

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

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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.

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## 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

76 Tmol/y from anthropogenic sources (Meybeck, 2003)). Thus in order to fully  
77 understand the secular changes in  $\delta^{34}\text{S}$  of seawater, we need to better constrain  
78 both the modern values for, and controls on, the isotopic composition of riverine  
79 sulfate.

80 The modern riverine sulfur isotopic composition can also inform  
81 estimates of chemical weathering fluxes, with important implications for the  
82 carbon cycle. Sulfur isotopes in rivers can provide insight into how much  
83 riverine S is sourced from dissolution of sedimentary sulfate minerals versus  
84 oxidative weathering of pyrite (OWP)(Calmels et al., 2007). OWP produces  
85 sulfuric acid, which is a source of acidity for chemical weathering and which,  
86 when it interacts with carbonate minerals, can lead to a net release of  $\text{CO}_2$ , in  
87 contrast to the sink of  $\text{CO}_2$  associated with silicate weathering (e.g. Calmels et al.,  
88 2007; Torres et al., 2016; 2015). Previous estimates of global OWP fluxes range  
89 from 0.5 to 0.65 Tmol/y (Berner and Berner, 1996; Francois and Walker, 1992;  
90 Lerman et al., 2007). However, recent studies that use sulfur isotopes (and  
91 sulfate-oxygen isotopes) from individual catchments indicate that estimates of  
92 global OWP flux are potentially much too low. The sum of OWP fluxes (0.15  
93 Tmol/y) from just three river basins (Mackenzie (Calmels et al., 2007), Kaoping  
94 (Das et al., 2012), and Jialing (Li et al., 2011)) can account for a third of previous  
95 global OWP flux estimates, despite covering less than 2% of global land area (Das  
96 et al., 2012). Underestimating global OWP by this magnitude may result in  
97 substantial overestimates of the modern-day sink of  $\text{CO}_2$  associated with  
98 chemical weathering.

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101 *1.1 Previous estimates of  $\delta^{34}\text{S}$  of river water*

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

118 Geochemical calculations tend to form the basis of the most commonly  
119 cited sulfur isotope compositions for modern riverine input estimates. Isotope  
120 mass balance models of the sulfur cycle have typically employed a riverine  $\delta^{34}\text{S}$   
121 value of around 7-8‰ (e.g. Garrels and Lerman, 1984; Halevy et al., 2012; Kump  
122 and Garrels, 1986; Kurtz et al., 2003). These values can be traced back to  
123 assumptions about the relative contributions of sulfide and sulfate weathering to  
124 the riverine sulfate budget. Specifically, it was assumed that the abundance of  
125 sedimentary sulfate minerals is equal to the abundance of sedimentary sulfide

126 minerals and that gypsum weathers twice as fast as pyrite (Berner and Berner,  
127 1996). These two assumptions imply that sulfate mineral weathering should  
128 contribute twice as much sulfate to rivers as pyrite weathering. Thus, if a  $\delta^{34}\text{S}$   
129 value of 17‰ is assumed for sulfate in evaporite minerals and a  $\delta^{34}\text{S}$  value of -  
130 12‰ is assumed for pyrite, then a simple river isotope mass balance predicts an  
131 average riverine  $\delta^{34}\text{S}$  of between 7 to 8‰ (ignoring anthropogenic and other  
132 minor sources of sulfate to rivers). It is important to note that because these  
133 calculations assumed a fixed ratio of riverine sulfur from sulfide weathering to  
134 sulfate weathering, this isotopic composition cannot then be used to calculate the  
135 relative proportion of sulfide weathering. Nonetheless, this approach and its  
136 origins are important and informative to the field.

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

144

## 145 **2 Methods**

### 146 *2.1 Measurement of river water sulfate and $\delta^{34}\text{S}$*

147         River waters were sampled either opportunistically or as part of a  
148 number of field campaigns between years 1993 – 2013. Details of all rivers  
149 measured in this study for sulfur isotopes can be found in Supplementary Table  
150 1. Previously published sulfur isotope data from main stems of rivers were

151 compiled from the literature, and can be found in Supplementary Table 2, along  
152 with the new main stem data from this study. The locations of the main stems of  
153 rivers included in this study can be seen in Figure 1.

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

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

172 Complete chemistry blanks were monitored along with every set of 10  
173 samples, and contained an average of 0.1 nmol of sulfate. As the smallest samples  
174 measured had 20 nmol of sulfate, the blank contamination contributes at most  
175 0.5% of the total sulfate measured, and typically contributes closer to 0.1%, as

176 most samples were analyzed with at least 100 nmol of sulfate. The  $\delta^{34}\text{S}$  of the  
177 blank is typically close to zero, with a long-term average for all blanks of  $2.4 \pm$   
178  $6.5\text{‰}$  (2 s.d.;  $n = 16$ ). The measured  $\delta^{34}\text{S}$  of all river samples have been blank  
179 corrected with the average of all blanks, and the uncertainty on both the amount  
180 of blank and its isotopic ratio is propagated through to the final uncertainties on  
181 the riverine  $\delta^{34}\text{S}$  values.

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

186

## 187 *2.2 End-member weathering calculation*

188 Previous studies have used coupled  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  in sulfate to estimate  
189 OWP fluxes in individual river catchments (Calmels et al., 2007; e.g. Karim and  
190 Veizer, 2000; Turchyn et al., 2013). These estimates do not rely on knowing the  
191  $\delta^{34}\text{S}$  of the pyrite being weathered which can have a large range within an  
192 individual basin (e.g. Calmels et al., 2007). This is a very powerful technique, but  
193 measurement by gas source mass spectrometry requires larger sample sizes, and  
194 has only been used on a few rivers, in contrast to the numerous  $\delta^{34}\text{S}$   
195 measurements on riverine sulfate that have been previously published. Thus, to  
196 maximize the number of rivers included in our global database, we used riverine  
197  $\delta^{34}\text{S}$  and major anion and cation concentrations in an end-member weathering  
198 calculation following Gaillardet et al. (1999) to further constrain the global  
199 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),

244 assuming congruent weathering of evaporites. These evaporite based ratios are  
245 consistent with the median ratio calculated from rivers that drain evaporites  
246 (Meybeck, 1984; 1979), giving additional support for our choice of end-  
247 members<sup>1</sup>. The S/Na value for carbonates is based on the S/Ca molar ratio of  
248 0.001 in marine carbonates (Volkov and Rozanov, 1983) and the Ca/Na value of  
249 carbonates of 60 (Negrel et al., 1993). Finally, the S/Na value of the silicate end-  
250 member is calculated from global estimates of the abundance of S and Na<sub>2</sub>O in  
251 continental igneous and metamorphic rocks (Holser and Kaplan, 1966; Rudnick  
252 and Gao, 2003). This estimate of S/Na in silicate rocks deliberately does not  
253 include sedimentary sulfides (e.g. from shales). Consequently, any sulfate  
254 derived from oxidative weathering of sedimentary pyrite would be incorporated  
255 into the excess sulfate parameter described above.

256

### 257 **3 Results**

258 The river waters analyzed in this study yield a large range of  $\delta^{34}\text{S}$  values,  
259 between -13.4‰ and 21.7‰ (Figures 1 and 2), and represent more than 46% of  
260 the global water discharge to the ocean ( $3.88 \times 10^4 \text{ km}^3/\text{y}$  (Peucker-Ehrenbrink,  
261 2009)). This dataset includes smaller tributaries, as well as time series  
262 measurements from individual major rivers (Fraser, Lena, Ob', Yenisei, Yukon,  
263 Mackenzie, Kolyma, and Congo rivers). Within an individual river basin, there  
264 can be a large range in the  $\delta^{34}\text{S}$  of tributaries. For instance,  $\delta^{34}\text{S}$  values from the

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<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).

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

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

280 The flux-weighted average of the rivers gives a  $\delta^{34}\text{S}$  value of  $4.4 \pm 4.5\%$   
281 (1 s.d.). If the polluted rivers ( $([\text{Na}] - [\text{Cl}])/[\text{Cl}] < 0.1$ ) are excluded<sup>2</sup> from this  
282 estimate, the average  $\delta^{34}\text{S}$  of riverine sulfate is  $4.8 \pm 4.9\%$ , and accounts for  
283 more than 43% of the water discharge to the ocean. The similarity between these  
284 two values suggests that the most polluted rivers do not meaningfully change the

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<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  $\delta^{34}\text{S} = -5\%$ , and a concentration of sulfate of 115  $\mu\text{M}$ . This pre-anthropogenic estimate is *lower* than the measured  $\delta^{34}\text{S} = -0.72\%$  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)).

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

293 We can assess how representative our subset of rivers is of global riverine  
294 discharge by comparing the flux-weighted Mg/Na and Ca/Na ratios and  
295 strontium isotopes from our dataset with global estimates of these values from  
296 previously published studies. Our flux weighted Mg/Na ratio of 0.66 and Ca/Na  
297 ratio of 1.63 are within the range of previous global estimates of these values of  
298 0.57 to 0.70 and 1.32 to 1.67, respectively (Meybeck and Ragu, 1995; Miller et al.,  
299 2011). The same is true if we scale the river fluxes by the large scale drainage  
300 regions (Graham et al., 1999; Peucker-Ehrenbrink and Miller, 2007) following  
301 Miller et al. (2011). In this case, our subset of rivers yields a Mg/Na ratio of 0.68  
302 and a Ca/Na ratio of 1.70, compared to previously published values of 0.55 to  
303 0.71 and 1.27 to 1.74, respectively (Meybeck and Ragu, 1995; Miller et al., 2011).  
304 Thus, our elemental ratios support the use of this subset of rivers for global  
305 budget estimates. The flux weighted average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio from our subset of  
306 rivers with published ratios (40% of global water discharge) is 0.7115, slightly  
307 higher than estimates of global riverine  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7111 to 0.7114 (Peucker-  
308 Ehrenbrink et al., 2010; Vance et al., 2009)). The slightly more radiogenic  
309  $^{87}\text{Sr}/^{86}\text{Sr}$  value likely reflects an underrepresentation of younger, more

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

316

### 317 *3.1 Weathering end-member decomposition*

318 End-member decomposition allows us to tease apart the different sources  
319 of sulfate to rivers. A plot of  $\delta^{34}\text{S}$  of riverine sulfate versus the percentage of Na  
320 derived from silicate weathering illustrates the importance of pyrite weathering  
321 in influencing the sulfur isotopic composition of rivers (Figure 5). For rivers  
322 with no Na derived from silicate weathering, the only other two sources of Na  
323 are evaporite and carbonate minerals. As both of these lithologies reflect the  
324 sulfur isotopic composition of seawater when they were formed, they should  
325 both have high  $\delta^{34}\text{S}$  values ( $\sim 17\text{‰}$ , (Holser and Kaplan, 1966)). Similarly, for  
326 rivers that derive 100% of their Na from silicate weathering (none from  
327 evaporites or carbonates), the  $\delta^{34}\text{S}$  of river water should be similar to the silicate  
328 value of 4‰ (Holser and Kaplan, 1966). These two end-members determine the  
329 red mixing lines in Figure 5. Most data plot below these mixing lines, implying a  
330  $^{34}\text{S}$ -depleted source of sulfate to the rivers that does not also add Na. The  
331 oxidative weathering of sedimentary pyrite could reasonably constitute such a  
332 source.

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

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

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

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

363 The flux weighted global percentage of excess sulfate is  $65 \pm 6\%$  ( $3.1 \pm 0.2$   
364 Tmol/y), which is dominated by pyrite weathering and pollution. The  
365 contributions to riverine sulfate from volcanoes and biogenic emissions are both  
366 relatively small (0.34 and 0.14 Tmol/y, respectively (Berner and Berner, 1996)).  
367 Using an estimate of the pollutive sulfate in rivers of 1.3 Tmol/y (Meybeck,  
368 2003), we estimate that the global contribution of oxidative weathering of pyrite  
369 to riverine sulfate is 1.3 Tmol/y, or about 28% of the total sulfate flux from all  
370 sources to the ocean (4.7 Tmol/y), and 46% of the flux of sulfate from  
371 weathering (i.e. 2.8 Tmol/y, excluding sulfate from pollution, volcanoes, biogenic  
372 emissions, and cyclic sea salts).

373

## 374 **4 Discussion**

### 375 *4.1 Controls on riverine sulfate $\delta^{34}\text{S}$*

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



385 Formation and equivalent units. Sedimentary evaporites are absent from the  
386 underlying strata, and thus sulfate in these rivers is likely dominated by the  
387 oxidation of pyrite and organic sulfur molecules, which, due to the biological  
388 isotope fractionations associated with sulfate reduction in organic-rich  
389 sediments during their diagenesis and lithification, results in lower overall  $\delta^{34}\text{S}$   
390 values. The lowest  $\delta^{34}\text{S}$  values measured in major rivers come from the Orinoco  
391 (-5.1‰) and the Kolyma (-4.2 to -5.6‰) rivers, which also drain catchments  
392 rich in sedimentary rocks, including black shales (Edmond et al., 1996; Huh et al.,  
393 1998a). These examples are consistent with the notion that local lithology plays  
394 a key role in setting the sulfur isotopic composition of rivers, and the important  
395 role of black shale weathering in the sulfur budget.

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

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

410 negative  $\delta^{34}\text{S}$  signatures (e.g. Ivanov et al., 1983). We screened for polluted  
411 rivers using ancillary anion and cation data (Fiege et al., 2009; Miller et al., 2011;  
412 Peterson et al., 2016; Voss et al., 2014). If the value of  $([\text{Na}] - [\text{Cl}])/[\text{Cl}]$  is less  
413 than 0.1, then the river is considered polluted. The main sources of Cl to rivers  
414 are sea salt aerosols, evaporites, and pollution. As both sea salt aerosols and  
415 evaporites deliver Na and Cl in roughly equal proportions, an excess of Cl relative  
416 to Na may be indicative of a polluted river. The following rivers have high Cl  
417 relative to Na: Connecticut, Danube, Indus, Doubs, Lena, Mississippi, Neman,  
418 Rhine, Seine, and St. Lawrence. These rivers are also located near large human  
419 populations or near industrial centers. The one exception to this is the Lena  
420 River, which is influenced by Cl-rich brines (Gaillardet et al., 1999). As shown in  
421 Figure 2, the polluted rivers tend to have high sulfate concentrations ( $>100 \mu\text{M}$ ,  
422 with the exception of the Doubs whose main sulfate sources are atmospheric  
423 (Calmels et al., 2014)). However, there is a large range of  $\delta^{34}\text{S}$  for these rivers;  
424 thus they do not simply populate the bottom left of the graph, as would be  
425 expected if pollution always had a low  $\delta^{34}\text{S}$  signature. Indeed, measurements of  
426  $\delta^{34}\text{S}$  on oil, gas, coal and sulphide ores range from -25 to +30‰ (Newman et al.,  
427 1991), and  $\delta^{34}\text{S}$  of fertilizers, another anthropogenic sulfate source, can range  
428 from -6.5 to 20.7‰ (Szynkiewicz et al., 2011; Vitoria et al., 2004). Since pollution  
429 cannot be the sole reason for the high sulfate concentration and low  $\delta^{34}\text{S}$ , it  
430 follows that the oxidation of pyrite is a major source of sulfate to these rivers.  
431 This is consistent with the abundance of shales and pyrites in the catchment  
432 areas of the rivers (e.g. the Kolyma (Huh et al., 1998a), Orinoco (Edmond et al.,

433 1996), Buller (Robinson and Bottrell, 1997), Kaoping (Das et al., 2012), Skeena  
434 (Spence and Telmer, 2005), and Stikine rivers (Calmels et al., 2007)).

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

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

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

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

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

485

#### 486 *4.2 Global dissolved sulfur isotope mass balance for rivers*

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

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

503

$$504 \quad f_{\text{owp}} = -(\delta_{\text{evap}} - \delta_{\text{riv}})/(\delta_{\text{py}} - \delta_{\text{evap}}) \quad \text{Equation 2}$$

505

---

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

506 where  $f_{\text{owp}}$  is the fraction of pyrite-derived sulfate,  $\delta_{\text{evap}}$  is the  $\delta^{34}\text{S}$  of evaporite  
507 (17‰ (Holser and Kaplan, 1966)),  $\delta_{\text{riv}}$  is the  $\delta^{34}\text{S}$  of riverine sulfate (4.8‰,  
508 above), and  $\delta_{\text{py}}$  is the  $\delta^{34}\text{S}$  of pyrite from sedimentary rocks (-12‰ (Holser and  
509 Kaplan, 1966)). This gives a  $f_{\text{owp}}$  in rivers of 0.42, substantially higher than the  
510 estimate of  $f_{\text{owp}}$  of 0.28 if the riverine  $\delta^{34}\text{S}$  value is taken to be 9‰ (Ivanov,  
511 1983).

512         These estimates are very sensitive to the assumption of the end-member  
513  $\delta^{34}\text{S}$  values of the oxidized (sulfate salts) and reduced (sulfide and disulfide)  
514 sedimentary reservoirs, which are difficult to constrain from a global  
515 perspective. Estimates of the global  $\delta^{34}\text{S}$  values of oxidized S in sediments range  
516 from 12.1‰ to 19‰, and of reduced sediments from -7.4‰ to -16‰ (Holser et  
517 al., 1988 and references therein). These different combinations of  $\delta_{\text{evap}}$  and  $\delta_{\text{py}}$   
518 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  
519 river  $\delta^{34}\text{S}$  value is taken to be 9‰), with a median  $f_{\text{owp}}$  of 0.41. Despite the large  
520 uncertainties in the correct end-member isotope values, the estimate of  $f_{\text{owp}} =$   
521 0.41 is broadly consistent with the independently derived fluxes from the  
522 weathering end-member decomposition that indicate that pyrite weathering  
523 contributes up to 46% of the sulfate flux in rivers due to weathering. The  
524 weathering end-member decomposition is based solely on major ion  
525 concentrations and not isotope values, and so is independent of the isotope mass  
526 balance calculation in Equation 2.

527

528 *4.3 Implications for the modern sulfur cycle and marine isotope mass balance*

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

543 It can be informative to investigate the derivation of previous estimates of  
544 the sulfate flux from OWP in order to understand why they were significantly  
545 lower than our new value. Previous estimates of global OWP from Berner and  
546 Berner (1996) and Lerman et al. (2007) both relied on assumptions of the  
547 relative abundance of pyrite in sedimentary rocks, though they do this  
548 differently. The 0.5 Tmol/y estimate (Berner and Berner, 1996) assumed that the  
549 riverine ratio of calcium from weathering of sedimentary rocks to pyrite-derived  
550 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



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

580

$$581 \quad f_{\text{pyr}} = (\delta_{\text{riv}} - \delta_{\text{sw}}) / (\Delta^{34}\text{S}_{\text{pyrite-seawater}}) \quad \text{Equation 3}$$

582

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

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

600 measurements from modern continental shelf, slope and rise sediments  
601 ( $\Delta^{34}\text{S}_{\text{pyrite-seawater}} = -48\text{‰}$  (Yu Lein et al., 1983)). Modelling studies that use  
602 constraints from  $\delta^{33}\text{S}$  also predict a greater difference between the  $\delta^{34}\text{S}$  values of  
603 seawater and bulk pyrite buried ( $\Delta^{34}\text{S}_{\text{pyrite-seawater}} = -56 \pm 5\text{‰}$ ) (Tostevin et al.,  
604 2014). These larger offsets in the isotopic composition of seawater and buried  
605 pyrite would imply that the fraction of pyrite buried is 0.29 and 0.34 for  $\Delta^{34}\text{S}_{\text{pyrite-}}$   
606  $\text{seawater} = -56$  and  $\Delta^{34}\text{S}_{\text{pyrite-seawater}} = -48$ , respectively (Figure 7), significantly less  
607 than our two independent estimates of the fraction of pyrite weathered. If  
608 correct, these estimates indicate that the biogeochemical sulfur cycle may not be  
609 balanced, and that more pyrite is being weathered than is being buried in  
610 modern marine sediments. This conclusion would be consistent with recent ice  
611 core evidence that shows a decrease in atmospheric  $\text{O}_2$  over the past 800,000  
612 years (Stolper et al., 2016). The magnitude of the imbalance between weathering  
613 and burial fluxes of reduced carbon and sulfur that is required to explain the long  
614 term oxygen trend in ice cores is  $\sim 2\%$  (Stolper et al., 2016); this number is well  
615 within uncertainties of the weathering flux estimates ( $\sim 0.2 \text{ Tmol/y}$ ). However,  
616 given the large range of estimates of  $\Delta^{34}\text{S}_{\text{pyrite-seawater}}$  more work constraining  
617 global  $\Delta^{34}\text{S}_{\text{pyrite-seawater}}$  from modern sediments would help to resolve this issue.

618 Our increased estimate of global OWP means that the previously  
619 published OWP rates from three river basins (Mackenzie (Calmels et al., 2007),  
620 Kaoping (Das et al., 2012), and Jialing (Li et al., 2011)) only account for  $\sim 12\%$   
621 (rather than a third) of the total global OWP flux estimate. Nonetheless, the fact  
622 that these rivers drain less than 2% of global surface area highlights the  
623 heterogeneity of pyrite weathering; simply put, some river basins will contribute  
624 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.

639

## 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

650 1.3 Tmol S/y, respectively. This estimate of pyrite weathering is twice as high as  
651 previous estimates, and is consistent with isotope mass balance constraints on  
652 the  $\delta^{34}\text{S}$  of river water that imply that ~40% of non-anthropogenic riverine  
653 sulfate derives from weathered pyrite. Since pyrite oxidation can act as a source  
654 of  $\text{CO}_2$  to the atmosphere, this new estimate should reduce the global carbon sink  
655 attributed to chemical weathering. Basin lithology exerts a strong control on the  
656  $\delta^{34}\text{S}$  values of riverine sulfate, questioning the validity of assuming constant  $\delta^{34}\text{S}$   
657 of riverine input to the ocean over geological time. Stratigraphic trends observed  
658 in sulfur isotopes in ancient sedimentary rocks might therefore reflect secular  
659 changes in the isotopic composition of the riverine inputs, rather than changes in  
660 the relative burial of marine pyrite versus sulfate salt evaporites.

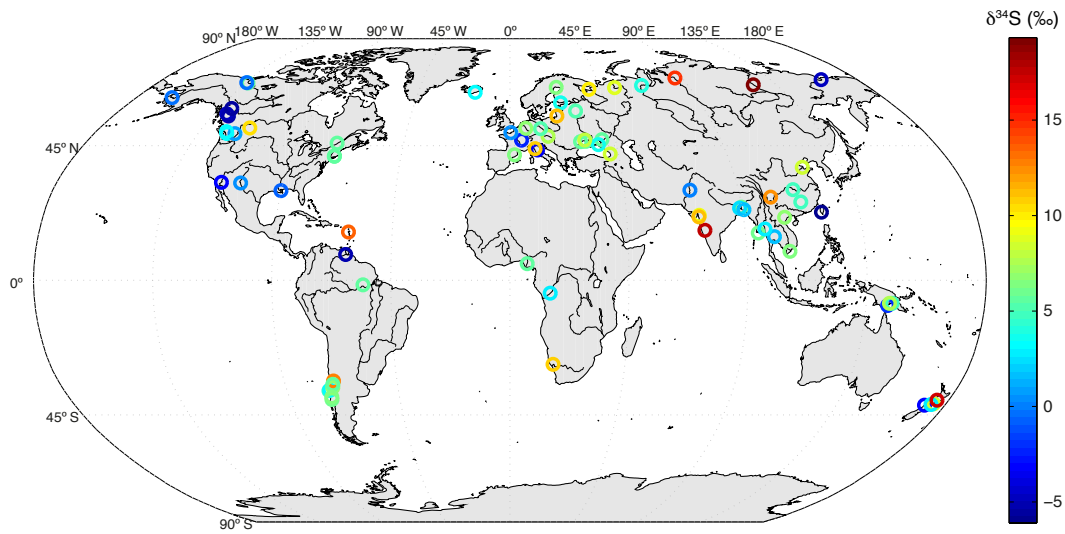
661

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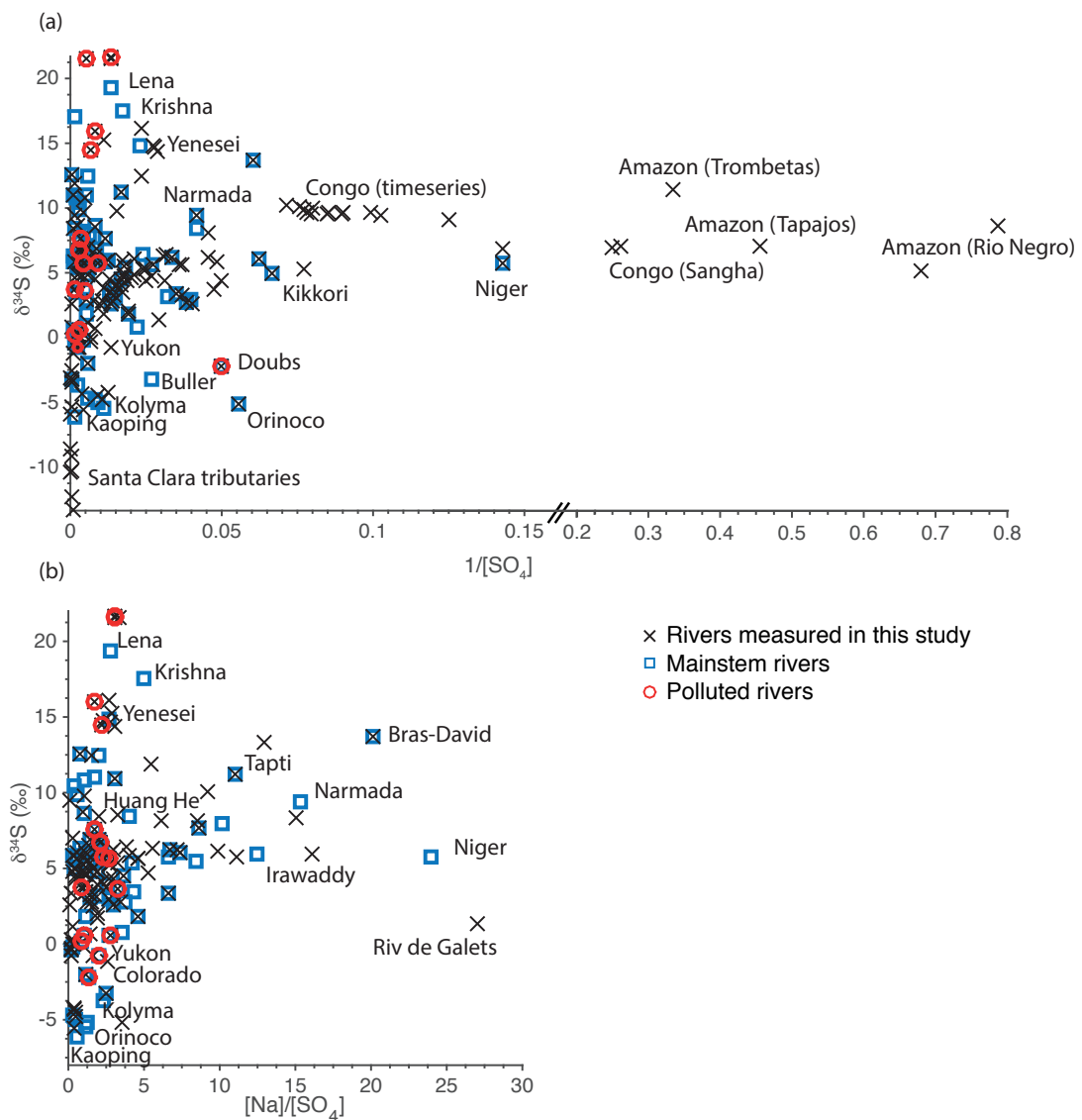
668

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.



675

676 **Figure 2.** (a)  $\delta^{34}\text{S}$  values (‰, V-CDT) of all rivers measured versus the inverse

677 concentration ( $\mu\text{M}^{-1}$ ) of sulfate (black x). Rivers designated as main stem rivers

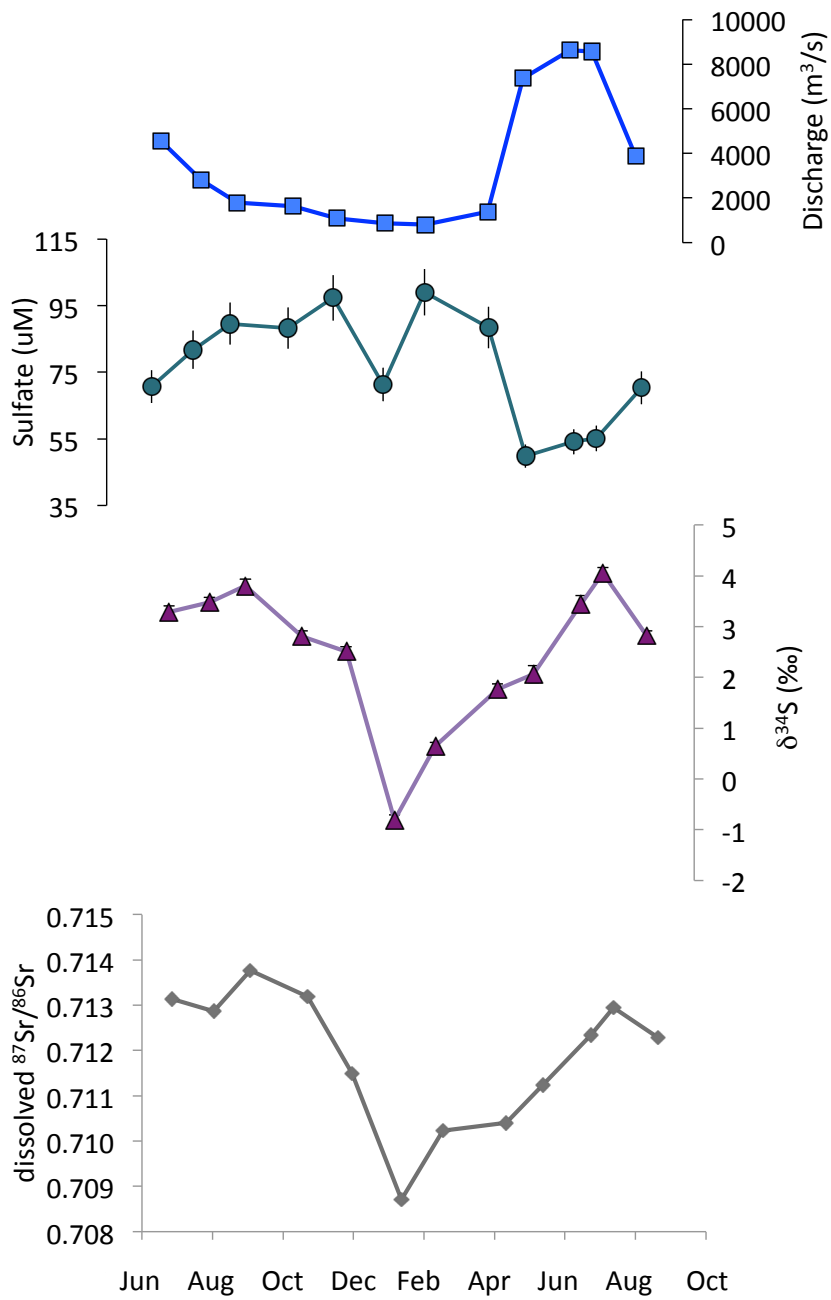
678 (compiled or measured) are shown as blue squares. Rivers identified as being

679 polluted (section 4.1) are circled in red. Note the change in scale on the X-axis

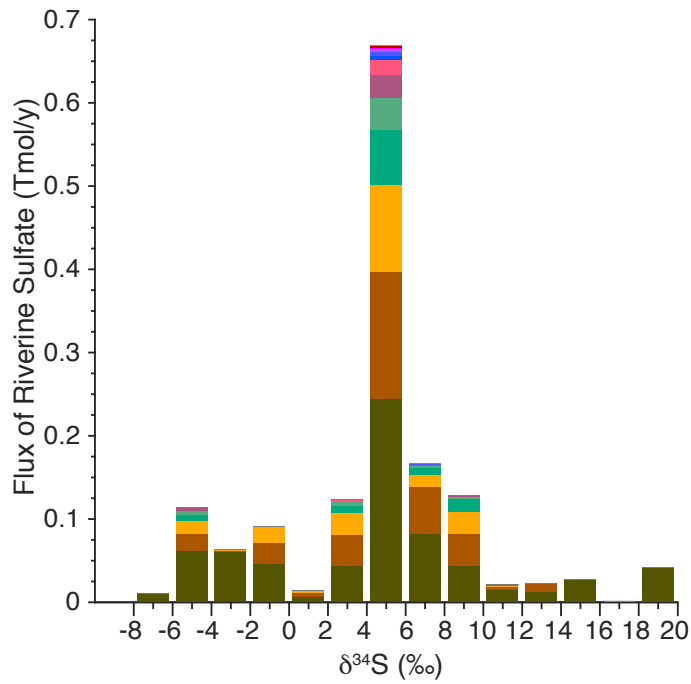
680 after the break. (b) Same as above but plotted against the Na/SO<sub>4</sub> molar value of

681 the riverine dissolved load.

682



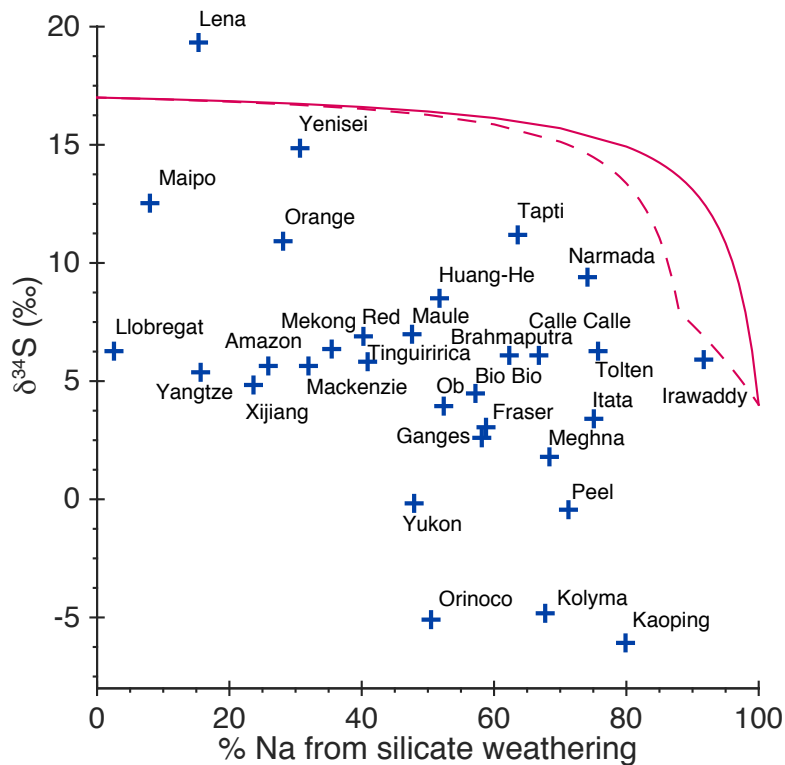
683  
 684 **Figure 3.** Time series data from Fraser River samples collected between June  
 685 2010 and August 2011. (a) Freshwater discharge (m<sup>3</sup>/s), (b) sulfate  
 686 concentration (µM); (c) δ<sup>34</sup>S values (‰, V-CDT), (d) <sup>87</sup>Sr/<sup>86</sup>Sr from (Voss et al.,  
 687 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.

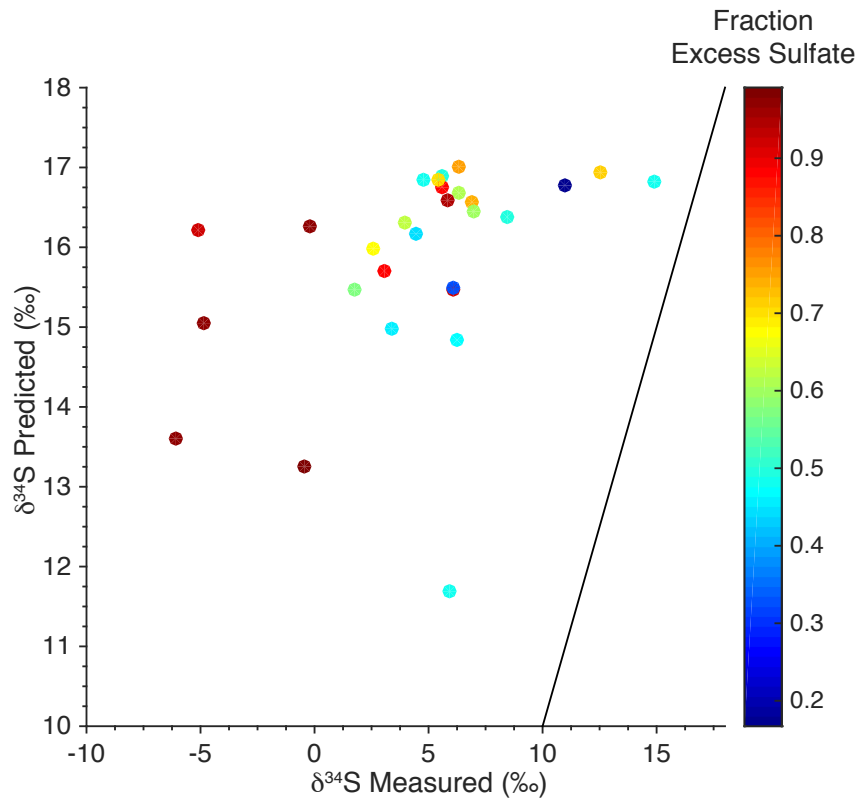




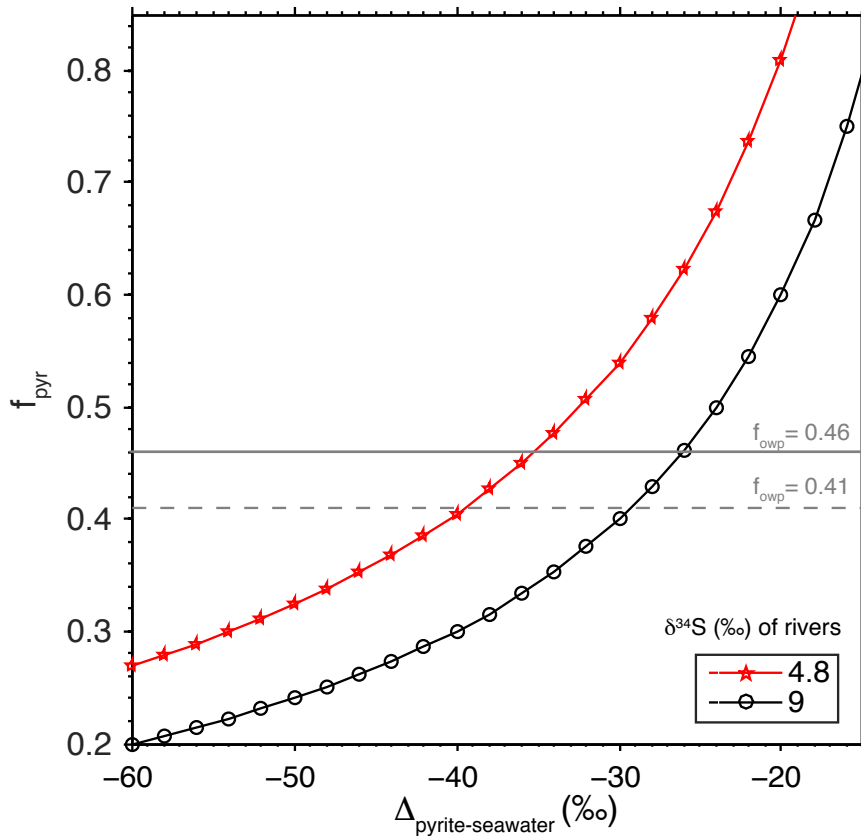
692

693 **Figure 5.** Riverine  $\delta^{34}\text{S}$  values (‰, V-CDT) of main stem rivers as a function of  
 694 the percent of Na attributed to silicate weathering from the end-member  
 695 decomposition. The red solid line is the predicted  $\delta^{34}\text{S}$  based on a riverine  
 696 isotope mass balance, using the S/Na end-member ratios from Table 1, and  
 697 assuming that the  $\delta^{34}\text{S}$  value of silicate rocks is 4‰, that the  $\delta^{34}\text{S}$  value of  
 698 evaporites is 17‰, and that there is no contribution of Na from carbonates. The  
 699 red dashed line is the predicted  $\delta^{34}\text{S}$  based on a riverine isotope mass balance,  
 700 using the S/Na end-member ratios from Table 1, and assuming that the  $\delta^{34}\text{S}$   
 701 value of silicate rocks is 4‰, that the  $\delta^{34}\text{S}$  value of evaporites and carbonates is  
 702 17‰, and that carbonates contribute 12% of the Na (maximum contribution  
 703 found for all rivers in this study), with the remainder coming from silicates and  
 704 evaporites.

705



706  
 707 **Figure 6.** Plot of predicted  $\delta^{34}\text{S}$  (based on assumptions of end-members from  
 708 mixing model, see section 4.1) versus measured  $\delta^{34}\text{S}$  values (‰, V-CDT). The  
 709 black line is the 1:1 line. The colors indicate the fraction of excess sulfate. Rivers  
 710 plotting to the left of the line have more negative  $\delta^{34}\text{S}$  values than predicted, and  
 711 thus are likely influenced by oxidative weathering of pyrite.



712

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

724

725

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