

Triple oxygen isotope insight into terrestrial pyrite oxidation

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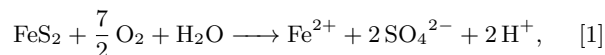
1 The mass-independent minor oxygen isotope compositions ($\Delta^{17}\text{O}$)
2 of atmospheric O_2 and CO_2 are primarily regulated by their rela-
3 tive partial pressures, $p\text{O}_2/p\text{CO}_2$. Pyrite oxidation during chemical
4 weathering on land consumes O_2 and generates sulfate that is car-
5 ried to the ocean by rivers. The $\Delta^{17}\text{O}$ values of marine sulfate
6 deposits have thus been proposed to quantitatively track ancient
7 atmospheric conditions. This proxy assumes direct O_2 incorpora-
8 tion into terrestrial pyrite oxidation-derived sulfate, but a mechan-
9 istic understanding of pyrite oxidation—including oxygen sources—
10 in weathering environments remains elusive. To address this issue,
11 we present sulfate source estimates and $\Delta^{17}\text{O}$ measurements from
12 modern rivers transecting the Annapurna Himalaya, Nepal. Sulfate
13 in high-elevation headwaters is quantitatively sourced by pyrite ox-
14 idation, but resulting $\Delta^{17}\text{O}$ values imply no direct tropospheric O_2
15 incorporation. Rather, our results necessitate incorporation of oxy-
16 gen atoms from alternative, ^{17}O -enriched sources such as reactive
17 oxygen species. Sulfate $\Delta^{17}\text{O}$ decreases significantly when moving
18 into warm, low-elevation tributaries draining the same bedrock lithol-
19 ogy. We interpret this to reflect overprinting of the pyrite oxidation-
20 derived $\Delta^{17}\text{O}$ anomaly by microbial sulfate reduction and reoxida-
21 tion, consistent with previously described major sulfur and oxygen
22 isotope relationships. The geologic application of sulfate $\Delta^{17}\text{O}$ as
23 a proxy for past $p\text{O}_2/p\text{CO}_2$ should consider both (i) alternative oxy-
24 gen sources during pyrite oxidation and (ii) secondary overprinting
25 by microbial recycling.

atmospheric O_2 | chemical weathering | $\Delta^{17}\text{O}$ | Himalayas | sulfur cycle

Atmospheric molecular oxygen (O_2) governs biogeochemical cycles, Earth's surface redox state, and the evolution of life; O_2 partial pressure ($p\text{O}_2$) has increased drastically in the geologic past in response to biologic and geologic drivers (1, 2). Despite this importance, quantitatively constraining $p\text{O}_2$ throughout Earth's history remains challenging due to a lack of direct proxies (2). Recently, the minor oxygen isotope composition ($^{17}\text{O}/^{16}\text{O}$, reported as $\Delta^{17}\text{O}$; Materials and Methods) of geologically preserved minerals has been proposed as one such proxy (1, 3–8). This approach utilizes the fact that photochemical reactions between O_2 , ozone (O_3), and carbon dioxide (CO_2) in the stratosphere generate anomalous, mass-independent ^{17}O signatures that are mixed into the troposphere (9). In particular, tropospheric O_2 carries a large negative $\Delta^{17}\text{O}$ anomaly, the magnitude of which reflects: (i) the ratio of O_2 to CO_2 partial pressures ($p\text{O}_2/p\text{CO}_2$), which determines the strength of the signal acquired during stratospheric photochemistry, and (ii) the amount of O_2 generated by oxygenic photosynthesis in the biosphere, which dilutes stratospheric inputs (1, 6). Thus, if $p\text{CO}_2$ and biospheric productivity can be independently constrained, then tropospheric O_2 $\Delta^{17}\text{O}$ is potentially a direct and quantitative $p\text{O}_2$ tracer.

Sulfate (SO_4^{2-}) bearing minerals are particularly attractive

reservoirs for this method of reconstructing $p\text{O}_2$ in the geologic past because oxidative pyrite (FeS_2) weathering consumes O_2 (10, 11). If oxidation of pyrite contained in exhumed sedimentary rocks on land follows the reaction:



then contemporaneous tropospheric O_2 —including its anomalous ^{17}O composition—could be directly incorporated into resulting sulfate (12). Isotopically labeled oxidation experiments support this idea; $\approx 8\%$ to 15% of sulfate oxygen atoms have been shown to be sourced directly from dissolved O_2 under well-oxygenated experimental conditions (12, 13). In light of these results and the fact that sulfate oxygen isotopes do not equilibrate with water on geologically relevant timescales, preserved barite (BaSO_4), gypsum (CaSO_4), and carbonate-associated sulfate $\Delta^{17}\text{O}$ values have been used to reconstruct $p\text{O}_2/p\text{CO}_2$ throughout Earth's history (3–8, 14, 15). Such interpretations require two criteria to be met: (i) this direct O_2 consumption mechanism (Eq. 1) contributes a significant proportion of pyrite oxidation-derived sulfate and (ii) primary $\Delta^{17}\text{O}$ signals are not overprinted or diluted in the environment prior to being preserved in the rock record. Tropospheric O_2 ^{17}O compositions in the geologic past are thus typically reconstructed using the most negative sulfate $\Delta^{17}\text{O}$ value from a given geologic unit (i.e., least overprinted) and scaling by a $\approx 8\%$ to 15% O_2 incorporation factor (7, 15).

However, anoxic laboratory experiments and modern field observations complicate this picture. Specifically, both biotic

Significance Statement

Pyrite is oxidized during weathering to form dissolved sulfate that is carried to the ocean by rivers. This process is thought to incorporate atmospheric O_2 -derived oxygen; geologically preserved sulfate has thus been proposed to directly trace past O_2 isotope compositions. However, this mechanism has not been thoroughly tested in modern weathering environments. We show that dissolved sulfate in Himalayan rivers is predominantly derived from pyrite, yet its oxygen isotope compositions preclude direct O_2 incorporation. Rather, alternative oxygen sources (e.g., reactive oxygen species) may be incorporated during oxidation, prompting reconsideration of the pyrite oxidation mechanism and the interpretation of geologically preserved sulfate as a direct O_2 tracer.

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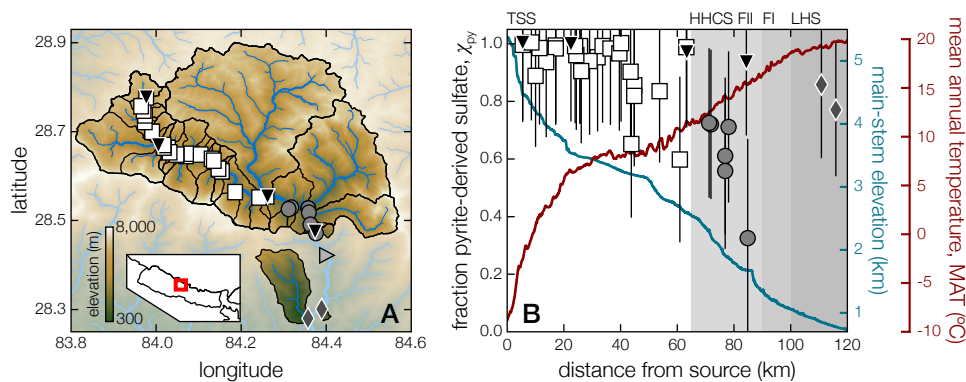
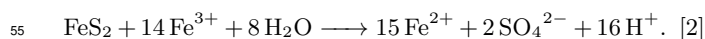


Fig. 1. (A) Marsiyandi basin map. Black lines delineate catchment areas upstream of each sample location. Background color represents elevation. Inset shows study location within Nepal. (B) Downstream evolution of elevation (blue line) and local MAT (red line) moving along the main-stem Marsiyandi. Also shown is the estimated fraction of sulfate derived from pyrite oxidation (χ_{py}) for each sample; tributaries are plotted at their confluence with the main-stem. Background shading indicates bedrock lithology. Symbols refer to: TSS tributaries (white squares), HHCS FII tributaries (gray circles), HHCS FI tributaries (light gray triangles), LHS tributaries (dark gray diamonds), and main-stem Marsiyandi (black triangles).

53 and abiotic experiments (10, 11, 13, 16, 17) imply that sulfate
54 oxygen can be quantitatively sourced from meteoric water:



56 O_2 is then consumed indirectly during subsequent oxidation
57 of Fe^{2+} to Fe^{3+} . If pyrite oxidation in the environment exclu-
58 sively follows Eq. 2, then product sulfate $\Delta^{17}\text{O}$ is decoupled
59 from atmospheric pO_2/pCO_2 . Recent studies using major
60 oxygen and sulfur isotope compositions ($\delta^{18}\text{O}$, $\delta^{34}\text{S}$; Materials
61 and Methods) suggest that pyrite oxidation in some modern
62 river systems occurs in suboxic groundwater aquifers and quan-
63 titatively incorporates meteoric water-derived oxygen (18–20).
64 Consistent with this interpretation, detailed studies of shale
65 bedrock drill cores indicate that pyrite oxidation occurs in
66 low- O_2 pores and microfractures within a deep, sharp reaction
67 front independent of erosion rate (21). Such results raise the
68 question as to why direct O_2 incorporation into sulfate is evi-
69 dent in the geologic past but is apparently absent from modern
70 pyrite weathering environments. Furthermore, pyrite oxida-
71 tion must proceed via 1-electron transfer steps regardless of the
72 exact mechanism involved (11, 22, 23), raising the possibility
73 that reactive oxygen species (ROS; e.g., H_2O_2 , $\text{O}_2^{\bullet-}$, OH^{\bullet})
74 may provide additional, isotopically unique oxygen sources
75 to sulfate (24, 25). ROS incorporation could help to recon-
76 cile modern and ancient observations, but its environmental
77 importance remains unknown.

78 To provide new insight, we constrain the sulfate budget in
79 a suite of highly erosive mountainous rivers. Building upon
80 previous work reporting $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ evolution (20), we doc-
81 ument sulfate source and $\Delta^{17}\text{O}$ values for samples collected
82 throughout the Marsiyandi River basin, Annapurna Himalaya,
83 Nepal. These results update our understanding of fluvial sul-
84 fate oxygen isotope systematics, with implications for modern
85 weathering budgets and geologic pO_2/pCO_2 reconstructions.

86 **Study Setting.** The Marsiyandi River is located in the South-
87 ern Flank of the Annapurna Himalaya, Central Nepal (Fig.
88 1A). Headwaters drain the Tethyan Sedimentary Series (TSS);
89 although some Manaslu granite exposures exist within our
90 study region, bedrock is primarily described as a continental
91 margin sequence containing variably metamorphosed lime-
92 stone and siliclastics with interbedded pyrite-rich black shales
93 (26–28). The TSS lies entirely within the Himalayan oro-
94 genic rain shadow; vegetation is sparse (29) and mean annual
95 precipitation (MAP) never exceeds 1000 mm yr^{-1} (average
96 $\approx 500 \text{ mm yr}^{-1}$) (30). Mean annual temperature (MAT) within
97 the TSS ranges from -10°C in the highest elevations to near

15 $^\circ\text{C}$ in the lowest elevations (Fig. 1B). Downstream of the
TSS, the Higher Himalayan Crystalline Series (HHCS) con-
tains two main bedrock units: Formation I (FI), dominated
by silicate gneiss, and Formation II (FII), dominated by calc-
silicate metamorphic rocks (26, 31). MAP increases markedly
due to the influence of the Indian Summer Monsoon, reaching
 2500 mm yr^{-1} (30), whereas MAT exhibits only modest in-
creases (Fig. 1B). Further downstream, the Lesser Himalayan
Series (LHS) is described as undifferentiated low- to medium-
grade metasedimentary and metavolcanic rocks (27) and by
MAP and MAT values near those within the HHCS. Import-
antly, evaporitic successions have never been reported in
Central Nepal (29)*.

Results

112 Samples were collected in May (pre-monsoon) and September
113 (monsoon season) 2002 across a $\approx 120 \text{ km}$ transect starting at
114 the Marsiyandi River headwaters in the TSS (5000 m elevation)
115 and ending in the LHS near the base of the Himalaya (750 m ele-
116 vation; Fig. 1B) (29, 33–35). Most samples were collected from
117 small tributaries draining single lithologies (median catchment
118 area = 20 km^2 ; Table S2) and are independent of one another.
119 Tributaries span a range of catchment slopes (24.0 to 41.1 deg),
120 MAP (407 to 1330 mm yr^{-1}), MAT (-10 to 15°C), and glacial
121 extent (0 to 46 % by area; Table S2). This approach allows us
122 to isolate the effect of geomorphic/environmental changes on
123 riverine chemistry while holding lithology and catchment area
124 roughly constant (36). To investigate main-stem evolution,
125 we additionally report results from the Marsiyandi River at 4
126 locations throughout the basin.

127 **Sulfate Sources.** Sulfate source contributions—including at-
128 mospheric inputs and carbonate, evaporite, granite, and shale
129 weathering—were estimated using a conservative tracer mix-
130 ing model and previously published major ion concentrations
131 (Materials and Methods) (29). Results indicate that the frac-
132 tion of riverine sulfate derived from pyrite oxidation in shale,
133 termed χ_{py} , ranges from 40 to 100 % (Fig. 1B). χ_{py} is highest
134 in sulfate-rich TSS tributaries, ranging from 60 to 100 % and
135 averaging $91 \pm 11\%$ ($\mu \pm 1\sigma$, $n = 25$; Table S1). Slightly
136 lower χ_{py} values in the most downstream TSS samples could
137 result from partial HHCS or Manaslu granite bedrock expo-
138 sure in these tributaries (29). Across the entire sample set,

*Chloride-rich hydrothermal hot springs along fault zones do suggest the presence of basinal brines or buried halite (33, 37). However, hot springs are deficient in both SO_4^{2-} and Ca^{2+} relative to Cl^- and Na^+ (37), indicating minimal contribution of gypsum dissolution to hydrothermal solutes and thus precluding evaporite weathering as a major driver of observed sulfate trends.

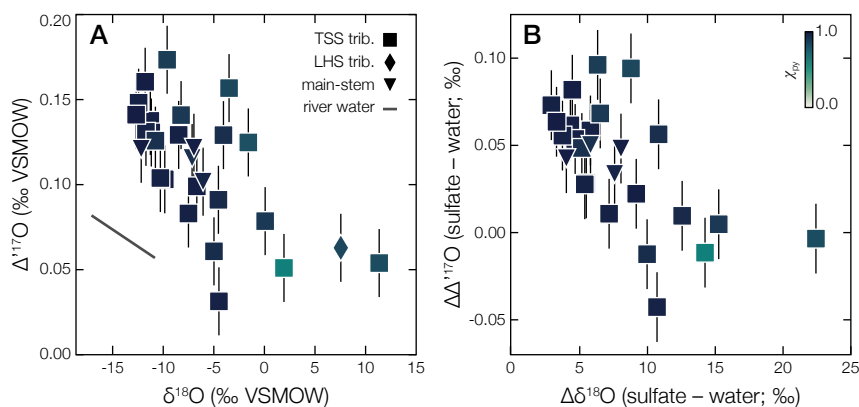


Fig. 2. Oxygen isotope compositions. (A) colored points: $\Delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ scatter plot for all sulfate samples; gray line: Marsiyandi basin river water isotope array. Water $\delta^{18}\text{O}$ was measured directly (20) and $\Delta^{17}\text{O}$ was calculated using the global meteoric water line (32). (B) Scatter plot of $\Delta\Delta^{17}\text{O}$ vs. $\Delta\delta^{18}\text{O}$, the offsets between sulfate and concomitant river water $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ (Materials and Methods). For both panels, symbol colors refer to the estimated fraction of sulfate derived from pyrite oxidation (χ_{py}) and shapes represent: TSS tributaries (squares), LHS tributaries (diamonds), and the main-stem Marsiyandi (triangles). $\Delta^{17}\text{O}$ and $\Delta\Delta^{17}\text{O}$ uncertainty ($\mu \pm 1\sigma$) is the long-term instrument reproducibility (Materials and Methods); $\delta^{18}\text{O}$ and $\Delta\delta^{18}\text{O}$ uncertainty is smaller than marker points (20). Both panels show that sulfate is generally enriched in ^{17}O relative to meteoric water, opposite of what would be expected from direct atmospheric O_2 incorporation.

χ_{py} decreases moving downstream (slope = $-0.003\% \text{ km}^{-1}$, $p = 6.5 \times 10^{-5}$), largely due to the sharp drop within tributaries draining HHCS FII calc-silicate metamorphic rocks. This drop coincides with the Southern Tibetan Detachment System and the Main Central Thrust (35) and is likely driven by contributions from limestone weathering in this region, as suggested by our weathering model results (Table S1). In contrast, when considering only TSS samples that are sufficiently upstream of potential HHCS and Manaslu granite influence ($\leq 40 \text{ km}$ from the the source) (29), χ_{py} remains near 100% and does not correlate with downstream distance ($p > 0.05$). Importantly, results account for precipitation-derived sulfate, including anthropogenic sources (i.e., acid rain). These inputs never exceed 11% of total sulfate in any sample, averaging only $2.0 \pm 2.5\%$ ($n = 38$) across the entire sample set and $1.0 \pm 1.1\%$ ($n = 25$) within the TSS, consistent with low measured sulfate concentrations in Himalayan rain water (38, 39). We thus primarily limit our sulfate ^{17}O isotope measurements to upstream TSS catchments.

Sulfate Isotopes. Riverine sulfate $\Delta^{17}\text{O}$ ranges from 0.041 to 0.180 ‰ VSMOW (average = $0.117 \pm 0.038\%$ VSMOW; $n = 29$; Table S1) and exhibits a significant decrease moving downstream (slope = $-0.001\% \text{ km}^{-1}$; $p = 3.8 \times 10^{-3}$; $R^2 = 0.35$; Fig. S1). Sulfate $\Delta^{17}\text{O}$ is negatively correlated with both $\delta^{18}\text{O}$ (slope = $-0.005\% \text{ ‰}^{-1}$; $p = 3.8 \times 10^{-3}$; $R^2 = 0.44$; Fig. 2A) and $\delta^{34}\text{S}$ (slope = $-0.002\% \text{ ‰}^{-1}$; $p = 1.6 \times 10^{-4}$; $R^2 = 0.41$; Table S1). Because sulfate oxygen can be sourced directly from water (Eq. 2) (10, 11, 16, 17, 40), we additionally report offsets between sulfate and concomitant river water $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$, termed $\Delta\delta^{18}\text{O}$ and $\Delta\Delta^{17}\text{O}$ (Fig. 2B; Materials and Methods). Water $\delta^{18}\text{O}$ was measured directly (20), whereas $\Delta^{17}\text{O}$ was calculated using the global meteoric water line (32). $\Delta\Delta^{17}\text{O}$ ranges from -0.033 to 0.103% (average = $0.048 \pm 0.034\%$; $n = 26$; Table S1) and displays a statistically significant decrease with increasing $\Delta\delta^{18}\text{O}$ (slope = $-0.008\% \text{ ‰}^{-1}$; $p = 8.3 \times 10^{-4}$; $R^2 = 0.39$; Fig. 2B). In contrast, both $\Delta^{17}\text{O}$ and $\Delta\Delta^{17}\text{O}$ values do not correlate with χ_{py} estimates nor with estimated fractional dolomite, gneiss/granite, limestone, or evaporite end-member weathering contributions ($p > 0.05$). Unlike χ_{py} , which is largely stable near 100% within the TSS, sulfate $\Delta^{17}\text{O}$ values in tributaries draining this region display large and systematic decreases moving downstream (Fig. S1).

Discussion

Fluvial Sulfate Oxygen Source. We observe spatially coherent sulfate oxygen isotope signals throughout the Marsiyandi River basin. Headwater sulfate exhibits large, positive $\Delta^{17}\text{O}$ values ($\Delta\Delta^{17}\text{O} \approx 0.10\%$) as well as $\delta^{18}\text{O}$ near that of local meteoric water ($\Delta\delta^{18}\text{O} \leq 5\%$). Consistent with previous observations based on sulfate $\delta^{18}\text{O}$ from a suite of global rivers (18–20), these results imply that pyrite weathering in mountainous headwaters occurs primarily within suboxic groundwater aquifers. Sulfate ^{17}O compositions indicate no appreciable O_2 incorporation during pyrite oxidation (Eq. 1). Any O_2 contribution would produce sulfate with $\Delta^{17}\text{O}$ below the meteoric water line (i.e., $\Delta\Delta^{17}\text{O} < 0$) since $\Delta^{17}\text{O} \approx -0.5\%$ VSMOW in modern tropospheric O_2 (6, 9). However, the opposite is observed (Fig. 2B). Furthermore, mass-dependent isotope fractionation associated with anoxic pyrite weathering (Eq. 2) likely cannot explain observed ^{17}O enrichment since this would require a mass law of $\theta \approx 0.54$ to 0.55 , considerably higher than any known low-temperature microbial or abiotic processes (1, 41). Rather, positive $\Delta\Delta^{17}\text{O}$ values require either (i) overprinting by atmospherically derived (precipitation or aerosol) sulfate inputs (1, 41) or (ii) an additional, ^{17}O -enriched oxygen source that is incorporated into sulfate during pyrite oxidation.

We first consider atmospheric inputs. Many oxygen-bearing gases carry positive ^{17}O anomalies that can be transferred to sulfate in the atmosphere. For instance, aqueous-phase SO_2 oxidation by ^{17}O -enriched H_2O_2 or O_3 in the atmosphere generates sulfate in rainwater and aerosols with positive $\Delta^{17}\text{O}$ values (41, 42). It is therefore possible that aerosol and/or rainwater inputs contribute to observed riverine sulfate signals. However, although correct in the required $\Delta^{17}\text{O}$ directionality, atmospheric deposition alone fails to explain our results for three reasons:

(1) According to our conservative tracer mixing model, precipitation accounts for $2.0 \pm 2.5\%$ of fluvial sulfate in the entire sample set and only $1.0 \pm 1.1\%$ within the TSS, where $\Delta^{17}\text{O}$ values are highest. If we assume all pyrite oxidation-derived sulfate follows Eq. 2 with no mass-independent isotope fractionation, then mass balance considerations require precipitation-derived sulfate with $\Delta^{17}\text{O}$ values up to $\approx 9\%$ VSMOW (higher if any contribution by Eq. 1 is invoked). This is nearly an order of magnitude higher than measured rainwater sulfate $\Delta^{17}\text{O}$ (41).

Still, it has previously been shown that $\approx 25\%$ of sulfate

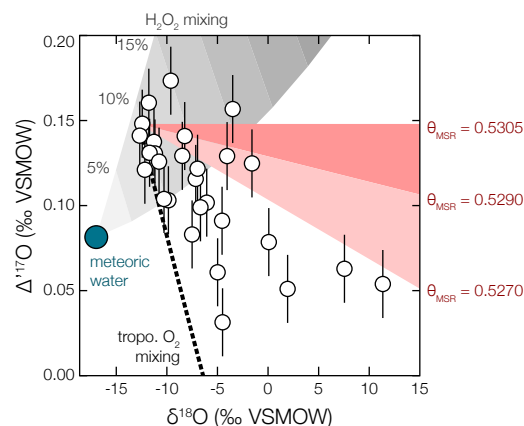
227 in Rocky Mountain headwater streams draining sulfate-poor
 228 gneiss and granite lithologies can be sourced from atmospheric
 229 deposition in snowpack (43). However, Marsiyandi headwater
 230 stream sulfate concentrations are $\approx 20\times$ higher than those of
 231 Ref. (43). Thus, if we assume snowpack sulfate $\Delta^{17}\text{O}$ values
 232 are similar in the Himalaya and Rocky Mountains (i.e., 0.8 ‰
 233 to 1.5 ‰), then mass balance considerations would require
 234 snowpack sulfate concentrations of $\approx 150\ \mu\text{M}$. This is an order
 235 of magnitude higher than reported Himalayan precipitation
 236 and Rocky Mountain snowpack concentrations (38, 39, 43).

237 (2) Riverine sulfate $\delta^{18}\text{O}$, $\delta^{34}\text{S}$, and $\Delta^{17}\text{O}$ trends are identical
 238 during pre-monsoon and monsoon seasons despite differences
 239 in air mass trajectories, precipitation amounts, and the
 240 importance of wet vs. dry deposition. In particular, we would
 241 expect significantly lower $\Delta^{17}\text{O}$ during the dry pre-monsoon
 242 season since atmospheric sulfate produced by gas-phase OH
 243 does not carry mass-independent $\Delta^{17}\text{O}$ signal (42). Similarly,
 244 if aerosol deposition were driving observed trends, then we
 245 would expect a much larger positive signal during the
 246 monsoon season when air masses cross the (heavily polluted)
 247 Indian subcontinent (41). This is not observed. Rather, for
 248 sites in which pre-monsoon and monsoon sampling can be
 249 compared directly, there exists no statistically significant
 250 seasonal difference in either sulfate $\delta^{18}\text{O}$ (May – September:
 251 -0.1 ± 2.8 ‰; $\mu \pm 1\sigma$; $n = 4$) or sulfate $\Delta^{17}\text{O}$ (May – September:
 252 -0.002 ± 0.030 ‰; $\mu \pm 1\sigma$; $n = 3$).

253 (3) Fluvial sulfate concentrations and $\Delta^{17}\text{O}$ values both
 254 decrease as MAP increases moving downstream, opposite of
 255 the expected atmospheric deposition trend. Highly erosive
 256 tributaries draining pyrite-rich TSS lithologies exhibit particularly
 257 positive $\Delta^{17}\text{O}$ values, up to 0.180 ‰ VSMOW, despite receiving
 258 only $\approx 400\ \text{mm yr}^{-1}$ MAP (Table S2). Similar to snowpack,
 259 it is possible that glacial meltwater contributes atmospheric
 260 precipitation- or aerosol-derived sulfate to headwater streams
 261 (44). However, we observe no statistical correlation between
 262 sulfate $\Delta^{17}\text{O}$ and aerial glacier extent across our sample set
 263 ($p > 0.05$; Table S1-S2), suggesting that glacier meltwater
 264 contributions alone cannot explain observed trends. Thus,
 265 while atmospheric deposition can contribute to fluvial sulfate
 266 with positive $\Delta^{17}\text{O}$ values (43), such contributions are likely
 267 negligible in the Marsiyandi River basin.

268 Marsiyandi River headwater sulfate is thus quantitatively
 269 rock-derived. The question then arises: what is the source
 270 of ^{17}O -enriched oxygen to pyrite oxidation-derived sulfate?
 271 Pyrite oxidation proceeds via 1-electron transfer steps
 272 occurring at anode sites on the mineral surface and thus involves
 273 oxygen-bearing sulfur intermediate species ($\text{S}_2\text{O}_2^{2-}$, $\text{S}_3\text{O}_6^{2-}$,
 274 SO_3^{2-}) (11). Sulfite (SO_3^{2-}), the most likely terminal
 275 precursor to sulfate, rapidly reaches isotopic equilibrium with
 276 water (46), raising the possibility that pyrite oxidation-derived
 277 sulfate ^{17}O is buffered to water regardless of the original
 278 oxygen source. However, the measured equilibrium sulfite-water
 279 ^{18}O effect (46) is significantly larger than headwater $\Delta\delta^{18}\text{O}$
 280 values observed here (≈ 5 ‰; Fig. 2B), suggesting sulfite-water
 281 isotope equilibrium cannot explain observed $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$
 282 trends.

283 Rather, we hypothesize that ROS isotope signatures are
 284 incorporated into pyrite oxidation-derived sulfate, consistent
 285 with laboratory experimental results (10, 11, 16, 17, 22, 40).
 286 Electrochemical studies treat pyrite as a semiconductor with
 287 a sulfur anode and an iron cathode; this model states that



288 Fig. 3. Sulfate oxygen source mixing diagram. White circles are measured riverine
 289 sulfate oxygen isotope compositions (Fig. 2A); blue circle is the high-elevation headwater
 290 meteoric water composition and the measured range of precipitation-derived H₂O₂ compositions
 291 (24); shading represents fraction of H₂O₂ contribution. Red region is a hypothesized
 292 MSR fractionation array starting from a "primary" headwater sulfate composition;
 293 shading represents the range of possible MSR θ values (45). The black dotted line is
 294 a mixing line between the same starting composition and tropospheric O₂. The primary
 295 composition used to define this mixing space was chosen such that the majority
 296 of data fall within the bounds defined by primary sulfate, MSR fractionation, and O₂
 297 incorporation. Measured sulfate compositions cannot be explained as a binary mixing
 298 between meteoric water and tropospheric O₂, especially in ^{17}O -enriched headwater
 299 TSS tributaries.

288 sulfate oxygen is quantitatively derived from H₂O or other
 289 O(-II) bearing species, whereas O₂ is reduced via ROS inter-
 290 mediates on iron cathode sites (22, 23). Furthermore, pyrite
 291 surfaces are almost always covered in Fe(III)-hydroxide patches
 292 (11, 47); these patches have been shown to disproportionate
 293 H₂O₂, generating O₂ and H₂O with unique isotope signatures
 294 relative to those of bulk fluid (23). If H₂O₂-derived H₂O is
 295 adsorbed onto pyrite surfaces, then these molecules could be
 296 preferentially incorporated into neighboring anode sulfur sites
 297 despite their low molarity relative to bulk water. In addition to
 298 explaining the origin of ^{17}O -enriched sulfate, this mechanism
 299 could potentially reconcile the apparent non-stoichiometric
 300 O₂ incorporation observed in isotope labeling pyrite oxida-
 301 tion experiments (i.e., values other than 25, 50, 75, or 100 %
 302 O₂-derived) (12, 13). That is, if isotopically labeled O₂ is
 303 reduced to H₂O via ROS intermediates on pyrite surfaces,
 304 then the apparent incorporation of this signature into sulfate
 305 would depend on the relative amount of adsorbed surface sites
 306 occupied by these molecules and would not be constrained by
 307 sulfate oxygen stoichiometry.

308 There are at least two pathways by which ROS incorpora-
 309 tion could explain our observed positive sulfate $\Delta^{17}\text{O}$ values:
 310 (1) *in situ* production of ^{17}O -enriched H₂O₂ during O₂ re-
 311 duction on pyrite surfaces, or (2) delivery of atmospheric
 312 H₂O₂ to the site of pyrite oxidation, for example by rainwater
 313 (24, 25, 42). Although the mass-dependent fractionation rela-
 314 tionships are currently not known for any step of the pyrite
 315 oxidation mechanism, the analogous H₂O₂-producing Mehler
 316 reaction has been shown to follow $\theta \approx 0.50$ (48). If O₂ reduc-
 317 tion on pyrite surfaces follows a similar θ value as that of the
 318 Mehler reaction, then this process would generate ^{17}O -enriched
 319 H₂O₂ that could be disproportionated and incorporated into
 320 sulfate. Future research is clearly needed to constrain these

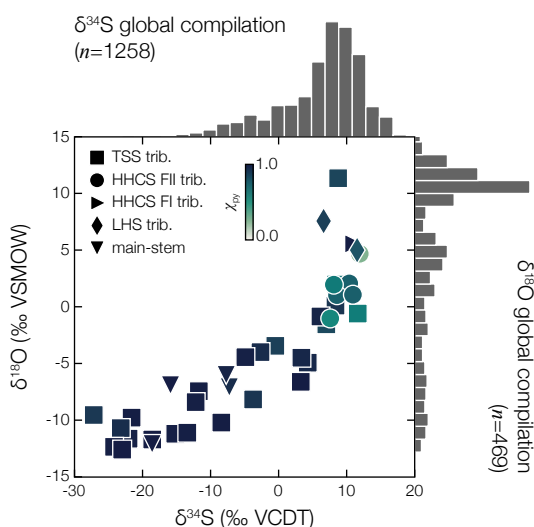


Fig. 4. Sulfate major isotope compositions. Colored points: $\delta^{18}\text{O}$ vs. $\delta^{34}\text{S}$ for all samples in Ref. (20). Symbol colors represent χ_{py} values and shapes refer to: TSS tributaries (squares), HHCS FI tributaries (circles), HHCS FI tributaries (right-pointing triangles), LHS tributaries (diamonds), and the main-stem Marsiyandi (down-pointing triangles). Histograms: literature compilations of all reported $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values from global rivers (Table S4; Materials and Methods). Marsiyandi River basin $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ compositions span nearly the entire global range and approach global median values moving downstream.

ogy (Fig. S1). Rather, microbial sulfate reduction (MSR) is more active in lower elevation, warmer catchments overlain by thicker, organic-rich soils. In particular, hyporheic zones— anoxic bank and bed sediments that are in hydrologic contact with river water (52)—are known to host highly active sulfate-reducing bacterial communities (53) and are thus a likely locus of MSR in the Marsiyandi River basin. MSR followed by sulfide precipitation or outgassing will increase residual sulfate $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values independent of the original sulfate source; the observed isotope fractionations are consistent in magnitude and direction with laboratory studies (54) and with previous field measurements (55). This mechanism is further supported by the strong positive relationships between local MAT and both sulfate $\delta^{34}\text{S}$ ($p = 2.9 \times 10^{-7}$; $R^2 = 0.53$) and $\delta^{18}\text{O}$ values ($p = 1.6 \times 10^{-6}$; $R^2 = 0.49$; Table S1, S2).

Resulting biogenic sulfide could be lost via H_2S outgassing from anoxic soils or retained locally as secondarily precipitated sulfide minerals and/or organic sulfur (56). For example, previous studies have utilized a network of bore holes in a temperate, first order stream to show that MSR can lead to an order-of-magnitude H_2S supersaturation with respect to sulfide mineral precipitation (FeS and FeS_2) in anoxic river bank sediments (53). The interpretation that sulfate reduction and subsequent loss is driving observed isotope trends is supported by strong negative correlations between sulfate concentration and both sulfate $\delta^{34}\text{S}$ ($p = 1.6 \times 10^{-10}$; $R^2 = 0.69$) and $\delta^{18}\text{O}$ values ($p = 3.6 \times 10^{-9}$; $R^2 = 0.63$; Table S1). If glacially carved valleys are being actively infilled by sediment in this region, then non-steady-state growth of secondarily precipitated sulfur reservoirs could exacerbate observed downstream sulfate isotope enrichments; this is likely occurring given such large $\delta^{34}\text{S}$ variability observed here (Fig. 4). However, in general, non-steady-state conditions are not required to explain progressive $\delta^{34}\text{S}$ enrichment as long as the standing stock of secondarily precipitated sulfur is significantly ^{34}S -depleted relative to inflowing sulfate (56), as would be expected with MSR (54, 55).

Interestingly, Marsiyandi River sulfate $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values span nearly the entire range measured in rivers across the globe (Fig. 4). The majority of this isotope variability occurs within a single lithologic unit, the TSS, despite all evidence to suggest sulfate is quantitatively derived from pyrite oxidation. This observation implies that riverine sulfate $\delta^{34}\text{S}$ compositions are an insufficient conservative tracer to estimate pyrite vs. evaporite weathering contributions to global fluvial sulfate export (20, 56, 57). In the TSS alone, MSR appears to increase $\delta^{34}\text{S}$ by $\approx 30\%$ within consistently pyrite-dominated lithology; this would traditionally be interpreted as a shift from pyrite-dominated to evaporite-dominated weathering (57). Furthermore, downstream Marsiyandi River tributary isotope compositions approach median values for global data sets, suggesting that global $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ distributions may more strongly reflect MSR intensity and secondary sulfur storage in floodplains than weathering lithology.

Sulfate $\Delta^{17}\text{O}$ trends corroborate the importance of MSR and secondary sulfur recycling in downstream catchments. Although the mass-dependent relationship describing MSR (θ_{MSR}) is poorly constrained, it likely lies between 0.5270 and 0.5305 (45). If we assume pyrite oxidation throughout the catchment generates primary sulfate with an isotope composition similar to that observed in high-elevation headwater

fractionation factors.

Alternatively, it has been shown that rainwater contains up to $\approx 30\ \mu\text{M}$ H_2O_2 with $\Delta^{17}\text{O}$ values near 1.0% VSMOW (25). A substantial fraction of this H_2O_2 is transferred to river water; measured concentrations reach $\approx 150\ \text{nM}$ (49, 50). If we assume (i) pyrite oxidation-derived sulfate oxygen is sourced from a mixture of river water and H_2O_2 , (ii) rainwater H_2O_2 $\Delta^{17}\text{O}$ values reported in the literature (25) are generally representative, and (iii) disproportionation and incorporation into sulfate molecules does not impart a mass-independent anomaly (12), then atmospherically derived H_2O_2 could contribute 7 to 15 % of sulfate oxygen in Marsiyandi headwaters (Fig. 3). This result satisfies both $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ observations. Still, it remains unclear how and to what extent rainwater H_2O_2 would survive to the site of pyrite oxidation; while this estimate based on the limited existing literature ROS $\Delta^{17}\text{O}$ data (24) appears reasonable, we emphasize that we do not quantitatively trust these results.

Regardless of the exact delivery mechanism invoked, pyrite oxidation-derived sulfate oxygen in mountainous rivers must be sourced primarily from meteoric water with supplemental contributions from a ^{17}O -enriched source. Electrochemical models and limited $\Delta^{17}\text{O}$ measurements suggest this source is likely H_2O_2 , but other ROS (e.g., $\text{O}_2^{\bullet-}$, OH^{\bullet}) or oxidants (e.g., NO_3^-) containing positive ^{17}O anomalies (51) could instead be driving observed signals. Future work is needed to provide detailed constraints on the importance of each of these species and pathways.

Downstream Evolution and Implications for Global Sulfur Budgets. Moving downstream, riverine sulfate becomes enriched in ^{34}S and ^{18}O and loses its positive ^{17}O anomaly. This transition occurs within tributaries draining the TSS and is therefore unlikely to result from changes in weathering lithol-

streams, then fractionation by MSR would lead to the observed increase in $\delta^{18}\text{O}$ as well as a slight decrease in $\Delta'^{17}\text{O}$ of residual sulfate (Fig. 3). Still, most downstream tributary data fall below the MSR fractionation line and imply secondary incorporation of ^{17}O -depleted oxygen into sulfate, most likely from O_2 .

Sulfide generated by MSR can be reoxidized either biotically or abiotically. Aerobic, chemolithoautotrophic sulfide oxidizing bacteria (SOB) are known to rapidly oxidize sulfide to sulfate in the presence of O_2 (58). However, aerobic SOB likely utilize an electron transport chain rather than an oxygenase enzyme (59); resulting sulfate oxygen atoms are thus exclusively derived from H_2O and not from O_2 directly (60). Alternatively, abiotic H_2S oxidation, while kinetically slower than oxidation by SOB (58), would directly incorporate O_2 and could explain observed downstream trends. This mechanism—MSR followed by secondary H_2S oxidation and abiotic O_2 incorporation—additionally reconciles our data with previous riverine sulfate $\Delta'^{17}\text{O}$ observations. Specifically, Mississippi River sulfate in Baton Rouge, Louisiana, USA displays a negative mean $\Delta'^{17}\text{O}$ of -0.091 ± 0.043 ‰ VSMOW ($n = 41$), which was previously interpreted to reflect tropospheric O_2 contributions during pyrite oxidation (61). We instead interpret this result as reflecting continued secondary sulfur recycling, although the potential for alternative sulfate sources and anthropogenic inputs in the Mississippi River cannot be discounted (61).

If the mechanism proposed here is true more generally, then the locus of O_2 incorporation into sulfate occurs not in erosive, pyrite-rich headwaters but rather during secondary sulfur recycling in lowland floodplains. This difference could carry implications for sulfate ^{17}O compositions through geologic time.

Conclusion and Implications for Earth History. The utility of sulfate $\Delta'^{17}\text{O}$ as a paleo- pO_2 tracer is predicated on tropospheric O_2 incorporation via oxidative pyrite weathering. In this study, we targeted highly erosive rivers draining pyrite-rich shale lithologies to isolate the ^{17}O signature of pyrite oxidation-derived sulfate; results under modern conditions suggest a complex reaction network that does not directly incorporate O_2 . However, O_2 is the only major atmospheric species that carries a negative ^{17}O anomaly; observed $\Delta'^{17}\text{O}$ values in Precambrian sulfate-bearing rocks therefore require atmospheric O_2 incorporation into sulfate precursors (3–8, 14, 15). Here we hypothesize that such incorporation may occur during secondary sulfur recycling in floodplains; this mechanism predicts that floodplain area could act as an additional, previously unrecognized control on sulfate ^{17}O composition. Still, open questions remain regarding the interpretation of geologic sulfate $\Delta'^{17}\text{O}$ records, including the dependence of ROS ^{17}O compositions on pO_2/pCO_2 and the implications for paleo-atmospheric compositions. Answering these questions will require mechanistic studies in modern settings in addition to new, high-resolution $\Delta'^{17}\text{O}$ measurements of geologic sulfate throughout the Phanerozoic Eon.

Materials and Methods

The materials and methods are summarized here; further details are provided in the Supporting Information.

Isotope Measurements and Data Reporting. Site location and sample collection details, as well as major ion, $^{18}\text{O}/^{16}\text{O}$, and $^{34}\text{S}/^{32}\text{S}$ ana-

lytical procedures, have been described previously (20, 29, 33–35). Sulfate $^{17}\text{O}/^{16}\text{O}$ ratios were measured by laser fluorination by F_2 coupled with isotope ratio mass spectrometry (IRMS) following Ref. (62). Uncertainty ($\pm 1\sigma$) was taken as the long-term reproducibility of a suite of primary sulfate standards ($\sigma = 0.016$). Isotope ratios are reported in conventional delta notation:

$$\delta^i\text{O} = \left(\frac{{}^{i/16}\text{R}_{\text{sample}}}{{}^{i/16}\text{R}_{\text{standard}}} - 1 \right) \times 1000\text{‰}, \quad [3]$$

where $i = 17, 18$ is the isotope of interest, ${}^{i/16}\text{R}$ is the ${}^i\text{O}/^{16}\text{O}$ ratio, and Vienna Standard Mean Ocean Water (VSMOW) is the reference standard. $\delta^{34}\text{S}$ is similarly reported using Vienna Canyon Diablo Triolite (VCDT) as the reference standard. To quantify small deviations from the expected mass-dependent $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ relationship, $^{17}\text{O}/^{16}\text{O}$ ratios are reported as

$$\Delta'^{17}\text{O} = \left[\ln \left(\frac{\delta^{17}\text{O}}{1000} + 1 \right) - \theta_{RL} \ln \left(\frac{\delta^{18}\text{O}}{1000} + 1 \right) \right] \times 1000\text{‰}, \quad [4]$$

where $\theta_{RL} = 0.5305$ is the high-temperature equilibrium reference line mass law (63) and $'$ indicates logarithmic notation (64). Isotope offsets between sulfate and concomitant water are reported as

$$\Delta\delta^{18}\text{O} = \delta^{18}\text{O}_{\text{SO}_4^{2-}} - \delta^{18}\text{O}_{\text{H}_2\text{O}}. \quad [5]$$

and

$$\Delta\Delta'^{17}\text{O} = \Delta'^{17}\text{O}_{\text{SO}_4^{2-}} - \Delta'^{17}\text{O}_{\text{H}_2\text{O}}. \quad [6]$$

All major ion concentrations and sulfate isotope compositions are reported in Table S1.

Geospatial Analysis. Geospatial data were analyzed using ArcGis Desktop v10.6 (ESRI Corporation); results are reported in Table S2. Catchment areas and geomorphic parameters upstream of each sampling location were calculated using the NASA Shuttle Radar and Topography Mission global digital elevation model v3.0 (1 arc-second resolution). Glacier extent was calculated using the Randolph Glacier Inventory v6.0. Mean annual precipitation (MAP) and mean annual temperature (MAT) were calculated using the WorldClim v2 global climate database (30 second resolution) (65). Local elevation, slope, MAT, and MAP for each sample were taken as the value of the raster pixel underlying each sampling location. Catchment-averaged elevation, slope, MAP, and MAT were calculated as the mean value for all pixels within a given catchment area. Main-stem distance, elevation, and MAT profiles (Fig. 1B) were generated using the flow-accumulation river network and underlying raster pixels. Sample downstream distances were calculated as the main-stem path length from the headwater source to the main-stem point nearest to each sample location.

Weathering Lithology Mixing Model. For each sample, the relative proportions of solutes derived from weathering of different end-member lithologies were estimated using a conservative tracer mixing model. The end members considered in this model were: dolomite, evaporites, gneiss/granite, limestone, and shale. Although evaporite lithologies in general—and gypsum in particular—have not been reported in the Marsiyandi basin (26), we nonetheless included them in the model since their presence would add non-pyrite-derived SO_4^{2-} . Our calculated pyrite-derived SO_4^{2-} contributions are thus minimum estimates. The conservative tracers considered in this model were: Ca^{2+} , K^+ , Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} , and the constraint that all fractional contributions sum to unity. This model was solved using a Monte Carlo approach similar to that of Ref. (56). In addition to end-member contributions to each sample, this approach estimated a *posteriori* end-member conservative tracer ranges. Finally, the fraction of pyrite-derived SO_4^{2-} in each sample, termed χ_{py} , was calculated as the relative proportion of shale weathering in that sample multiplied by the *a posteriori* SO_4^{2-} concentration for the shale end member. *A priori* and *a posteriori* end-member conservative tracer ranges are reported in Table S3.

Major Isotope Compilation and Data Analysis

All published fluvial sulfate $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ compositions, along with paired water $\delta^{18}\text{O}$ where available, were compiled from Refs.

537 (18–20, 57, 61, 66–70) (Table S4). Regression slopes were calculated
 538 using either weighted least squares regression if the ordinate is
 539 known perfectly (i.e., downstream distance; Fig. S1) or reduced
 540 major axis regression if the ordinate is known to contain uncertainty
 541 (i.e., isotope cross plots). Reported p values are the probability that
 542 regression slopes are statistically equal to zero and regressions with
 543 $p \leq 0.05$ are deemed significant. See Ref. (71) for regression details
 544 and equations.

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