J., 1999. Global silicate weathering  
764 and CO<sub>2</sub> consumption rates deduced from the chemistry of large rivers.  
765 *Chemical Geology* 159, 3–30.
- 766 Galy, A., France-Lanord, C., 1999. Weathering processes in the Ganges–  
767 Brahmaputra basin and the riverine alkalinity budget. *Chemical Geology*.
- 768 Garrels, R.M., Lerman, A., 1984. Coupling of the sedimentary sulfur and carbon  
769 cycles; an improved model. *Am J Sci* 284, 989–1007.  
770 doi:10.2475/ajs.284.9.989
- 771 Garrels, R.M., Lerman, A., 1981. Phanerozoic Cycles of Sedimentary Carbon and  
772 Sulfur. *Proc. Natl. Acad. Sci. U.S.A.* 78, 4652–4656.
- 773 Graham, S.T., Famiglietti, J.S., Maidment, D.R., 1999. Five-minute, 1/2°, and 1°  
774 data sets of continental watersheds and river networks for use in regional

775 and global hydrologic and climate system modeling studies. *Water Resources*  
776 *Research* 35, 583–587. doi:10.1029/1998WR900068

777 Habicht, K.S., Canfield, D.E., 2001. Isotope fractionation by sulfate-reducing  
778 natural populations and the isotopic composition of sulfide in marine  
779 sediments. *Geology* 29, 555–558. doi:10.1130/0091-  
780 7613(2001)029<0555:IFBSRN>2.0.CO;2

781 Halevy, I., Peters, S.E., Fischer, W.W., 2012. Sulfate Burial Constraints on the  
782 Phanerozoic Sulfur Cycle. *Science* 337, 331–334.  
783 doi:10.1126/science.1220224

784 Herut, B., Spiro, B., Starinsky, A., Katz, A., 1995. Sources of sulfur in rainwater as  
785 indicated by isotopic  $\delta^{34}\text{S}$  data and chemical composition, Israel.  
786 *Atmospheric Environment* 29, 851–857. doi:10.1016/1352-2310(94)00307-  
787 7

788 Holser, W.T., Kaplan, I.R., 1966. Isotope geochemistry of sedimentary sulfates.  
789 *Chemical Geology* 1, 93–135. doi:10.1016/0009-2541(66)90011-8

790 Holser, W.T., Schidlowski, M., Mackenzie, F.T., Maynard, J.B., 1988. Geochemical  
791 cycles of carbon and sulfur, in: Gregor, C.B., Garrels, R.M., Mackenzie, F.T.,  
792 Maynard, J.B. (Eds.), *Chemical Cycles in the Evolution of the Earth*. Wiley,  
793 New York, pp. 105–173.

794 Huh, Y., Panteleyev, G., Babich, D., Zaitsev, A., Edmond, J.M., 1998a. The fluvial  
795 geochemistry of the rivers of Eastern Siberia: II. Tributaries of the Lena,  
796 Omoloy, Yana, Indigirka, Kolyma, and Anadyr draining the  
797 collisional/accretionary zone of the Verkhoyansk and Cherskiy ranges.  
798 *Geochimica et Cosmochimica Acta* 62, 2053–2075. doi:10.1016/S0016-  
799 7037(98)00127-6

800 Huh, Y., Tsoi, M.Y., Zaitsev, A., Edmond, J.M., 1998b. The fluvial geochemistry of  
801 the rivers of eastern Siberia: I. Tributaries of the Lena River draining the  
802 sedimentary platform of the Siberian Craton. *Geochimica et Cosmochimica*  
803 *Acta* 62, 1657–1676.

804 Ivanov, M.V., 1983. Major Fluxes of the Global Biogeochemical Cycle of Sulphur  
805 , in: Ivanov, M.V., Freney, J.R. (Eds.), *The Global Biogeochemical Sulphur Cycle*.  
806 New York, pp. 449–463.

807 Ivanov, M.V., Grinenko, V.A., Rabinovich, A.P., 1983. The Sulphur Cycle in  
808 Continental Reservoirs, in: Ivanov, M.V., Freney, J.R. (Eds.), *The Global*  
809 *Biogeochemical Sulphur Cycle, Sulphur Flux From Continents to Oceans*. New  
810 York, pp. 331–356.

811 Kampschulte, A., Strauss, H., 2004. The sulfur isotopic evolution of Phanerozoic  
812 seawater based on the analysis of structurally substituted sulfate in  
813 carbonates. *Chemical Geology* 204, 255–286.  
814 doi:10.1016/j.chemgeo.2003.11.013

815 Karim, A., Veizer, J., 2000. Weathering processes in the Indus River Basin:  
816 implications from riverine carbon, sulfur, oxygen, and strontium isotopes.  
817 *Chemical Geology* 170, 153–177.

818 Killingsworth, B.A., Bao, H., 2015. Significant Human Impact on the Flux and  $\delta$   
819  $^{34}\text{S}$  of Sulfate from the Largest River in North America. *Environ. Sci. Technol.*  
820 49, 4851–4860. doi:10.1021/es504498s

821 Kump, L.R., Garrels, R.M., 1986. Modeling Atmospheric  $\text{O}_2$  in the Global  
822 Sedimentary Redox Cycle. *Am J Sci* 286, 337–360.

823 Kurtz, A.C., Kump, L.R., Arthur, M.A., Zachos, J.C., Paytan, A., 2003. Early Cenozoic

824 decoupling of the global carbon and sulfur cycles. *Paleoceanography* 18, n/a–  
825 n/a. doi:10.1029/2003PA000908

826 Lerman, A., Wu, L., Mackenzie, F.T., 2007. CO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> consumption in  
827 weathering and material transport to the ocean, and their role in the global  
828 carbon balance. *Marine Chemistry* 106, 326–350.  
829 doi:10.1016/j.marchem.2006.04.004

830 Li, X.D., Liu, C.Q., Liu, X.L., Bao, L.R., 2011. Identification of dissolved sulfate  
831 sources and the role of sulfuric acid in carbonate weathering using dual-  
832 isotopic data from the Jialing River, Southwest China. *Journal of Asian Earth*  
833 *Sciences*. doi:10.1016/j.jseaes.2011.06.002

834 Li, Y.H., 1972. Geochemical mass balance among lithosphere, hydrosphere and  
835 atmosphere. *Am J Sci*.

836 Longinelli, A., Edmond, J.M., 1983. Isotope geochemistry of the Amazon basin: a  
837 reconnaissance. *Journal of Geophysical Research* 88, 3703–3717.

838 Meybeck, M., 2003. Global Occurrence of Major Elements in Rivers, in: Drever, J.I.  
839 (Ed.), *Treatise on Geochemistry*. Elsevier, pp. 207–223.

840 Meybeck, M., 1984. Les fleuves et le cycle géochimique des éléments.

841 Meybeck, M., 1979. Concentrations des eaux fluviales en éléments majeurs et  
842 apports en solution aux océans. *Revue de Géologie Dynamique et de*  
843 *Géographie Physique* 21, 215–246.

844 Meybeck, M., Ragu, A., 1995. GEMS/Water contribution to the global register of  
845 river inputs (GLORI), Provisional Final Report. UNEP/WHO/UNESCO,  
846 Geneva, Geneva. doi:10.1029/2010GC003259/full

847 Miller, C.A., Peucker-Ehrenbrink, B., Walker, B.D., Marcantonio, F., 2011. Re-  
848 assessing the surface cycling of molybdenum and rhenium. *Geochimica et*  
849 *Cosmochimica Acta* 75, 7146–7179. doi:10.1016/j.gca.2011.09.005

850 Moller, D., 1990. The Na/Cl ratio in rainwater and the seasalt chloride cycle.  
851 *Tellus, Series B* 42 B, 254–262. doi:10.1034/j.1600-0889.1990.t01-1-00004.x

852 Negrel, P., Allegre, C.J., Dupré, B., Lewin, E., 1993. Erosion Sources Determined by  
853 Inversion of Major and Trace-Element Ratios and Strontium Isotopic-Ratios  
854 in River Water - the Congo Basin Case. *Earth and Planetary Science Letters*  
855 120, 59–76.

856 Newman, L., Krouse, H.R., Grinenko, V.A., 1991. Sulphur Isotope Variations in the  
857 Atmosphere, in: Krouse, H.R., Grinenko, V.A. (Eds.), *Stable Isotopes: Natural*  
858 *and Anthropogenic Sulphur in the Environment*. John Wiley & Sons, pp. 133–  
859 176.

860 Paris, G., Adkins, J.F., Sessions, A.L., Webb, S.M., Fischer, W.W., 2014. Neoproterozoic  
861 carbonate-associated sulfate records positive <sup>33</sup>S anomalies. *Science* 346,  
862 739–741. doi:10.1126/science.1258211

863 Paris, G., Sessions, A.L., Subhas, A.V., Adkins, J.F., 2013. MC-ICP-MS measurement  
864 of δ<sup>34</sup>S and Δ<sup>33</sup>S in small amounts of dissolved sulfate. *Chemical Geology*  
865 345, 50–61. doi:10.1016/j.chemgeo.2013.02.022

866 Peterson, B., Holmes, R.M., McClelland, J.W., Tank, S., Raymond, P.A., 2016. Arctic  
867 Great Rivers Observatory 1 Biogeochemistry Data (2009 - 2011).  
868 doi:10.18739/A2ZQ03

869 Peucker-Ehrenbrink, B., 2009. Land2Sea database of river drainage basin sizes,  
870 annual water discharges, and suspended sediment fluxes. *Geochem.-*  
871 *Geophys.-Geosyst.* 10, n/a–n/a. doi:10.1029/2008GC002356

872 Peucker-Ehrenbrink, B., Miller, M.W., 2007. Quantitative bedrock geology of the

873 continents and large-scale drainage regions. *Geochem.-Geophys.-Geosyst.* 8,  
 874 doi:10.1029/2006GC001544  
 875 Peucker-Ehrenbrink, B., Miller, M.W., Arsouze, T., Jeandel, C., 2010. Continental  
 876 bedrock and riverine fluxes of strontium and neodymium isotopes to the  
 877 oceans. *Geochem.-Geophys.-Geosyst.* 11, doi:10.1029/2009GC002869  
 878 Robinson, B.W., Bottrell, S.H., 1997. Discrimination of sulfur sources in pristine  
 879 and polluted New Zealand river catchments using stable isotopes. *Applied*  
 880 *Geochemistry* 12, 305–319. doi:10.1016/S0883-2927(96)00070-4  
 881 Rudnick, R.L., Gao, S., 2003. Composition of the continental crust. *Treatise on*  
 882 *Geochemistry* 3, 1–64. doi:10.1016/B0-08-043751-6/03016-4  
 883 Sim, M.S., Ono, S., Donovan, K., Templer, S.P., Bosak, T., 2011. Effect of electron  
 884 donors on the fractionation of sulfur isotopes by a marine *Desulfovibrio* sp.  
 885 *Geochimica et Cosmochimica Acta* 75, 4244–4259.  
 886 doi:10.1016/j.gca.2011.05.021  
 887 Spence, J., Telmer, K., 2005. The role of sulfur in chemical weathering and  
 888 atmospheric CO<sub>2</sub> fluxes: Evidence from major ions,  $\delta^{13}\text{CDIC}$ , and  $\delta^{34}\text{SSO}_4$  in  
 889 rivers of the Canadian Cordillera. *Geochimica et Cosmochimica Acta* 69,  
 890 5441–5458. doi:10.1016/j.gca.2005.07.011  
 891 Stolper, D.A., Bender, M.L., Dreyfus, G.B., Yan, Y., Higgins, J.A., 2016. A Pleistocene  
 892 ice core record of atmospheric O<sub>2</sub> concentrations. *Science* 353, 1427–1430.  
 893 doi:10.1126/science.aaf5445  
 894 Szyrkiewicz, A., Szyrkiewicz, A., Witcher, J.C., Witcher, J.C., Modelska, M.,  
 895 Modelska, M., Borrok, D.M., Borrok, D.M., Pratt, L.M., 2011. Anthropogenic  
 896 sulfate loads in the Rio Grande, New Mexico (USA). *Chemical Geology* 283,  
 897 194–209. doi:10.1016/j.chemgeo.2011.01.017  
 898 Torres, M.A., West, A.J., Clark, K.E., Paris, G., Bouchez, J., Ponton, C., Feakins, S.J.,  
 899 Galy, V., Adkins, J.F., 2016. The acid and alkalinity budgets of weathering in  
 900 the Andes–Amazon system: Insights into the erosional control of global  
 901 biogeochemical cycles. *Earth and Planetary Science Letters* 450, 381–391.  
 902 doi:10.1016/j.epsl.2016.06.012  
 903 Torres, M.A., West, A.J., Li, G., 2015. Sulphide oxidation and carbonate dissolution  
 904 as a source of CO. *Nature* 507, 346–349. doi:10.1038/nature13030  
 905 Tostevin, R., Turchyn, A.V., Farquhar, J., Johnston, D.T., Eldridge, D.L., Bishop,  
 906 J.K.B., McIlvin, M., 2014. Multiple sulfur isotope constraints on the modern  
 907 sulfur cycle. *Earth and Planetary Science Letters* 396, 14–21.  
 908 doi:10.1016/j.epsl.2014.03.057  
 909 Turchyn, A.V., Tipper, E.T., Galy, A., Lo, J.-K., Bickle, M.J., 2013. Isotope evidence  
 910 for secondary sulfide precipitation along the Marsyandi River, Nepal,  
 911 Himalayas. *Earth and Planetary Science Letters* 374, 36–46.  
 912 doi:10.1016/j.epsl.2013.04.033  
 913 Vance, D., Teagle, D.A., Foster, G.L., 2009. Variable Quaternary chemical  
 914 weathering fluxes and imbalances in marine geochemical budgets. *Nature*  
 915 458, 493.  
 916 Vitoria, L., Otero, N., Soler, A., Canals, À., 2004. Fertilizer Characterization:  
 917 Isotopic Data (N, S, O, C, and Sr). *Environ. Sci. Technol.* 38, 3254–3262.  
 918 doi:10.1021/es0348187  
 919 Volkov, I.I., Rozanov, A.G., 1983. The Sulfur Cycle in Oceans, in: *The Global*  
 920 *Biogeochemical Sulphur Cycle, Reservoirs and Fluxes*. John Wiley & Sons,  
 921 New York, pp. 357–423.



922 Voss, B.M., Peucker-Ehrenbrink, B., Eglinton, T.I., Fiske, G., Wang, Z.A., Hoering,  
923 K.A., Montluçon, D.B., LeCroy, C., Pal, S., Marsh, S., Gillies, S.L., Janmaat, A.,  
924 Bennett, M., Downey, B., Fanslau, J., Fraser, H., Macklam-Harron, G., Martinec,  
925 M., Wiebe, B., 2014. Tracing river chemistry in space and time: Dissolved  
926 inorganic constituents of the Fraser River, Canada. *Geochimica et*  
927 *Cosmochimica Acta* 124, 283–308. doi:10.1016/j.gca.2013.09.006  
928 Yu Lein, A., Grinenko, V.A., Migdisov, A.A., 1983. The Sulphur Cycle in Oceans, in:  
929 The Global Biogeochemical Sulphur Cycle, The Mass-Isotopic Balance of  
930 Sulphur in Oceanic Sediments. John Wiley & Sons, New York, pp. 423–448.  
931