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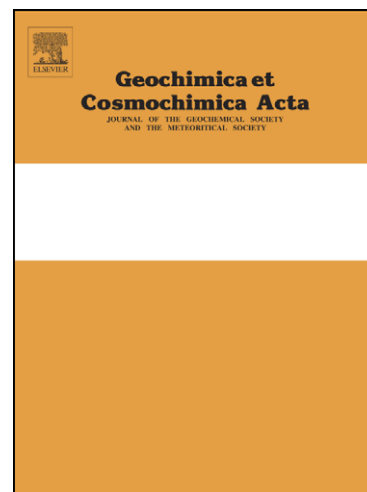
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1 The impact of igneous bedrock weathering on the Mo
 2 isotopic composition of stream waters : Natural samples
 3 and laboratory experiments

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15 **Abstract**

16 River waters have been shown to be systematically enriched in the heavy molyb-
 17 denum (Mo) isotopes when compared to typical granites and basalts, which
 18 generally possess Mo isotopic compositions ($\delta^{98/95}\text{Mo}$) of around 0‰. This in-
 19 consistency has been used to argue against weathering of crustal rocks as the
 20 cause for heavy riverine $\delta^{98/95}\text{Mo}$ signatures. Incongruent dissolution of pri-
 21 mary bedrock, however, may be an important process by which the anomalous
 22 Mo signatures of the river dissolved load are produced. This study therefore in-
 23 vestigates the effect of igneous crustal rock weathering on the aquatic $\delta^{98/95}\text{Mo}$
 24 signal by comparing stream water and bedrock Mo isotope data to results of
 25 bulk rock leach experiments. For this purpose, stream water and bedrock (or-
 26 thogneiss, granite, basalt), as well as soil and vegetation samples were collected
 27 in a small catchment in the French Massif Central. In accordance with the
 28 results of earlier studies on riverine Mo, both streams are isotopically heavier
 29 ($\delta^{98/95}\text{Mo} = 0.5$ to 1.1%) than the typical granites and basalts. The excellent
 30 agreement of these data with those of Mo released during experimental leaching

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31 of the basalt bedrock (0.6 to 1.0‰) identifies a predominance of basalt weath-
32 ering over the stream water Mo geochemistry, while other processes (i.e. soil
33 formation, secondary mineral precipitation and adsorption) are subordinate in
34 this catchment. Given that the basalt bulk rock $\delta^{98/95}\text{Mo}$ reflects a value typi-
35 cal for crustal magmatic rocks (ca. 0.1‰), Mo isotope fractionation during the
36 incongruent dissolution of basalt can explain the observed isotopically heavy
37 aquatic Mo signatures. Laser ablation analyses demonstrate that the volumet-
38 rically minor magmatic sulfides can be highly enriched in Mo and mass balance
39 calculations identify the sulfide melt inclusions as the principal Mo source for
40 the leach solutions. These data suggest that the magmatic sulfides possess a dis-
41 tinctly heavier $\delta^{98/95}\text{Mo}$ signature than the coexisting silicate melt. In this case,
42 Mo would behave like Fe by showing a detectable isotope fractionation at mag-
43 matic temperatures. Incongruent crustal bedrock weathering may thus cause a
44 preferential release of heavy Mo isotopes. This effect, however, is highly depen-
45 dent on the primary bedrock mineralogy. Consequently, the average continental
46 runoff may have been significantly affected by incongruent weathering during
47 periods when the Earth system was exceptionally far from steady state, e.g.,
48 large glaciations with enhanced physical weathering or large subaerial basalt
49 eruptions such as the Deccan and the Siberian plateau.

50 1. Introduction

51 River transport is the main process controlling fluxes of most elements from
52 continents to oceans (Garrels & Mackenzie, 1971; Gaillardet et al., 2003). The
53 marine isotope and element inventory is thus strongly dependent on continental
54 weathering processes and subsequent river transport to the ocean basins. In the
55 case of the highly redox sensitive molybdenum (Mo), the continental contribu-
56 tion accounts for the predominant part of the marine Mo budget (Morford &

57 Emerson, 1999; McManus et al., 2002, 2006). Once dissolved Mo has entered
58 the oceans, redox-dependent isotope fractionation accompanies its incorpora-
59 tion into sediments, covering all environments from oxic to strongly euxinic.
60 As each of these environments shows characteristic isotope signatures (Barling
61 et al., 2001; Barling & Anbar, 2004; Siebert et al., 2003, 2006; Neubert et al.,
62 2008), Mo isotopes in marine sediments have been used to investigate the evo-
63 lution of atmospheric O₂ and to quantify the extent of seafloor anoxia in the
64 geological record (e.g., Arnold et al., 2004; Siebert et al., 2005; Wille et al., 2007;
65 Pearce et al., 2008; Voegelin et al., 2010). All of these models rely upon the
66 assumption of a fairly uniform long-term riverine Mo isotope input signature
67 of around 0‰ based on the available $\delta^{98/95}\text{Mo}$ data of crustal igneous rocks
68 (-0.1 to +0.3‰; Siebert et al., 2003). Arnold et al. (2004) additionally included
69 continental molybdenites (average of -0.1‰, Barling et al., 2001) in their model.
70 Recent publications by Archer & Vance (2008), Pearce et al. (2010) and Neu-
71 bert et al. (2011), however, have revealed not only a preferential enrichment of
72 river waters in the heavy isotopes but also a large variability of their $\delta^{98/95}\text{Mo}$
73 signature (-0.13 to 2.3‰). The pronounced discrepancy between the assumed
74 crustal background and the aquatic signature thus emphasizes the need for a
75 more thorough investigation of isotope fractionation processes during chemical
76 rock weathering in the terrestrial environment.

77 The heavy Mo isotopic composition of sedimentary source rocks was found
78 to be reflected in the associated river water $\delta^{98/95}\text{Mo}$, suggesting a predominant
79 control of catchment outcrop weathering (Neubert et al., 2011). Thereby, sulfate
80 weathering and sulfide oxidation were proposed to play a crucial role in liberat-
81 ing Mo from the different source rock types. Leach experiments performed by
82 Liermann et al. (2011) on black shales document an enrichment of the solution
83 in heavy Mo isotopes. The offset between the starting material and the leach

84 solutions was interpreted to be caused by adsorption of dissolved Mo to Fe-
85 and Mn-(oxyhydr)oxides, as they preferentially adsorb light Mo (Barling et al.,
86 2001; Siebert et al., 2003; Goldberg et al., 2009). An analogous process, i.e. ad-
87 sorption of Mo onto the suspended load during river transport, was suggested
88 as a potential removal process of light Mo in natural environments (Archer &
89 Vance, 2008; Pearce et al., 2010). Finally, the same authors proposed that soil
90 retention of light Mo is an important process to control river water Mo.

91 This study investigates Mo isotope fractionation processes during weathering
92 of crustal igneous rocks (basalt, granite, orthogneiss) in a small catchment basin
93 located in the French Massif Central. Although weathering of magmatic rocks
94 has in the past not been associated with significant Mo isotope fractionation due
95 to their small $\delta^{98/95}\text{Mo}$ variability, stream waters analyzed here are enriched in
96 the heavy isotopes. In order to identify the role of various Mo sources and
97 weathering processes, stream water and bedrock data were complemented by
98 measurements of the suspended load, soil material and vegetation. The Mo
99 data of natural samples were compared to results of successive bulk rock leaching
100 experiments. These experiments were conducted on all three bedrock lithologies
101 in order to simulate the weathering behavior of different crustal igneous rock
102 types and their role in generating the observed heavy aquatic $\delta^{98/95}\text{Mo}$ signals.
103 Special emphasis was thereby placed on the effect of mineral dissolution and
104 adsorption effects. To identify the Mo hosting phases and to constrain mass
105 balance, laser ablation ICP-MS was used to obtain element concentrations of
106 single mineral grains and sulfidic melt inclusions.

107 2. Study site and sampling

108 2.1. Geological setting

109 The mixed basaltic-granitic catchment basin is located in the southern part
110 of the French Massif Central (Fig. 1). It covers an area of around 68 km² and
111 includes two streams, the Séjallières and the Malaval. The eastern and most
112 elevated part (1301 m a. s. l.) is formed by Quaternary basalts. Downstream
113 and to the west the catchment basin drops to an altitude of 714 m a. s. l.
114 and is characterized by deep and narrow valleys with Hercynian granitic and
115 orthogneissic bedrock. Due to its low inclination, the basalt plateau is covered
116 by well developed soils and swampy areas. The steep orthogneissic and granitic
117 hillsides to the west are covered by forests and exhibit a poorly developed soil
118 cover.

119 2.2. Sampling

120 Stream water was collected during two field campaigns in June 2003 (see
121 Steinmann & Stille, 2008) and June 2010. Sampling locations are shown in
122 Fig. 1 and listed with respect to their upstream distances from the catchment
123 outlet in Table 1. All waters were filtered on site using 0.45 μm nylon filters
124 and Nalgene™ filtering units. Subsequently, they were acidified with distilled
125 nitric acid and stored in pre-cleaned LDPE bottles for isotope and trace element
126 analysis. Anion determinations were done on filtered, non-acidified aliquots.
127 Filters were dried and weighed prior to and after water sampling in order to
128 determine the suspended load for each filter. Basaltic bedrock samples were
129 collected in the riverbed of the study area. Additional basalt material was
130 collected in a quarry located north of the catchment outlet (Fig. 1) as these
131 rocks were particularly fresh. Well preserved granite and orthogneiss samples
132 were collected during earlier fieldwork. One soil sample was taken in a swampy

133 area on the basalt plateau. A soil sampler was used to recover the topmost ca.
134 30 cm. In the lab, root material for Mo analyses was extracted from the soil.

135 *2.3. Rock sample descriptions*

136 Basalt sample PA-1 is a fine grained olivine basalt, containing medium sized
137 phenocrysts of olivine and clinopyroxene and small phenocrysts of plagioclase,
138 embedded in a dense microcrystalline matrix. The opaque phases are pre-
139 dominantly titanomagnetites. Opaque sulfidic melt inclusions occur as small
140 ($<30\mu\text{m}$) droplets as identified in silicate phenocrysts. Basalt M29-R is miner-
141 logically identical with smaller olivine, pyroxene and plagioclase phenocrysts
142 when compared to sample PA-1. The biotite rich orthogneiss (AR-7) has a
143 medium to coarse grained texture. It is composed of quartz, potassium feldspar
144 and plagioclase and contains only few oxides and sulfides. The fine grained
145 granite (LC-1) is dominated by quartz, potassium feldspar, biotite, plagioclase
146 and contains some muscovite. Apatite and zircon occur as accessory phases and
147 oxides and sulfides are rare.

148 **3. Analytical methods**

149 *3.1. Leach experiments*

150 In order to investigate the behavior of Mo isotopes during progressive rock
151 weathering, rock samples were exposed to acid leach experiments under oxidiz-
152 ing conditions using 0.3 and 2 mol L⁻¹ HCl and HNO₃. The experiments were
153 performed at low pH (≤ 1) to preclude secondary mineral formation (Pistiner
154 & Henderson, 2003) and adsorption related Mo isotope fractionation (see sec-
155 tion 5.2.3). These conditions should insure that the impact of primary mineral
156 dissolution on the leach solution $\delta^{98/95}\text{Mo}$ is isolated.

157 Experiments were conducted on both basalt grains and powders, and or-
158 thogneiss and granite powders. Samples were prepared by cutting off sections

159 affected by rock weathering. Subsequently, slabs were crushed in a hydraulic
160 press. Grains of 0.1-0.5 mm in size were separated, sonicated and rinsed repeat-
161 edly with high purity H₂O ($>18.2 \text{ M } \Omega\text{cm}^{-1}$). Powders were ground in an agate
162 ball mill, and multiple aliquots were processed to determine representative bulk
163 rock $\delta^{98/95}\text{Mo}$ compositions and concentrations for all rocks. All sample splits
164 were weighed into screw-top PTFE beakers prior to leaching. Up to eight grams
165 of basalt grains were immersed in 50 ml 0.3 mol L⁻¹ HNO₃ and 0.3 mol L⁻¹
166 HCl at room temperature for a period between 10 minutes and 2 months. Pow-
167 der samples were processed using 0.3 mol L⁻¹ HNO₃ at room temperature and
168 2 mol L⁻¹ HNO₃ at a constant temperature of 50 °C. Periods of between 2 min-
169 utes and 7 days were chosen for these experiments. This setup produced leach
170 solutions with a considerable range of fractional Mo release. Due to the overall
171 low Mo content, particularly of the orthogneiss and granite ($<0.4 \mu\text{g g}^{-1}$), each
172 leach experiment was performed on an individual sample split. Separation of
173 acid solutions from rock materials was done by centrifugation and subsequent
174 filtering through 0.2 μm nylon syringe filters. Finally, the Mo isotopic compo-
175 sitions and concentrations of leach solutions as well as selected residues were
176 analyzed.

177 3.2. Preparation of water, rock, soil and vegetation samples

178 Prior to any sample processing and chemical Mo purification procedures a
179 double spike with masses $^{100}\text{Mo} + ^{97}\text{Mo}$ (see Siebert et al., 2001 for details)
180 was added to all sample types in order to account for any potential Mo isotope
181 fractionation during column chemistry (Anbar et al., 2001; Siebert et al., 2001)
182 and to correct for instrumental mass bias during measurement. Double (HF)
183 and triple (HCl and HNO₃) distilled acids and 30% suprapure hydrogen peroxide
184 were used for all digestion and purification steps. Powdered bulk rock samples
185 were treated with concentrated HCl + H₂O₂ and HF + HNO₃ dissolution steps

186 to ensure complete digestion of the silicate matrix (Siebert et al., 2001; Wille
187 et al., 2007). Soil material was dried at 60°C and subsequently sieved to separate
188 it from rock pebbles and root material. Roots were cleaned in an ultrasonic bath
189 and rinsed repeatedly with high purity H₂O to remove any residual soil particles.
190 Soil and root samples were digested using multiple HNO₃ and HF steps closely
191 following the procedure described in Cenki-Tok et al. (2009). Between 0.5 and
192 2 liters of filtered stream water were evaporated prior to column chemistry.

193 3.3. Chemical purification and isotope analysis of Mo and Sr

194 Mo was purified from all samples using an anion exchange column (1 mL
195 Dowex 1X8 resin, 200-400 mesh). A cation exchange column (2 mL Dowex
196 50WX8 resin, 200-400 mesh) was used additionally to remove any residual iron
197 (procedure after Siebert et al., 2001 and Wille et al., 2007). For Sr purification,
198 eluted matrix solutions, obtained from Mo anion column separation, were evap-
199 orated and loaded onto Sr Spec™ columns. For MC-ICP-MS measurements, the
200 evaporated Mo and Sr fractions were re-dissolved in 0.5 mol L⁻¹ HNO₃. Mo iso-
201 topic compositions and concentrations as well as Sr isotopic compositions were
202 measured at the University of Bern on a double-focusing [®]Nu-Instruments
203 MC-ICP-MS connected to an Apex™ desolvating nebulizer. The Mo isotopic
204 composition is measured relative to a standard solution (Johnson Matthey,
205 1000 μg mL⁻¹ (±0.3%) ICP standard solution, lot 602332B). This standard is
206 2.3‰ below modern open ocean seawater (Siebert et al., 2003). Final Mo iso-
207 topic data are reported as $\delta^{98/95}\text{Mo} = \left[\frac{(^{98}\text{Mo}/^{95}\text{Mo})_{\text{Sample}}}{(^{98}\text{Mo}/^{95}\text{Mo})_{\text{Standard}}} - 1 \right] \times 10^3$. The data presented were acquired with a preferred quantity of >60 ng
208 and a minimum of 30 ng of Mo in solution. Total chemistry Mo blank was
209 <1 ng. The external standard reproducibility of the $\delta^{98/95}\text{Mo}$ ratio is ±0.1%
210 at the 2σ level (Siebert et al., 2003). For Sr isotope analyses the samples were
211 diluted down to an optimum amount of 50 to 100 ng. The external reproducibil-
212

ity of the NIST SRM 987 standard during the period of the present analyses was 0.710235 ± 0.000029 (2σ). The external reproducibility of of the NIST SRM 987 standard measured by Steinmann & Stille (2008) was at 0.710259 ± 0.000016 (2σ).

3.4. Major anion and cation analyses of stream waters and leach solutions

Major anion and cation contents of all river water samples (except M31-Ft and M31-Fu) were determined on $0.22\mu\text{m}$ filtered sample fractions at the laboratory of Chrono-Environnement, CNRS / University of Franche-Comté, Besançon (France). Na^+ , K^+ , Ca^{2+} and Mg^+ were analyzed with a Perkin Elmer A Analyst 100 atomic absorption spectrometer (AAS) on sample aliquots acidified with HNO_3 to pH 2 after filtering. F^- , Cl^- , NO_3^- and SO_4^{2-} were measured with a Dionex DX100 high-pressure ion chromatograph on unacidified sample aliquots. HCO_3^- concentrations were determined in the field within a few hours after sampling (in order to limit exchange with atmospheric CO_2) on unfiltered and unacidified samples by standard titrimetric methods considering total and carbonate alkalinity as equivalent and equal to HCO_3^- . Typical uncertainties including all error sources for major cations, anions and alkalinity lie between $\pm 4\%$ and $\pm 6\%$, depending on the concentration levels (Steinmann & Stille, 2008; Binet et al., 2009). Major anion and cation concentrations of river water samples M31-Ft and M31-Fu as well as SO_4^{2-} concentrations of the leach solutions were determined using a Metrohm®861 Advanced Compact Ion Chromatograph at the University of Bern.

3.5. Laser ablation ICP-MS analyses of bedrock minerals

LA-ICP-MS analyses were performed on silicate phenocrysts, oxides, sulfide melt inclusions (entirely enclosed in the host mineral) and the fine grained matrix of basalt sample PA-1. Measurements were performed on a GeoLas-Pro 193

239 nm ArF excimer laser system in combination with a Perkin Elmer Elan DRC-e
240 quadrupole mass spectrometer at the University of Bern. Instrumental condi-
241 tions were similar to those reported in Pettke (2008). Major and trace element
242 concentrations were measured using spot sizes between 16 and 120 μm , with
243 the 120 μm beam used for bulk matrix compositions. Bracketing standardiza-
244 tion using SRM 610 from NIST was used for instrument sensitivity calibration
245 and drift correction. The standard contains sixty-one trace elements doped in
246 a Si-Na-Ca-Al matrix, most of which are homogeneously distributed (Eggins &
247 Shelley, 2002). Data quantification used the SILLIS software package (Guillong
248 et al., 2008), employing the major element oxide total of 100 wt% for internal
249 standardization. For sulfide melt inclusions, data were treated following Halter
250 et al. (2002). The mixed inclusion plus host mineral signal was deconvolved by
251 assuming that no SiO_2 is present in the sulfide melt inclusion; hence, the Mo
252 concentrations obtained are those present in the pure sulfide inclusion.

253 4. Results

254 4.1. Natural samples

255 4.1.1. Stream water and bedrock geochemistry

256 All stream water Mo data are given in Table 1 and shown in Fig. 2. Overall,
257 the waters show a moderate $\delta^{98/95}\text{Mo}$ variability between 0.55 and 1.1 ‰. The
258 waters of both streams sampled in 2003 show a tendency towards slightly higher
259 $\delta^{98/95}\text{Mo}$ values. Mo concentrations were also higher in 2003 (0.17-0.81 ng g^{-1})
260 than in 2010 (0.02-0.15 ng g^{-1}). Field parameters and further chemical compo-
261 sitions of the stream waters are listed in Table 2.

262 Analyses performed on multiple splits of all three igneous rock types (Table
263 3) reveal different signatures ranging from a minimum of -0.28 ‰, detected in
264 an orthogneiss split (median $\delta^{98/95}\text{Mo}$ = -0.2 ‰, n=7), to a maximum of 0.70 ‰

265 (median $\delta^{98/95}\text{Mo}=0.58\text{ ‰}$, $n=5$) in the granite. By contrast, the two basalts
266 PA-1 and M29-R show median $\delta^{98/95}\text{Mo}$ values of 0.14 ($n=6$) and 0.07 ‰ ($n=5$),
267 respectively. Hence, the basalts are the only igneous bedrock to comply with
268 the Mo isotope signature of the basalts and granites measured by Siebert et al.
269 (2003) ($\delta^{98/95}\text{Mo} = -0.1$ to 0.3 ‰). The three different bedrocks exhibit strongly
270 variable Mo concentrations, with median values of $0.08\ \mu\text{g g}^{-1}$ and $0.33\ \mu\text{g g}^{-1}$
271 for the orthogneiss and the granite. The basalts show median Mo concentrations
272 of $3.5\ \mu\text{g g}^{-1}$ (PA-1) and $2.4\ \mu\text{g g}^{-1}$ (M29-R). Two basalt sample splits reached
273 Mo concentrations as high as 7.7 and $4.8\ \mu\text{g g}^{-1}$, indicating a nugget effect on
274 bulk rock Mo concentrations. The concentrations measured in this study are
275 more variable compared to the assumed upper crust value of 0.78-1.5 $\mu\text{g g}^{-1}$
276 (Rudnick & Gao, 2004, and references therein).

277 Bedrock Sr isotope data are taken from Steinmann & Stille (2008). Table 3
278 lists values typical for the individual rock types. A pronounced difference exists
279 between the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of orthogneiss and granite (typically between
280 0.720-0.750) and the low ratios of the basalt (ca. 0.703). The stream waters
281 show the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio typical of basalt on the plateau and a small increase of
282 the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio downstream (Table 1), reflecting the contribution of gneiss
283 and granite.

284 4.2. *Single grain and matrix element concentrations determined by LA-ICP-MS*

285 Element concentrations of single minerals and the basalt matrix (averages)
286 are given in Table 4, data of sulfidic melt inclusions in Table 5. The silicate
287 phenocrysts have Mo concentrations reaching 0.1 to $0.2\ \mu\text{g g}^{-1}$ in olivine and
288 pyroxene, and between 1 and $2\ \mu\text{g g}^{-1}$ in plagioclase. The Fe-Ti oxides contain
289 between 0.5 and $1.2\ \mu\text{g g}^{-1}$ Mo. The fine grained basalt matrix has an average
290 Mo concentration of $3.5\ \mu\text{g g}^{-1}$ with minimum values at $2.7\ \mu\text{g g}^{-1}$ and a
291 maximum at $5.5\ \mu\text{g g}^{-1}$. The sulfide melt inclusions have strongly variable Mo

292 contents ranging from values $<0.05\mu\text{g g}^{-1}$ to as high as $250\mu\text{g g}^{-1}$. According
293 to their Fe, Cu and Ni concentrations they can be subdivided into three different
294 inclusion types. Type 1 has high Fe/Cu and Ni/Cu ratios and Mo concentrations
295 $<2\mu\text{g g}^{-1}$, type 2 exhibits moderate Fe/Cu and Ni/Cu ratios and very variable
296 Mo concentrations between 0.3 and $250\mu\text{g g}^{-1}$, type 3 shows very low Fe/Cu and
297 Ni/Cu ratios and intermediate Mo concentrations between 16 and $80\mu\text{g g}^{-1}$.

298 4.3. Soil, vegetation and suspended load

299 The soil sample, as well as root material extracted from it, show moderately
300 negative $\delta^{98/95}\text{Mo}$ values of -0.33 and -0.14‰ (Table 6). A concentration of
301 $0.67\mu\text{g g}^{-1}$ was found in the roots, the soil is more enriched with a concentration
302 of $2.4\mu\text{g g}^{-1}$. Data of the suspended load are given in Table 7. The amount
303 of suspended load lies between 1.3 and 19.7mg L^{-1} in the 2003 samples, while
304 in 2010 the suspension weight was below detectable limits by weighing. Also,
305 most of the suspended load samples taken in 2010 had Mo concentrations not
306 exceeding Mo blank levels ($<1\text{ng}$). Due to the low amount of suspended load
307 in 2010, no Mo isotope composition and concentrations could be determined.
308 Samples taken in 2003 were not available for measurement.

309 4.4. Laboratory leach experiments

310 4.4.1. Basalt leach solutions and residues

311 Data of all leach solutions and residues are listed in Table 8. Experiments
312 performed on grains of sample PA-1 show identical leach solution $\delta^{98/95}\text{Mo}$ val-
313 ues for both the HCl and the HNO_3 leach (Fig. 4), all of which are isotopically
314 significantly heavier than the starting material. Mo isotopic compositions lie
315 between 0.61 and 0.84‰ with up to 9% of the total rock Mo inventory ex-
316 tracted. Powder leach solutions of the same basalt reveal a similarly narrow
317 range of Mo isotopic compositions (0.42 - 0.88‰). In these experiments, up to

318 54 % of the total bedrock Mo were released (Fig. 4). Leaching of basalt M29-R
319 liberated up to around 30 % of Mo and shows solution $\delta^{98/95}\text{Mo}$ signals consis-
320 tent with those of PA-1 (0.53-0.97 ‰; Fig. 5). The evolution of the Mo isotope
321 ratio as a function of increased leach fractions is nearly identical for both basalt
322 samples. Between the initial, extremely rapid Mo release and Mo extraction of
323 30 %, no significant trend appears in the $\delta^{98/95}\text{Mo}$ signal of PA-1. Only at a Mo
324 release of approximately 54 % Mo the $\delta^{98/95}\text{Mo}$ decreases. In the leach series
325 of sample M29-R, the isotope compositions are slightly higher at lower leach
326 fractions ($\leq 15\%$) and decrease at higher fractions. Leach residues of PA-1
327 experiments show a broad range of $\delta^{98/95}\text{Mo}$ values from 0.12 to -0.29 ‰ (Fig.
328 4). The lowest values were observed at the longest leach times, corresponding
329 to the highest proportion of extracted heavy Mo.

330 The different leach setups produced different Mo release patterns (Fig. 6A).
331 HCl and HNO_3 grain leach solutions show increasing concentrations reaching
332 a maximum of $0.3 \mu\text{g g}^{-1}$. After a rapid initial Mo release the leaching rate
333 slowed. The largest Mo release occurred during the $2 \text{ mol L}^{-1} \text{HNO}_3$ pow-
334 der experiments where maximum Mo concentrations of $1.9 \mu\text{g g}^{-1}$ (PA-1) and
335 $0.7 \mu\text{g g}^{-1}$ (M29-R) were extracted from the basalts. The interaction between
336 basalt powders and $0.3 \text{ mol L}^{-1} \text{HNO}_3$ produced solutions with considerably
337 lower Mo concentrations ($0.2\text{-}0.4 \mu\text{g g}^{-1}$). Also, a quick initial Mo release is
338 followed by a concentration decrease with time. Sulfate concentrations of leach
339 solutions increased with time, correlating with increasing Mo concentrations
340 ($R^2=0.9$ linear correlation; Fig. 6B).

341 4.4.2. Orthogneiss and Granite leach solutions

342 Powder leach experiments performed on the orthogneiss (AR-7) extracted
343 between 1 and ca. 100% of the bedrock Mo inventory (Table 8, Fig. 5C). The
344 isotopic compositions of the leach solutions vary between 0.11 ‰ and -0.15 ‰.

345 Leach rates for the granite (LC-1) are much lower since only approximately
346 1-8 % of the total Mo were released applying the same leach times. Showing
347 values between 1.03 and 1.38 ‰, the granite leach solutions are isotopically
348 much heavier than those of the orthogneiss (Fig. 5A).

349 5. Discussion

350 5.1. Natural samples: bedrock and stream waters

351 The catchment morphology promotes the formation of well developed weath-
352 ering profiles on the plateau and hampers rock-water interaction in the steep
353 granitic and orthogneissic hillsides. As a consequence, the mafic rocks, highly
354 susceptible to weathering processes (Gislason & Eugster, 1987), are favored as
355 the primary lithological control on the stream water geochemistry. Their pre-
356 dominance is shown by the aquatic Nd and Sr isotope data of Steinmann & Stille
357 (2008) and Sr data of this study (Table 1), which mainly reflect the signature
358 of the basalt; the contribution from granites and orthogneisses is subordinate.
359 Data collected on all three riverbed rock types indicate an analogous basalt dom-
360 inance for the river dissolved Mo system as the median Mo concentration of the
361 mafic rocks of 2.4 and 3.5 $\mu\text{g g}^{-1}$ is about one order of magnitude higher than
362 that of the felsic bedrock types ($<0.4 \mu\text{g g}^{-1}$; Fig. 3). However, unlike the Sr
363 and Nd isotope signatures, the $\delta^{98/95}\text{Mo}$ of both the Malaval and the Séjallières
364 do not concur with the isotopic composition of the basalt but are enriched in the
365 heavy isotopes. With a median value of 0.58 ‰ the granite is isotopically slightly
366 heavier than the previously reported magmatic rocks by Siebert et al. (2003)
367 and represents the only rock type with a $\delta^{98/95}\text{Mo}$ signature approximating that
368 of the stream waters. Yet the granite cannot account for the isotopically heavy
369 waters of the Séjallières, as it is crosscut only by the Malaval. The orthogneiss
370 potentially contributes Mo to both the Séjallières and the lower segment of the

371 Malaval. Nevertheless, the extremely low concentrations (median=0.08 $\mu\text{g g}^{-1}$,
372 n=7) exclude the orthogneiss from being an important contributor to the over-
373 all aquatic Mo budget. The moderate stream water $\delta^{98/95}\text{Mo}$ variations do not
374 coincide with the sampling distance from the catchment outlet (Fig. 2). The
375 lack of any systematic $\delta^{98/95}\text{Mo}$ downstream trend of the river dissolved load,
376 despite changing environmental conditions (i.e. bedrock type, soil cover, to-
377 pography), as well as the overall small variability of the aquatic Mo signature
378 may further support the idea of a single dominant source rock. The waters
379 of both streams sampled in 2003 show a tendency to slightly higher $\delta^{98/95}\text{Mo}$
380 values and a greater variability (0.7-1.1 ‰) than in 2010 (0.6-0.9 ‰). This
381 marginal isotopic shift coincides with an increase in the amount of suspended
382 particles, which was generally higher in 2003 than in 2010 (Table 7). Mo isotope
383 fractionation through adsorption of Mo to (oxyhydr-)oxide particles (Barling &
384 Anbar, 2004; Goldberg et al., 2009) might thus be considered a process con-
385 tributing to the isotopic composition of the river dissolved load. This process
386 was previously proposed to cause the suspended load to be isotopically lighter
387 than the dissolved load (Pearce et al., 2010), in return increasing the stream
388 water $\delta^{98/95}\text{Mo}$ values. While this may explain the small difference in $\delta^{98/95}\text{Mo}$
389 between 2003 and 2010, it cannot account for the 0.5 to 1 ‰ offset between
390 the basalt bedrock and the stream waters. Even in 2010, when the amount of
391 suspended load is negligible, a large $\delta^{98/95}\text{Mo}$ offset exists between the bedrock
392 and the river dissolved load.

393 5.2. Experimental primary mineral dissolution

394 5.2.1. Incongruent bedrock weathering

395 Mild acid leach experiments performed by Siebert et al. (2003) on granite
396 did not generate a heavy dissolved Mo pool, but released Mo with a $\delta^{98/95}\text{Mo}$
397 composition indistinguishable from that of the crustal starting material. These

398 data have consequently been used to assume that igneous crustal rock weath-
399 ering has no importance in producing the heavy $\delta^{98/95}\text{Mo}$ of river waters (e.g.,
400 Nagler et al., 2005; Pearce et al., 2010). In contrast to the data of Siebert et al.
401 (2003), the basalt and granite leach solutions produced in the present study are
402 not identical to the $\delta^{98/95}\text{Mo}$ compositions of the bulk rock but show a consid-
403 erable enrichment in the heavy isotopes (Figs. 4 and 5 A & B). In contrast,
404 Mo freed from the orthogneiss matrix is only very weakly fractionated when
405 compared to the starting material (Fig. 5C). These results indicate that the
406 isotopic composition of Mo released during the partial dissolution of igneous
407 rocks is dependent on the bedrock mineralogy. Accordingly, the weathering of
408 igneous crustal rocks is incongruent and likely controls the river dissolved Mo
409 signature. In fact, the striking consistency between the $\delta^{98/95}\text{Mo}$ of the basalt
410 leach solutions (0.5 to 1 ‰; Figs. 4 and 5B) and that of the stream waters (0.6
411 to 1.1 ‰; Fig. 2) strongly suggests that the $\delta^{98/95}\text{Mo}$ in these streams is con-
412 trolled by bedrock weathering. Furthermore, it corroborates the interpretation
413 that basalt is the single most important source contributing to the stream water
414 Mo geochemistry in the catchment investigated here. Consequently, Mo host
415 phases and their respective importance for mass balance need to be constrained.

416 5.2.2. Mo released from basalts: host phases and mass balance

417 The interpretation of the basalt leach patterns (Figs. 4 and 5B) requires
418 knowing the Mo content of the individual rock components. This permits
419 the performance of mass balance calculations to identify the relevant Mo host
420 phases. The discussion focuses on basalt PA-1 (Fig. 4), as the larger sized phe-
421 nocrysts facilitate a precise determination of Mo concentrations of individual
422 components by LA-ICP-MS. Note, that although the two basalts have identical
423 mineralogical compositions and their leach solutions show the same $\delta^{98/95}\text{Mo}$
424 variability, the modal abundance of the individual rock components may vary

425 between samples M29-R and PA-1. This is expressed by the difference in the
426 fraction of Mo released at identical leach times (2 mol L⁻¹ HNO₃ leach: 20-30%
427 in M29-R and 30-55% in PA-1; Table 4).

428 The Mo distribution among the different rock components is fairly hetero-
429 geneous. Thereby, moderately to strongly enriched phases can be distinguished
430 from depleted phases (Tables 4 and 5). Also, while the Mo content of the sul-
431 fide melt inclusions is highly diverse, all other rock constituents show minor
432 Mo variability. Mass balance calculations indicate that when combined, the low
433 concentration oxides and silicate phenocrysts only account for a minor fraction
434 of the total Mo rock inventory (3-4 %; Table 4) and, hence, their role in pro-
435 ducing the leach patterns is irrelevant. The Mo content of basalts is intimately
436 connected to how evolved the parent basalt magma is (Arnórsson & Oskars-
437 son, 2007; Audétat, 2010). Therefore, the offset between the generally depleted
438 silicate phenocrysts and the moderately enriched silicate matrix is attributed
439 to fractional crystallization, which results in a progressive Mo enrichment of
440 the magma (Audétat, 2010). Accordingly, the depleted phenocrysts are likely
441 to record the composition of the early magma, while the matrix represents the
442 evolved, residual melt, where Mo accumulated due to its incompatibility. The
443 three types of sulfide melt inclusions (Table 5) reflect different stages of sili-
444 cate melt evolution because of their magmatic equilibrium coexistence. They
445 show distinct Mo concentration patterns with each stage, finally resulting in the
446 pronounced Mo variability.

447 Due to the low Mo concentrations of silicate phenocrysts and oxides, the sul-
448 fide phases and the matrix remain primary sources of Mo and, hence, dominate
449 the Mo budget of the solution. It has been argued previously that sulfide disso-
450 lution is an important weathering process, very likely to generate distinguishable
451 geochemical patterns of the riverine dissolved load (Neubert et al., 2011). The

452 elevated Mo contents found in some of the melt inclusions and the rapid pro-
453 gression of sulfide weathering in oxygenated environments (Anbar et al., 2007)
454 here leads to the hypothesis that the preferential dissolution of the magmatic
455 sulfides causes the isotopically heavy Mo in the basalt leachates. Increasing
456 SO_4^{2-} concentrations, which go along with heavy $\delta^{98/95}\text{Mo}$ and increasing Mo
457 concentrations of the liquid phase (Fig. 6A), support this interpretation. If the
458 sulfides are the primary and most readily dissolved Mo source, then the isotopic
459 composition of the leachates would require them to host at least 25 to 30 % of
460 the total bedrock Mo (Fig. 4) despite being rare (<1 % modal abundance).
461 Mass balance calculations are therefore used to check whether the experimen-
462 tally derived data can be explained by the sulfides alone. Within the limits
463 set by the geochemical and optical data (Tables 4 and 5) the system shows a
464 very high sensitivity to changes of both sulfide concentration and abundance.
465 Changing these parameters for all other components has a much smaller effect.
466 The calculations presented in Table 9 are thus based on constant, representative
467 values for silicate phenocrysts, oxides and the matrix. By changing the sulfide
468 parameters, the entire range of experimentally released heavy dissolved Mo can
469 be reproduced. These data demonstrate that even few magmatic sulfide grains
470 can account for a large fraction of the total bedrock Mo inventory. As leaching
471 progresses the contribution from other rock components becomes progressively
472 more important. Supporting evidence is given by the significant $\delta^{98/95}\text{Mo}$ drop
473 observed in the residues at leach amounts >30 %, suggesting that the heavy
474 sulfide reservoir is exhausted and that the influence of an isotopically lighter
475 component increases. This component is most likely the matrix, since it ac-
476 counts for the largest fraction of the bulk rock Mo inventory associated with
477 preferentially weathered devitrified glass. Gradual admixture of isotopically
478 lighter matrix-derived Mo also explains the lowered $\delta^{98/95}\text{Mo}$ of the solution at

479 a leach amount of 54 % ($\delta^{98/95}\text{Mo} = 0.42 \text{ ‰}$, Fig. 4).

480 On its own, the experimental data (Figure 4) could theoretically be recon-
481 ciled with equilibrium fractionation. In the context of all available information
482 (sulfate and LA-ICPMS data as well as mass balance calculations), however,
483 the proposed model is the most likely. A simple two-component model (solid-
484 liquid) does not realistically describe the data, as we are dealing with a three-
485 component system (solution-sulfides-silicate matrix). Finally, sulfide is identi-
486 fied as the source of heavy $\delta^{98/95}\text{Mo}$ due to the correlation with sulfate ($R^2=0.9$
487 linear correlation; Fig. 6B).

488 These data strongly suggest that Mo isotopes are fractionated between co-
489 existing silicate and sulfide melts in basaltic systems, with sulfide melt being
490 isotopically heavier than silicate melt. Therefore, the results indicate that Mo
491 isotope fractionation is likely to occur at hot magmatic conditions. Iron isotope
492 fractionation of similar magnitude has previously been observed at magmatic
493 temperatures between sulfide (pyrrhotite) and silicate melt (Schuessler et al.,
494 2007) as well as between silicate (fayalite) and magnetite (Shahar et al., 2008).
495 It remains to be established whether the observed Mo isotope fractionation is
496 primarily due to crystallographic control of phases involved in such processes or
497 is rather a consequence of changing intensive properties such as density.

498 5.2.3. *The role of Mo adsorption to Fe-Ti oxide surfaces during experimental* 499 *dissolution*

500 As mentioned earlier, the low pH of the leaching agents should prevent sec-
501 ondary mineral formation during the experiments (Pistiner & Henderson, 2003)
502 and isolate Mo isotope fractionation related to primary mineral dissolution. In
503 particular, Fe^{3+} does not precipitate and form additional phases (Johnson et al.,
504 2004). Mo adsorption to metal (oxyhydr)oxide surfaces, however, is increased
505 under these conditions (e.g., Goldberg et al., 1996; Xu et al., 2006; Kim & Jang,

2010) and thus Mo adsorption to the preexisting titanomagnetite surfaces may have caused Mo isotope fractionation unrelated to mineral dissolution. Since Mo adsorption to Fe-Mn (oxyhydr)oxide surfaces preferably removes the light isotopes from solution (Siebert et al., 2003; Barling & Anbar, 2004; Goldberg et al., 2009), the observed isotope fractionation ($\Delta^{98}\text{Mo}$) between leach solutions and basalt could potentially be attributed to adsorption rather than to the dissolution of specific bedrock minerals. Assuming that the experimentally determined fractionation factor between magnetite and the dissolved phase ($\Delta^{98}\text{Mo}=0.83 \pm 0.6 \text{ ‰}$; Goldberg et al., 2009) is applicable to Ti bearing magnetite as well, the predicted basalt-leachate isotope fractionation agrees with the isotope fractionation between solid and solution observed in this study ($\Delta^{98}\text{Mo}=0.4\text{-}0.9$). However, fractionation factors of Goldberg et al. (2009) were determined at high pH (6.9-8) with Mo present as the tetrahedrally coordinated MoO_4^{2-} . At the low pH, at which the experiments of this study were conducted (≤ 1), Mo is exclusively present in the octahedral form (Cruywagen & Heyns, 1989, 2000; Ozeki et al., 1996). Since fractionation of Mo isotopes during adsorption to (oxyhydr)oxide surfaces occurs dominantly as a result of the transition from the tetrahedrally to the octahedrally coordinated Mo species (Tossel, 2005; Goldberg et al., 2009), the fractionation factor between solid and solution decreases with more acidic pH, i.e. high proportions of octahedral Mo in solution. Consequently, $\Delta^{98}\text{Mo}$ is expected to be strongly reduced in the present experiments and the observed large fractionation cannot be attributed to adsorption onto the Fe-Ti oxide surfaces. This prediction is supported by the Mo concentration as well as isotope data. First, although the decreasing Mo contents observed in the 0.3 mol L⁻¹ powder experiments is compatible with adsorption, no concomitant change in $\delta^{98/95}\text{Mo}$ occurs (Fig. 4). Secondly, the increasing Mo concentrations observed in all other experiments suggest that adsorption is not significant. Fi-

533 nally, in a two phase closed system equilibrium process exhibiting a constant
534 fractionation factor, as it is the case in the experiments here, any liquid will
535 show increased $\delta^{98/95}\text{Mo}$ values with increasing Mo adsorption. The $\delta^{98/95}\text{Mo}$
536 of the leach solutions, however, show no such trend (Fig. 4). Hence, the ob-
537 served large isotope fractionation cannot be attributed to adsorption onto the
538 Fe-Ti oxide surfaces. The discrepancy between the concentration data of the
539 0.3 mol L^{-1} and the 2 mol L^{-1} leaches (decreasing vs. increasing Mo concen-
540 trations, Fig. 6B) may conceivably be a function of variable pH. Adsorption
541 reaches a maximum between pH 2 and 4 (Goldberg et al., 1996) and the subse-
542 quent implied decrease could gradually limit adsorption at $\text{pH} \leq 2$, resulting in
543 the differing concentration patterns of the leachates.

544 *5.3. Implications for the natural environment*

545 The interpretation of the leach patterns indicates that incongruent phase
546 dissolution of bulk rocks in general, and fast magmatic sulfide dissolution in par-
547 ticular, greatly influences how Mo isotopes are disproportionated during crustal
548 bedrock weathering. With respect to the natural environment, the close match
549 between the $\delta^{98/95}\text{Mo}$ signatures of stream waters and experimental leach so-
550 lutions suggests that the dissolution of isotopically heavy magmatic sulfides
551 during basalt outcrop weathering is likely to be the key factor in producing
552 the aquatic signatures of the Malaval and the Séjallières. These results raise
553 important questions pertaining to the relevance of soil formation and adsorp-
554 tion processes, which have been considered vital in producing heavy river water
555 $\delta^{98/95}\text{Mo}$ signatures (Archer & Vance, 2008; Pearce et al., 2010). According to
556 the combined results of leach solutions and stream waters, soil formation and ad-
557 sorption appear to have a minor effect on the isotopic signature of the dissolved
558 Mo in the catchment basin under investigation. However, the soil sampled on
559 the plateau exhibits a negative $\delta^{98/95}\text{Mo}$, typically produced by Mo adsorption

560 to Fe-Mn (oxyhydr)oxides. Even so, this is most probably not the primary pro-
561 cess causing the two streams to be enriched in the heavy Mo isotopes, and based
562 on the experimental data an alternative process is proposed here. Incongruent
563 chemical basalt weathering preferentially releases isotopically heavy magmatic
564 sulfide Mo that dominates the dissolved Mo inventory. In the case of the Malaval
565 and the Séjallières, the extraction of sulfide-bound Mo within the regolith cover
566 is reflected in the aquatic sulfate concentrations, which are elevated in the lower
567 parts of the catchment where streams are affected by regolith-derived waters
568 (Table 2). Similarly, other stream water parameters also show an enrichment in
569 the lower regions. This effect may be additionally amplified by rain water ad-
570 mixture to the surface waters on the plateau, because precipitation is generally
571 depleted in Mo (e.g., Kawakubo et al., 2001).

572 The isotopically heavy Mo of river waters is most likely the result of a com-
573 plex interplay between various processes involved, and the mass balance between
574 the competing factors likely controls the aquatic $\delta^{98/95}\text{Mo}$. The local system is
575 highly dependent on rock mineralogy, degree of rock weathering and soil devel-
576 opment, secondary mineral precipitation and the availability of mineral surfaces
577 for adsorption. In the case presented here, magmatic sulfide mineral dissolution
578 within the basaltic riverbed and regolith appears to dominate all other processes.
579 Finally, future studies will not only have to focus on Mo isotope fractionation
580 during mineral dissolution and soil formation, but also on the importance of
581 vegetation in the terrestrial Mo cycle, because the role of Mo as an essential
582 micronutrient required by plants is well known (e.g., Mendel & Bittner, 2006;
583 Fitzpatrick et al., 2008). The root and soil Mo isotope and concentration data
584 presented here indicate that Mo uptake into the biomass is considerable and,
585 therefore, may be an important additional pathway for the removal isotopically
586 light Mo in the weathering environment.

587 *5.4. Consequences for the global Mo isotope budget*

588 The observation that most Mo isotopic compositions of dissolved river loads
589 are heavier than most of the silicate magmatic rocks analysed so far raises
590 two related problems. Firstly, the fate of the light Mo isotopes missing in the
591 balance needs to be evaluated; secondly, the effect of isotopically heavy river
592 water on the constancy of the continental input needs to be quantified. Different
593 explanations for the heavy Mo isotopic composition of river waters have been
594 put forward. Archer & Vance (2008) proposed retention of light Mo isotopes
595 in soils, while Neubert et al. (2011) proposed the Mo isotopic composition of
596 catchment source rocks as the predominant control on the dissolved riverine
597 $\delta^{98/95}\text{Mo}$, stressing that sedimentary rocks (especially marine carbonates and
598 sulfates) have a different $\delta^{98/95}\text{Mo}$ from the magmatic silicates. The hypothesis
599 of incongruent rock weathering presented in this paper is not meant to be a
600 substitute for the former explanation, but rather a complementary process. The
601 relative effect of the processes that affect the Mo isotopic composition of rivers
602 on the global Mo isotopic cycle depends on the time scale. On a global scale, the
603 total volume of soil (or weathered rock volume) at any given time is limited. If
604 light Mo isotopes are preferentially retained in soil and/or weathering residues,
605 erosion will liberate them sooner or later. When the integrated volume of soil
606 formation is equal to the integrated soil erosion, the net Mo isotope effect will
607 be zero. This is certainly true for very long time-scales. Likewise, whenever
608 the globally integrated incongruent weathering of (sulfide bearing) fresh rocks
609 is balanced by erosion of already weathered rocks, the Mo isotope effect will
610 also be zero. The fact that to date there are no reports of magmatic rocks with
611 a particularly low $\delta^{98/95}\text{Mo}$ (i.e. residues of intense sulfide weathering) may
612 well be related to an intentional sampling bias: to constrain the magmatic Mo
613 isotopic composition of such rocks, fresh samples were collected and measured,

614 not highly weathered ones. The only way to bias the total continental runoff
615 towards an isotopic composition heavier than the continental crust (magmatic
616 plus sedimentary rocks) requires a continuous net increase of the volume of
617 soils and weathered rocks on a global scale, which, however, is not a long-term
618 steady state that can be maintained over geological times. On the other hand,
619 the hypothesis that the $\delta^{98/95}\text{Mo}$ of catchment rocks accounts for the heavy Mo
620 isotopic composition of river water is independent of the need to achieve a steady
621 state. It applies to the whole geological period, for which marine sediments
622 exposed to subaerial erosion show a heavy $\delta^{98/95}\text{Mo}$ signature; basically this
623 includes post Archean times.

624 Even if soil processes and incongruent weathering are transient, there is
625 ample possibility that they do influence the Mo isotopic composition of the con-
626 tinental runoff in selected periods of Earth's history, namely when the Earth sys-
627 tem was exceptionally far from steady state. Amongst the conceivable examples
628 are large subaerial basaltic eruptions (LIPs: e.g., Deccan, Siberian plateau, etc.).
629 Large volumes of magmatic rocks were first produced and then weathered. The
630 short-lived ocean anoxic events at the Permo-Triassic or Cretaceous-Paleogene
631 transitions are temporally related to LIP volcanism. Modelling of anoxic events
632 could potentially be refined by testing for a short-period $\delta^{98/95}\text{Mo}$ modification,
633 which could be attributed to a weathering "peak". As another example, physi-
634 cal weathering during large glaciations could lead to non-steady-state intensive
635 sulfide weathering on the newly exposed rock surfaces. This is in line with
636 the observation of an increased Mo concentration in the Tista river (Neubert
637 et al., 2011), which was interpreted by the authors as physical weathering by a
638 glacier. In any case, it remains to be established if disseminated sulfide minerals
639 generally have a heavier Mo isotopic composition than the coexisting silicates
640 because of equilibrium fractionation, or if this effect is restricted to basalts. In

641 this respect, the study presented here is rather an identification of a process
642 than the quantification of a Mo source.

643 6. Conclusions

644 The combined results of natural samples and bulk rock leaching experiments
645 have identified bedrock-controlled heavy aquatic $\delta^{98/95}\text{Mo}$ in a catchment un-
646 derlain exclusively by igneous crustal rocks. The most important finding con-
647 cerns the weathering of the basaltic bedrock, which dominates the dissolved Mo
648 geochemistry in the catchment basin. While the basalts display a bulk rock
649 signature with a $\delta^{98/95}\text{Mo} \sim 0.1 \text{ ‰}$, the basalt leach solutions are enriched in
650 the heavy isotopes. The consistency between these experimental data and the
651 stream water $\delta^{98/95}\text{Mo}$ are evidence that incongruent catchment outcrop weath-
652 ering generates heavy isotope signatures of river dissolved Mo. Mass balance
653 calculations based on LA-ICP-MS data of individual rock phases indicate that
654 the preferential dissolution of magmatic sulfides drives the river dissolved load
655 towards the observed heavy $\delta^{98/95}\text{Mo}$ values. Consequently, the magmatic sul-
656 fides need to have prominently fractionated Mo isotopes relative to coexisting
657 silicates. This makes it likely that Mo isotope fractionation also occurs at mag-
658 matic conditions similarly to reports of Fe fractionation in magmatic systems.
659 Oxidative weathering of igneous crustal rocks can thus produce substantial Mo
660 isotope fractionation through preferential dissolution of magmatic sulfides. It is
661 clear, however, that the effect of incongruent chemical rock weathering strongly
662 depends on primary rock composition, as illustrated by the significant differ-
663 ences in leach behavior of the three crustal bedrock types found in the study
664 area. The excellent match between the $\delta^{98/95}\text{Mo}$ values from the experiments
665 and stream water samples deemphasizes soil formation, vegetation, adsorption
666 processes and secondary mineral formation as important contributors to the

667 overall Mo isotope budget of the catchment studied here. On a global scale, the
668 total weathered rock volume at any given time is limited. If light Mo isotopes are
669 preferentially retained in weathering residues, erosion will liberate them sooner
670 or later. Thus, whenever the globally integrated incongruent weathering of sul-
671 fide bearing fresh rocks is balanced by erosion of already weathered rocks, the
672 Mo isotope effect will be zero. However, during periods of Earth's history when
673 the Earth system was exceptionally far from steady state, incongruent weather-
674 ing may have influenced the global continental runoff significantly. Conceivable
675 examples are periods of large subaerial basalt eruptions (e.g., Deccan, Siberian
676 plateau), or physical weathering related to large glaciations, with intensive sul-
677 fide weathering on the newly exposed rock surfaces. This study reiterates the
678 importance of (igneous) bedrock weathering for the aquatic $\delta^{98/95}\text{Mo}$ signa-
679 ture, while at the same time acknowledging the role of all other processes which
680 contribute to a heavy aquatic Mo signature. River water $\delta^{98/95}\text{Mo}$ signatures
681 are thus expected to be variable in space and time and may be controlled by
682 processes of incongruent magmatic rock weathering.

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690 language and outline. This manuscript benefited from the comments of two
691 anonymous reviewers.

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719 6 Time dependence of Mo release during basalt leach experiments.
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721 ple PA-1; left axis = 0.3 and 2 mol L⁻¹ HNO₃ leach of M29-R
722 and 0.3 mol L⁻¹ HNO₃ leach of PA-1. (B) Grain leach; left
723 axis = Mo concentrations, right axis= sulfate concentrations.
724 Note the proportionality between both. The Mo concentrations
725 of the 2 mol L⁻¹ HNO₃ powder leaches (PA-1) are plotted on
726 the right side axis due to their higher Mo concentrations. Grain
727 and strong acid leach experiments produce increasing Mo concen-
728 trations. The weak acid experiments produce Mo concentrations
729 which decrease with time. 34

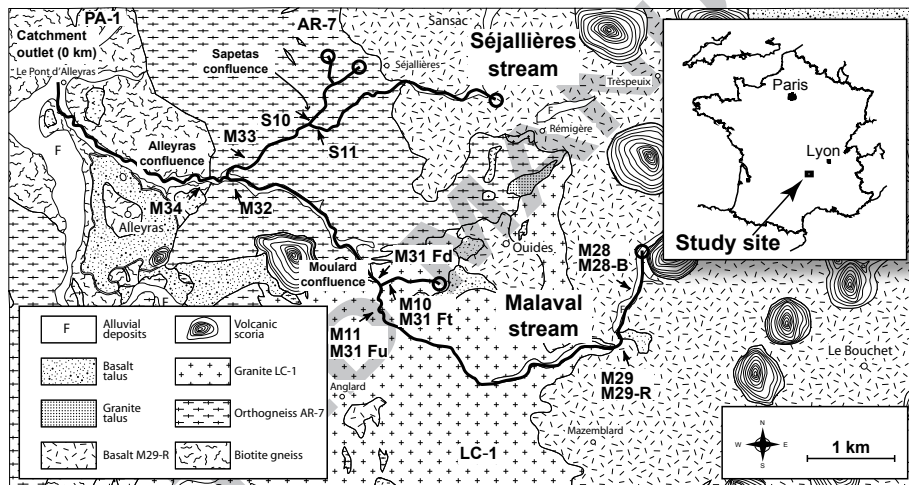


Figure 1:

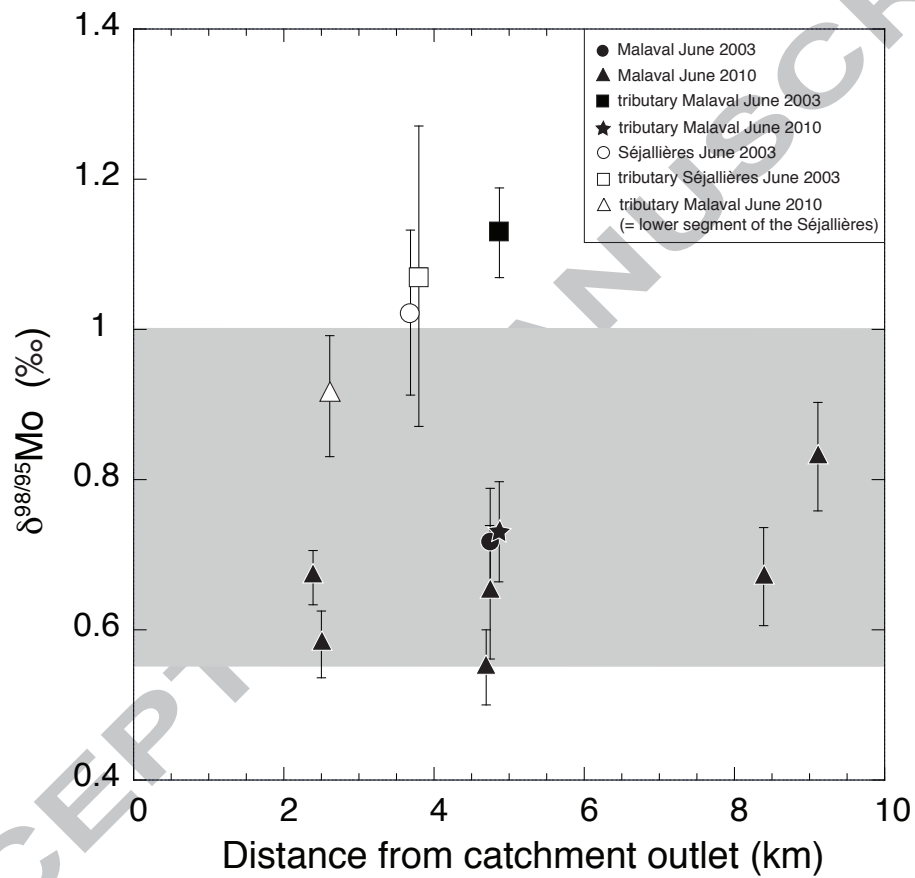


Figure 2:

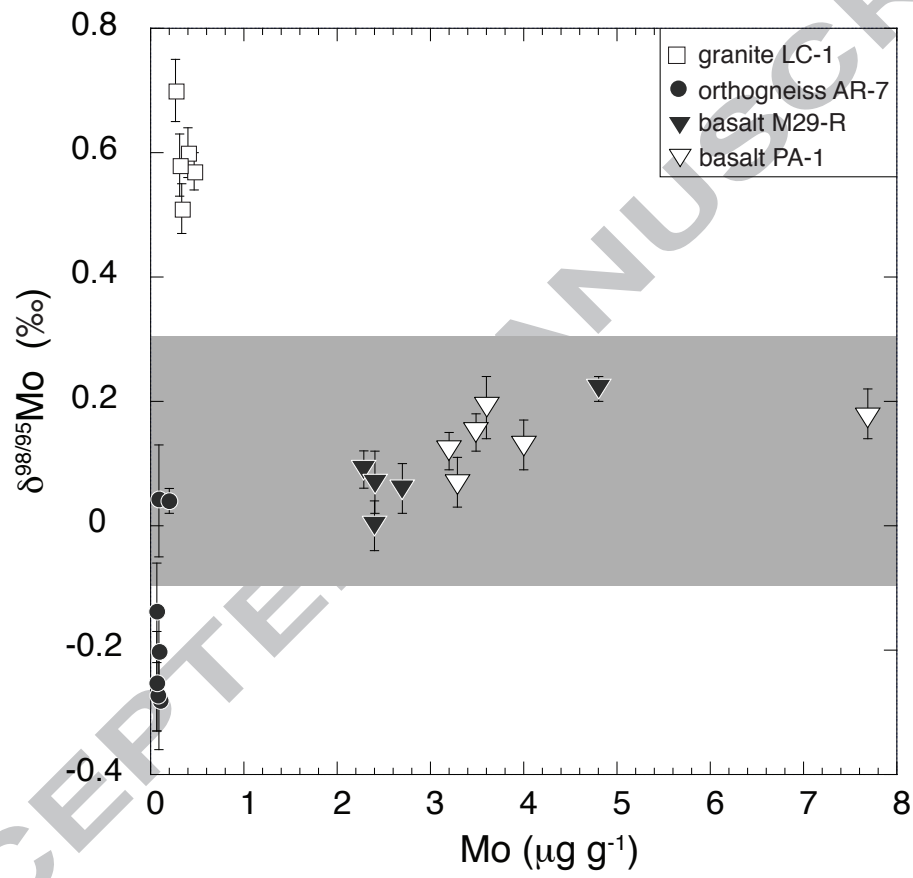


Figure 3:

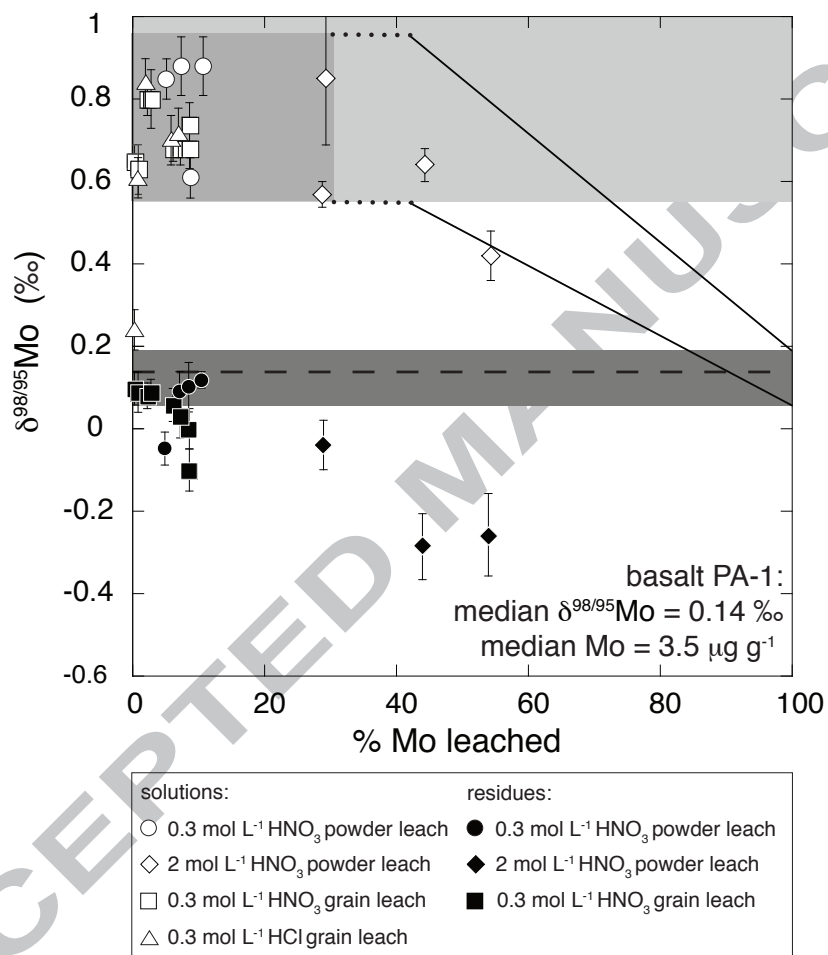


Figure 4:

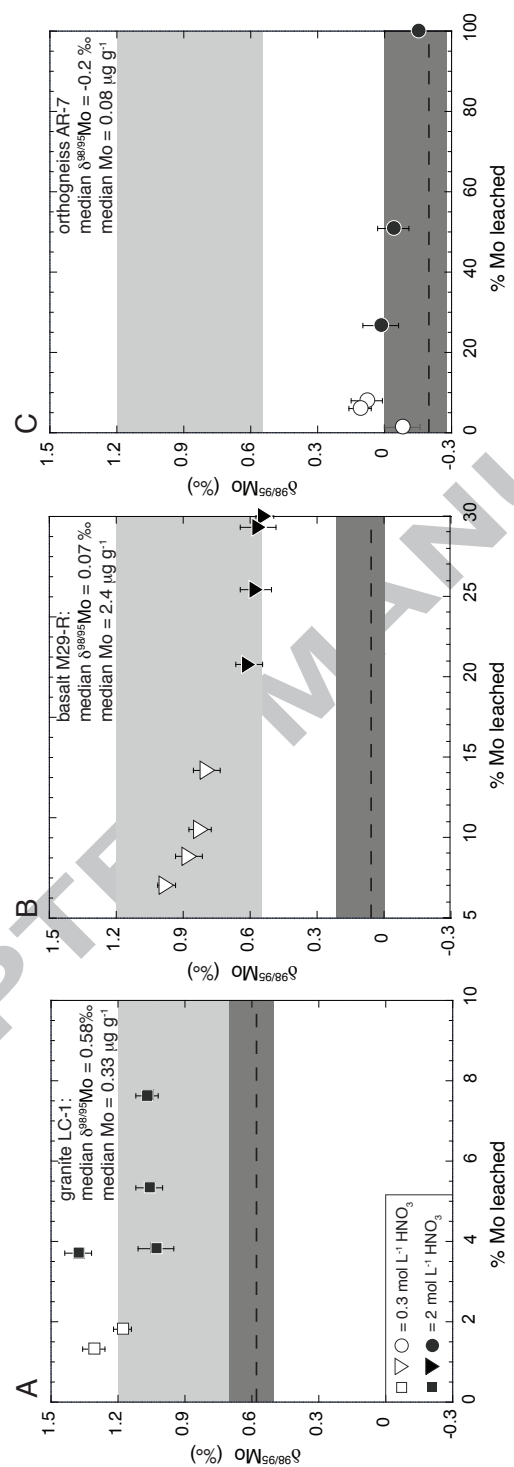


Figure 5:

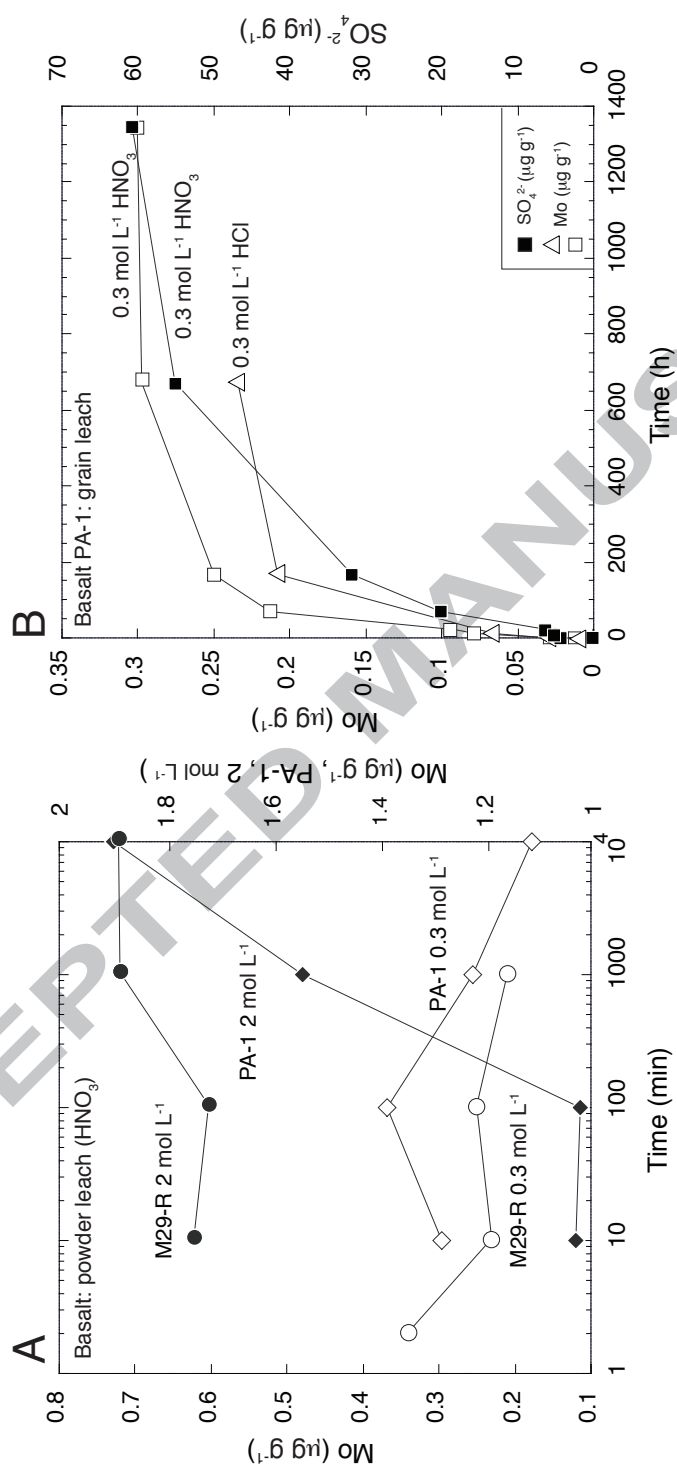


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Table 1:

	Rock type	Upstream distance [km]	$\delta^{98/95}\text{Mo}$ [‰]	2SE ^a	Mo [ng g ⁻¹]	$^{87}\text{Sr}/^{86}\text{Sr}$	2SE ^a
<i>Water Samples June 2003</i>							
M10	GSC	4.9	1.13	0.06	0.81	0.709749 ^b	10
M11	GSC	4.8	0.72	0.07	0.30	0.706340 ^b	10
S10	OG	3.8	1.07	0.20	0.20	0.704790 ^b	10
S11	OG	3.7	1.02	0.11	0.17	0.704450 ^b	10
<i>Water Samples June 2010</i>							
M28	BA	8.9	0.83	0.07	0.02	0.703853	36
M29	BA	8.4	0.67	0.07	0.04	0.703759	34
M31-Ft	GSC	4.9	0.73	0.07	0.15	0.709332	28
M31-Fu	GSC	4.8	0.65	0.09	0.12	0.705535	24
M31-Fd	GSC	4.7	0.55	0.01	0.12	0.705692	38
M32	OG	2.5	0.58	0.05	0.15	0.705322	34
M33	OG	2.6	0.91	0.08	0.07	0.704813	26
M34	OG	2.4	0.67	0.04	0.14	0.705175	38

^a2SE of individual measurements, the external reproducibility of the analytical procedure is $\pm 0.1\text{‰}$ (2σ). The 2SE of the Sr-isotope ratios refer to the last two digits.

^b $^{87}\text{Sr}/^{86}\text{Sr}$ data from Steinmann & Stille (2008).

Table 2:

Upstream distance [km]	Rock type	pH	Eh [mV]	EC [$\mu\text{S cm}^{-1}$]	T [$^{\circ}\text{C}$]	F ⁻ [mg L ⁻¹]	Cl ⁻ [mg L ⁻¹]	NO ₃ ⁻ [mg L ⁻¹]	SO ₄ ²⁻ [mg L ⁻¹]	HCO ₃ ⁻ [mg L ⁻¹]	Ca ²⁺ [mg L ⁻¹]	Na ⁺ [mg L ⁻¹]	K ⁺ [mg L ⁻¹]	Mg ²⁺ [mg L ⁻¹]	Charge Balance
<i>Water samples June 2003</i>															
M10	4.9	GSC	7.7	180	14.5	0.20	2.8	0.7	6.8	95	14.9	11.3	1.0	6.5	0.0 %
M11	4.8	GSC	7.5	265	12.8	0.09	3.3	2.5	5.9	36	5.6	5.3	0.9	4.6	-4.1 %
S10	3.8	OG	8.2	250	16.8	0.05	7.5	3.1	5.5	89	13.4	7.6	4.9	11.6	-6.7 %
S11	3.7	OG	8.1	258	14.5	0.07	6.9	8.1	5.9	73	11.0	5.4	3.3	11.1	-4.0 %
<i>Water samples June 2010</i>															
M28	9.1	BA	7.0	220	9.4	0.00	1.3	0.5	1.7	41	4.6	4.2	0.1	4.0	0.7 %
M29	8.4	BA	8.1	160	9.3	0.00	2.3	2.3	2.4	51	6.0	3.4	0.3	5.0	6.5 %
M31-Ft	4.9	GSC	-	-	-	<0.50	4.8	-	7.3	-	6.3	4.2	<1	3.2	-
M31-Fu	4.8	GSC	-	-	-	0.15	3.2	3.8	5.7	-	6.3	4.1	<1	4.7	-
M31-Fd	4.7	GSC	7.9	280	10.3	0.15	3.0	4.5	5.2	44	5.8	6.8	0.6	4.6	0.4 %
M32	2.5	OG	8.1	-	11.6	0.18	3.2	4.8	5.7	51	7.8	6.4	0.9	5.6	-0.9 %
M33	2.6	OG	8.3	-	12.1	0.16	3.4	4.3	6.8	67	8.6	4.8	1.1	7.8	3.5 %
M34	2.4	OG	8.2	-	11.9	0.16	3.3	4.7	5.9	54	7.6	5.2	0.9	6.2	1.4 %

Table 3:

Split	$\delta^{98/95}\text{Mo}$ [‰]	2SE ^a	Mo [$\mu\text{g g}^{-1}$]	$^{87}\text{Sr}/^{86}\text{Sr}$
<i>Basalt: PA-1</i>				
1	0.15	0.03	3.5	-
2	0.07	0.04	3.3	-
3	0.18	0.04	7.7	-
4	0.19	0.05	3.6	-
5	0.12	0.03	3.2	-
6	0.13	0.04	4.0	-
Median	0.14		3.5	-
<i>Basalt: M29-R</i>				
1	0.07	0.05	2.4	-
2	0.09	0.03	2.3	-
3	0.06	0.04	2.7	-
4	0.22	0.02	4.8	-
5	0.00	0.04	2.4	-
Median	0.07		2.4	0.703348 ± 12^b
<i>Orthogneiss: AR-7</i>				
1	-0.25	0.08	0.07	-
2	0.04	0.02	0.19	-
3	-0.28	0.08	0.08	-
4	0.04	0.09	0.09	-
5	-0.20	0.06	0.08	-
6	-0.27	0.06	0.07	-
7	-0.14	0.08	0.07	-
Median	-0.2		0.08	0.751991 ± 13^b
<i>Granite: LC-1</i>				
1	0.57	0.03	0.47	-
2	0.70	0.05	0.26	-
3	0.60	0.04	0.41	-
4	0.58	0.05	0.31	-
5	0.51	0.04	0.33	-
Median	0.58		0.33	0.722319 ± 13^b

^a2SE of individual measurements, the external reproducibility of the analytical procedure is $\pm 0.1\text{‰}$ (2σ)

^btypical $^{87}\text{Sr}/^{86}\text{Sr}$ values taken from Steinmann & Stille (2008). 2SE of the Sr-isotope ratios refer to the last two digits.

Table 4:

Mineral Phase	avg. Mo [$\mu\text{g g}^{-1}$]	1SE	Modal abundances ^a	Model parameters
Olivine	0.14	0.03	15% – 20%	15%
Pyroxene (cpx)	0.14	0.03		
Plagioclase	1.25	0.43		
Titanomagnetite	0.92	0.18	3% – 7%	5%
Matrix	3.53	0.69	75% – 80%	79.2 – 79.5%

^adetermined by optical microscopy

Table 5:

Analysis No.	Mo [$\mu\text{g g}^{-1}$]	S ^a [wt%]	Fe [wt%]	Cu [wt%]	Ni [wt%]	Zn [$\mu\text{g g}^{-1}$]	Ti [$\mu\text{g g}^{-1}$]	Pb [$\mu\text{g g}^{-1}$]	Fe/Cu	Ni/Cu
Inclusion type 1										
26ala03.xl	1.1	29	60	0.5	3.2	140	440	<0.2	123	6.6
26ala04.xl	1.5	29	61	0.3	2.8	150	71	<0.2	239	10.9
26ala05.xl	1.1	27	60	0.4	3.6	170	210	<0.4	165	10.0
26ala06.xl	<0.05	28	60	0.5	3.0	180	660	<0.6	117	5.9
Inclusion type 2										
26ala07.xl	2.0	22	53	7.6	3.4	320	2700	140	7	0.4
26ala08.xl	0.8	28	59	1.5	3.5	60	<93	<1	39	2.3
26ala09.xl	200	22	57	4.3	2.4	360	22000	15	13	0.6
26ala10.xl	22.0	29	61	1.7	1.0	103	<50	2	36	0.6
26ala11.xl	52.4	30	61	1.6	1.1	99	<40	6	38	0.7
26ala12.xl	39.8	33	61	1.6	1.1	103	2900	<3	37	0.7
26alc14.xl	0.3	18	60	1.2	2.6	260	1700	0.2	50	2.2
26alc15.xl	2.0	21	60	2.0	2.0	300	250	4	30	1.0
24mrb06.xl	250	27	61	1.5	0.8	150	<1000	1	42	0.5
Inclusion type 3										
24mrb03.xl	35	25	34	30	0.7	430	<84	320	1.2	0.0
24mrb05.xl	78	23	29	35	1.1	750	<44	670	0.8	0.0
24mrb07.xl	28	23	30	32	3.1	740	44000	500	0.9	0.1
24mrb09.xl	16	22	32	28	4.4	1500	<263	30	1.1	0.2

^acalculated based on (Fe, Ni, Cu)S stoichiometry

Table 6:

Sample	Type	$\delta^{98/95}\text{Mo}$	2SE [‰]	Mo [$\mu\text{g g}^{-1}$]
M28-B	top soil	-0.33	0.1	2.38
M28-BW	root material	-0.14	0.0	0.67

Table 7:

	Upstream distance [km]	Rock type	Suspension weight [mg L ⁻¹]
<i>Samples June 2003</i>			
M10	4.9	GSC	1.3 ^a
M11	4.8	GSC	5.5 ^a
S10	3.8	OG	19.7 ^a
S11	3.7	OG	5.6 ^a
<i>Samples June 2010</i>			
M28	8.9	BA	b.d.l.
M29	8.4	BA	b.d.l.
M31-Ft	4.9	GSC	b.d.l.
M31-Fu	4.8	GSC	b.d.l.
M31-Fd	4.7	GSC	b.d.l.
M32	2.5	OG	b.d.l.
M33	2.6	OG	b.d.l.
M34	2.4	OG	b.d.l.

^a2003 data taken from Steinmann & Stille (2008)

Table 8:

leach time	leaching agent	Temp.	Mo leached [%]	$\delta^{98/95}\text{Mo}$ in solution [‰]	2SE	Mo in solution [$\mu\text{g g}^{-1}$] ^a	$\delta^{98/95}\text{Mo}$ in residue [‰]	2SE	SO_4^{2-} in solution [$\mu\text{g g}^{-1}$] ^a	$\delta^{98/95}\text{Mo}_{MB}$ [%] ^b
<i>Basalt: PA-1 grain leach</i>										
10min	0.3 mol L ⁻¹ HNO ₃	cold	0.4	0.65	0.04	0.01	0.10	0.04	b.d.l.	-0.04
0.5h	0.3 mol L ⁻¹ HNO ₃	cold	0.8	0.63	0.06	0.03	0.09	0.05	4.4	-0.05
12h	0.3 mol L ⁻¹ HNO ₃	cold	2.3	0.80	0.04	0.08	0.08	0.03	5.6	-0.05
24h	0.3 mol L ⁻¹ HNO ₃	cold	2.7	0.80	0.07	0.09	0.09	0.03	6.3	-0.04
72h	0.3 mol L ⁻¹ HNO ₃	cold	6.1	0.68	0.03	0.21	0.06	0.04	20.0	-0.05
1w	0.3 mol L ⁻¹ HNO ₃	cold	7.1	0.68	0.04	0.25	0.03	0.05	31.7	-0.07
1m	0.3 mol L ⁻¹ HNO ₃	cold	8.5	0.68	0.05	0.30	-0.10	0.05	55.0	-0.18
2m	0.3 mol L ⁻¹ HNO ₃	cold	8.7	0.74	0.05	0.30	0.00	0.05	61.7	-0.09
10min	0.3 mol L ⁻¹ HCl	cold	0.3	0.24	0.05	0.01	-	-	-	-
0.5h	0.3 mol L ⁻¹ HCl	cold	0.8	0.61	0.05	0.03	-	-	-	-
12h	0.3 mol L ⁻¹ HCl	cold	1.9	0.84	0.06	0.07	-	-	-	-
1w	0.3 mol L ⁻¹ HCl	cold	5.8	0.70	0.06	0.21	-	-	-	-
1m	0.3 mol L ⁻¹ HCl	cold	7.0	0.72	0.06	0.23	-	-	-	-
<i>Basalt: PA-1 powder leach</i>										
10min	0.3 mol L ⁻¹ HNO ₃	cold	8.5	0.61	0.05	0.30	0.10	0.06	-	0.00
100min	0.3 mol L ⁻¹ HNO ₃	cold	10.5	0.88	0.07	0.37	0.12	0.02	-	0.05
1000min	0.3 mol L ⁻¹ HNO ₃	cold	7.3	0.88	0.07	0.26	0.09	0.05	-	0.00
10'000min	0.3 mol L ⁻¹ HNO ₃	cold	5.1	0.85	0.05	0.18	-0.05	0.04	-	-0.15
10min	2 mol L ⁻¹ HNO ₃	50°C	28.6	0.57	0.03	1.03	-	-	-	-
100min	2 mol L ⁻¹ HNO ₃	50°C	29.2	0.85	0.16	1.02	-0.04	0.06	-	0.03
1000min	2 mol L ⁻¹ HNO ₃	50°C	44.1	0.64	0.04	1.54	-0.29	0.08	-	-0.09
10'000min	2 mol L ⁻¹ HNO ₃	50°C	54.3	0.42	0.06	1.90	-0.26	0.10	-	-0.09
<i>Basalt: M29-R powder leach</i>										
2min	0.3 mol L ⁻¹ HNO ₃	cold	14.2	0.79	0.06	0.34	-	-	-	-
10min	0.3 mol L ⁻¹ HNO ₃	cold	7.0	0.97	0.04	0.23	-	-	-	-
100min	0.3 mol L ⁻¹ HNO ₃	cold	10.5	0.82	0.05	0.25	-	-	-	-
1000min	0.3 mol L ⁻¹ HNO ₃	cold	8.8	0.87	0.06	0.21	-	-	-	-
10min	2 mol L ⁻¹ HNO ₃	50°C	25.4	0.57	0.07	0.62	-	-	-	-
100min	2 mol L ⁻¹ HNO ₃	50°C	20.8	0.60	0.06	0.60	-	-	-	-
1000min	2 mol L ⁻¹ HNO ₃	50°C	29.4	0.56	0.08	0.72	-	-	-	-
10'000min	2 mol L ⁻¹ HNO ₃	50°C	30.0	0.53	0.04	0.72	-	-	-	-
<i>Orthogneiss: AR-7 powder leach</i>										
10min	0.3 mol L ⁻¹ HNO ₃	cold	7.9	0.08	0.07	0.01	-	-	-	-
100min	0.3 mol L ⁻¹ HNO ₃	cold	6.3	0.11	0.05	0.005	-	-	-	-
10'000min	0.3 mol L ⁻¹ HNO ₃	cold	1.4	-0.08	0.10	0.001	-	-	-	-
100min	2 mol L ⁻¹ HNO ₃	50°C	26.8	0.02	0.08	0.02	-	-	-	-
1000min	2 mol L ⁻¹ HNO ₃	50°C	50.9	-0.04	0.07	0.04	-	-	-	-
10'000min	2 mol L ⁻¹ HNO ₃	50°C	100	-0.15	0.15	0.10	-	-	-	-
<i>Granite: LC-1 powder leach</i>										
10min	0.3 mol L ⁻¹ HNO ₃	cold	1.8	1.18	0.04	0.01	-	-	-	-
100min	0.3 mol L ⁻¹ HNO ₃	cold	1.3	1.31	0.05	0.004	-	-	-	-
10min	2 mol L ⁻¹ HNO ₃	50°C	3.7	1.38	0.06	0.01	-	-	-	-
100min	2 mol L ⁻¹ HNO ₃	50°C	3.8	1.03	0.08	0.01	-	-	-	-
1000min	2 mol L ⁻¹ HNO ₃	50°C	5.3	1.06	0.06	0.02	-	-	-	-
10'000min	2 mol L ⁻¹ HNO ₃	50°C	7.6	1.07	0.05	0.03	-	-	-	-

^aConcentrations relative to grams of sample material leached.

^bdifference between bulk rock $\delta^{98/95}\text{Mo}$ composition and $\delta^{98/95}\text{Mo}$ composition of calculated mass balance.

Table 9:

Modal abundances				Concentrations				Fraction of bulk rock Mo inventory				
oxides	sulfides ^a	phenocrysts ^b	matrix	oxides	sulfides	phenocrysts ^b	matrix	Total	oxides	sulfides	phenocrysts ^b	matrix
[%]	[%]	[%]	[%]	[$\mu\text{g g}^{-1}$]	[$\mu\text{g g}^{-1}$]	[$\mu\text{g g}^{-1}$]	[$\mu\text{g g}^{-1}$]	[$\mu\text{g g}^{-1}$]	[%]	[%]	[%]	[%]
5	0.5	15	79.5	1.0	40	0.5	3.5	3.1	1.6	6.5	2.4	89.5
5	0.5	15	79.5	1.0	70	0.5	3.5	3.2	1.5	10.8	2.3	85.3
5	0.5	15	79.5	1.0	100	0.5	3.5	3.4	1.5	14.8	2.2	81.6
5	0.5	15	79.5	1.0	150	0.5	3.5	3.6	1.4	20.6	2.1	76.0
5	0.8	15	79.2	1.0	40	0.5	3.5	3.2	1.6	10.0	2.3	86.1
5	0.8	15	79.2	1.0	70	0.5	3.5	3.5	1.5	16.2	2.2	80.1
5	0.8	15	79.2	1.0	100	0.5	3.5	3.7	1.4	21.7	2.0	75.0
5	0.8	15	79.2	1.0	150	0.5	3.5	4.1	1.2	29.3	1.8	67.7

^atotal content <1% based on XRD analysis^bsum of plagioclase, pyroxene and olivine

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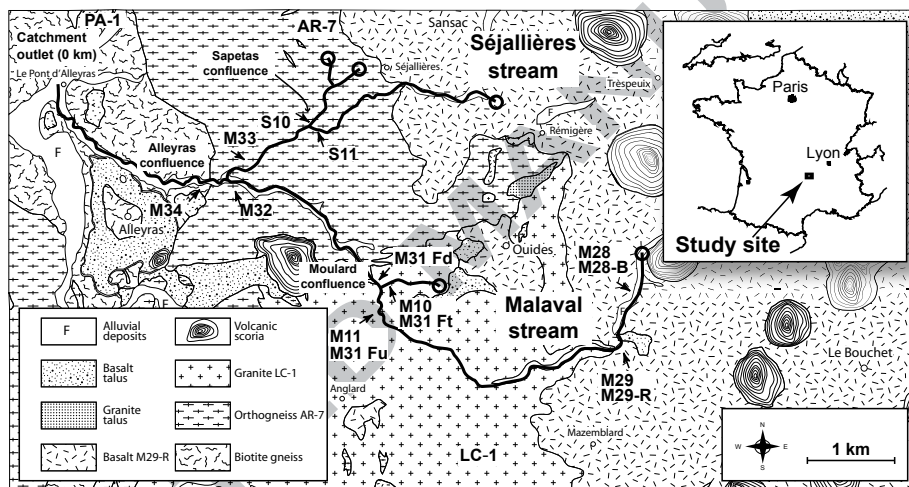


Figure 1: