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Philippe Négrel, Romain Millot

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1 **BEHAVIOUR OF LI ISOTOPES DURING REGOLITH FORMATION ON**
2 **GRANITE (MASSIF CENTRAL, FRANCE): CONTROLS ON THE**
3 **DISSOLVED LOAD IN WATER, SAPROLITE, SOIL AND SEDIMENT**

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5
6 **NÉGREL, Ph., MILLOT, R.**

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8 BRGM, Laboratories Division, Orléans, France -- p.negrel@brgm.fr,
9

10 **Abstract**

11
12 Lithium (Li) contents and isotopes were studied in all environments of a small river catchment draining
13 granite in the Margeride mountains of the French Massif Central. This covered surface waters, primary
14 and accessory minerals of the granites, the whole rock, and soil and sediment samples developed in the
15 catchment, completed with regional data for mineral waters and rainwater. The integrated investigation
16 aimed at evaluating the potential of Li isotopes as effective tracers of water/rock interaction processes
17 within a granitic environment. The $\delta^7\text{Li}$ values and Li concentrations were measured on sediment- and
18 soil samples, following standard acid-dissolution procedures and chemical purification of Li using the
19 cationic exchange resin protocol in a clean lab. Lithium-isotope compositions were measured with a
20 Neptune MC-ICP-MS and Li concentrations by ICP-MS. The samples represented different stages of
21 granite weathering, including fresh granite, weathered-rock, surface saprolite, and sediments in
22 riverbanks and fields bordering the streams. The extent of Li mobility during granite weathering was
23 first evaluated through determining the percentage change relative to Ti, with a range from -31 to -66%
24 in the collected samples. The weathered-rock was depleted by -47% for Li with negative $\delta^7\text{Li}$ values
25 ranging from -1.9 to -3.4‰. Soil to riverbank sediment samples were characterized by less negative $\delta^7\text{Li}$
26 values, indicating that Li is enriched in soil with fractionation of Li isotopes and changes of the mineral
27 abundance in the samples. To complement this first view, we i) Modelled the theoretical Li isotope
28 signature of water interacting with granite, using a weathering model based on dissolution; ii) Applied
29 an atmospheric-input correction to surface waters; iii) Applied a Raleigh equation for modelling the Li
30 isotope fractionation when compared with corrected surface water and mineral water; and iv) Compared
31 Li isotopes with Sr-isotope data in a larger weathering framework.

32
33 **Keywords:** weathering, isotopes, lithium, groundwater, soil, sediment, granite
34

35 **1 – Introduction**

36 Continental silicate weathering is one of the major processes controlling the chemical evolution
37 of the Earth's surface (Gaillardet et al., 1999), because crystalline basement rocks represent
38 over 50% of the earth's terrestrial surface (Amiotte Suchet et al., 2003). Weathering leads to the
39 formation of unconsolidated alterite or saprolite, usually representing a thickness of up to
40 several tens of metres (Velbel, 1988). The study of alteration processes combines the use of
41 several tools, such as geochemistry (e.g., Nesbitt and Markovics, 1980), isotopic tracing (e.g.,
42 Négrel et al., 2018), mineralogy (e.g., Braga et al., 2002), and the notions of space and scale,
43 ranging from a small watershed (White and Blum, 1995; Ackerer et al., 2016) to continental
44 river basins like the Amazon, Ganges or Congo basins (Gaillardet et al., 1999; Abbas and
45 Subramanian, 1984; Négrel et al., 1993).

46 The links and relationships between weathering, development of saprolite on hill slopes
47 and large-scale dissolved-load transport by streams are very complex. Despite the existence of
48 numerous tools for studying weathering processes (e.g., isotopes of Sr, U, etc.), the increasing
49 need for proxies has underpinned the development of chemical—such as rare earth elements—
50 and isotopic tools, such as lithium and, more recently, silicon, calcium and magnesium (see
51 Sullivan et al., 2016, for synthesis).

52 Lithium has two stable isotopes of mass 6 and 7, with natural abundances of 7.5% and
53 92.5%, respectively; it is a mobile element that tends to incorporate into the fluid phase during
54 water/rock interactions. The relative mass difference between the two isotopes is considerable
55 at 17%, generating significant mass-dependant fractionation during geochemical processes.
56 Tomascak (2004) noted that the range of variation in lithium-isotope compositions is over 50‰
57 in geological materials. Silicate rocks have Li-isotope compositions ranging from -2 to +10‰
58 (Coplen et al., 2002; Teng et al., 2004). The Li isotope of seawater is about +31‰ (Millot et
59 al., 2004); river water has a large range (-6.0 to +32.2‰, Huh et al., 1998); and (saline) thermo-

60 mineral water generally has isotopic compositions of 0 to +15‰ (Millot and Négrel, 2007;
61 Millot et al., 2010b).

62 In the context of water/rock interactions, numerous studies have clearly shown that Li
63 isotopes are a promising proxy for tracing silicate weathering reactions (e.g. Huh et al., 1998,
64 2001; Pistiner and Henderson, 2003; Kisakurek et al., 2004; Rudnick et al., 2004; Pogge von
65 Strandmann et al., 2012; Millot et al., 2007, 2010a, 2010b; Vigier et al., 2009; Wang et al.,
66 2015; Clergue et al. 2015). Silicate minerals host Li and chemical weathering induces isotopic
67 fractionation. This results in enrichment of the heavy isotope (^7Li) in solution, the light isotope
68 (^6Li) being preferentially retained in secondary weathering mineral phases (Huh et al., 2004;
69 Vigier et al., 2008; Weynell et al., 2017), similar to other non-traditional stable-isotope systems
70 such as Ca, Fe and B (Sullivan et al., 2016). Today, lithium isotopes are applied to a wide range
71 of geochemical processes, such as weathering (Pistiner and Henderson, 2003; Huh et al., 2004;
72 Hathorne and James, 2006; Lemarchand et al., 2010; Wanner et al., 2017; Wimpenny et al.,
73 2010; Ryu et al., 2015; Pogge von Strandmann et al., 2019). Other applications are to the study
74 of erosion processes, either in large river-basin studies (Huh et al., 1998, 2001; Kisakurek et
75 al., 2005; Millot et al., 2010a; Dellinger et al., 2015; Henchiri et al., 2014; 2016; Wang et al.,
76 2015; Murphy et al., 2019), or in smaller streams (Vigier et al., 2009; Pogge von Strandmann
77 et al., 2010; Liu et al., 2015); to studying anthropogenic disturbance in soils (Négrel et al., 2010;
78 Tsai et al., 2014); and as geothermometer proxies in mineral waters (Millot and Négrel, 2007),
79 or for tracing groundwater flowpaths (Négrel et al., 2012; Pogge von Strandmann et al., 2014).
80 However, studies on granitic bedrock and its associated weathering products are very scarce
81 (Rudnick et al., 2004; Lemarchand et al., 2010).

82 At the basic scale of a watershed, the challenge is to integrate all the reservoirs and parts
83 of the watershed affected by the weathering processes. This has been the case in studies
84 involving classic tools, such as strontium isotopes, but not when working with newly developed

85 tools. In this study, we measured lithium and its isotope values in all reservoirs and parts of a
86 catchment draining granite. This included surface- and mineral waters, primary minerals and
87 accessory phases of the granites, the whole rock, and samples of soil and sediment generated
88 within the watershed, completed with additional data for rainwater.

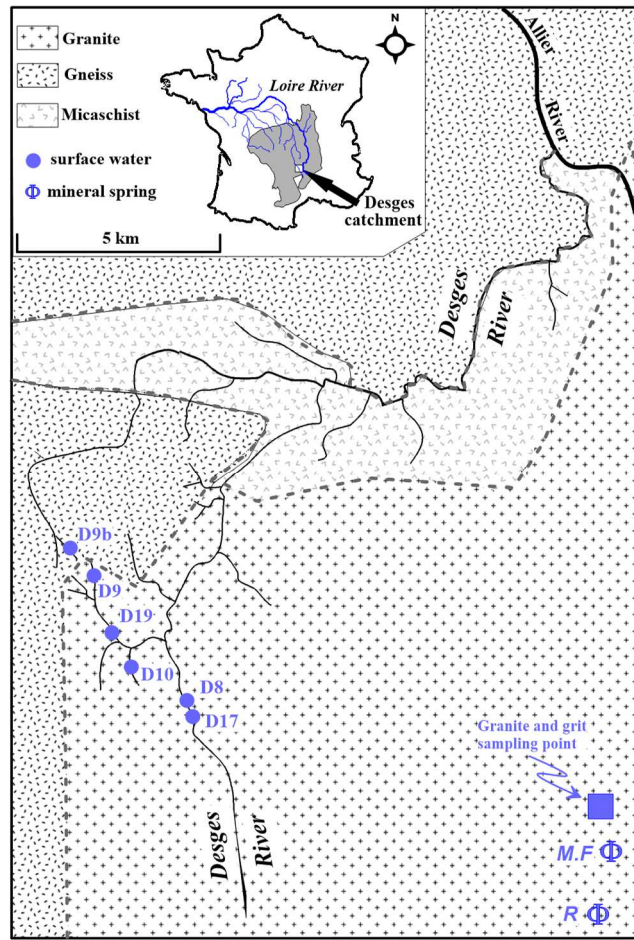
89 Our study has used Li-isotope data for tracing silicate weathering processes at the basic
90 scale of a watershed, considering all its components. This is a novel approach for Li isotopes,
91 which earlier were partly limited due to the difficulty of collecting and analysing samples from
92 all reservoirs. This systematic work is part of a long-term, wide-ranging and integrated
93 geochemical study covering major and trace elements, Sr isotopes, Nd isotopes and rare earth
94 elements, in water, sediment and soil within the Margeride mountains of central France (Négrel,
95 1999; 2006; Négrel et al., 2000); this also includes incorporation of all relevant outside data,
96 such as on separated minerals and long-term monitoring of rainfall.

97 Isotopic investigation of weathering products generally provides good information on
98 the chemical reactions taking place during such processes. This is further demonstrated by
99 recent studies on the Li isotope systematics of silicate-rock weathering, in complement to
100 investigations covering regolith production and the development of weathering profiles
101 (Vázquez et al., 2016; Ackerer et al., 2016).

102 In order to apply Li isotopes as effective tracers of water/rock interaction processes in a
103 small mono-lithological catchment, the effect of atmospheric input was investigated to correct
104 the lithium values of surface- and mineral waters. This allowed replacing Li isotopes with Sr
105 isotopes in a larger weathering framework. We also tested a steady-state weathering model and
106 fractionation process modelling on the Margeride granite-gneiss, prerequisites for our reactive-
107 transport model computer simulations that coupled a large number of chemical reactions with
108 mass transport, a key challenge for the effective use of Li isotopes as a tool in weathering
109 studies.

110 **2 - General setting**

111 The granite-gneiss Margeride massif is located in the south of the French Massif Central
112 (Figs. 1a, b). It consists of light and dark granite-gneiss with an average mineral composition
113 of the light facies of 37% quartz, 30% oligoclase, 23% K-feldspar and 10% biotite, and of 31%
114 quartz, 30% andesine, 20% K-feldspar and 19% biotite in the dark facies (Marchand et al.,
115 1985). The mineralogy and chemistry of Margeride granite and gneiss are similar, although the
116 relative abundance of minerals may fluctuate slightly. The presence of a micaschist unit in the
117 massif is worth noting, composed of quartz, muscovite and biotite. Couturié et al. (1979)
118 reported that the different facies of the Margeride granite (323 ± 12 Ma., Rb-Sr isochron)
119 resulted from fractional crystallization of a crustal magma in a subhorizontal laccolith. The
120 Desges River, a tributary of the Allier, flows approximately 40 km between the upper part of
121 the Margeride massif and its confluence with the Allier (Négrel, 1999; Fig. 1b). The watershed
122 covers 89 km^2 and ranges in altitude from 1250 m (headwaters) to 650 m (outlet); the dense N-
123 S-oriented drainage pattern mainly on the top of the Margeride plateaus receives an average
124 annual precipitation of 1000 to 1200 mm/yr^{-1} .



125

126 *Figure 1. General location map of the Massif Central (in blue-grey), and detailed map of the*
 127 *Desges watershed showing the sampling sites, modified from Négrel (1999; 2006). The main*
 128 *geological units are granite, gneiss, and micaschist. The different sampling points are:*
 129 *bedrock and granitic grit of the Desges watershed, mineral springs (Mazel and Fontaine*
 130 *Basses (M.F) and Ranc (R), surface waters, soils and sediments (Dx).*

131 **3 – Material and methods**

132 In a temperate climate, granite usually weathers into grit (Sequeira Braga et al., 1990; 2002; Le
 133 Pera et al., 2001; Paquet and Clauer, 2012). Unweathered bedrock and granitic grit were
 134 collected at the same place (Fig. 1, blue square). The Mazel grit sample, collected on top of a
 135 granite outcrop, has a fabric skeleton structure retaining the original granitic one, which is
 136 commonly observed in the lower (45-100 cm depth) part of the soil profile here. Although the
 137 texture of the parent rock was largely preserved, the main transformations are chloritization of
 138 biotite, kaolinization of plagioclase, and the presence of oxy-hydroxides (Sarazin, 1979). This
 139 is reflected in our sample that is mainly composed of quartz (20%), K-feldspar (20%),

140 plagioclase (20%) and chlorite (5%), and for which we adopt the classification of Begonha and
141 Sequeira Braga (2002) as “weathered rock”.

142 Samples A0, A1 and A2 were collected around station D17, and samples B0, B1 and B2
143 around station D19 (Fig. 1). A0 and B0 (Négre, 2006), collected from a weathering profile, are
144 not a direct skeleton-fabric material of the granite, but are surface saprolite mainly composed
145 of sand and silt. Samples A1 and B1 are riverbank sediments, classified as sandy-silt. All four
146 samples mainly consist of quartz, K-feldspar, plagioclase and illite-micas, with dramatic
147 changes in relative abundances (Négre, 2006).

148 The soils in this catchment are podzol and peat, varying in thickness from a few
149 centimetres at the top of the profile to a few metres farther down. They mainly consist of
150 kaolinite, hydroxides and vermiculite, K feldspar and biotite (isolated from the matrix), and
151 ubiquitous organic and amorphous phases (Bourrié, 1978; Sarazin, 1979). Soil samples A2 and
152 B2, collected in fields bordering the streams, can be classified as silty-sand and contain small
153 amounts of quartz, K-feldspar, plagioclase and illite-micas.

154 The sample-preparation procedure was described in detail by Negrel and Deschamps
155 (1996) and Négre (1999; 2006). Briefly, weathered rock (Mazel) and surface saprolite (A0 and
156 B0) were powdered, the other soil and sediment samples being oven-dried at 70 °C,
157 homogenized, quartered and dry-sieved through a 165 µm nylon mesh, and powdered before
158 analysis. The $\delta^7\text{Li}$ values were measured on the sediment- and soil samples following standard
159 acid-dissolution. For rock and sediment, total sample digestion was necessary before separation
160 of Li from the matrix. About 50 mg of crushed sample was dissolved in a closed beaker with
161 an ultrapure mixture of three acids [4 ml HF (23N), 1 ml HNO₃ (14N) and 0.1 ml HClO₄ (12N)]
162 for four days at 100 °C. After this, once the acid mixture had evaporated, 4 ml of HCl (6N) was
163 added for four days at 100 °C. A sample aliquot (30 ng of Li) of the acid-dissolution residue

164 was then dissolved in 0.5 ml of HCl (0.2N) before being placed in a column containing cationic
165 resin for Li separation.

166 Surface-water samples were collected from the river according to the protocol in Négrel
167 (1999); groundwater samples were thermo-mineral waters from naturally flowing springs, taken
168 according to the protocol in Négrel (2006). Briefly, water samples were collected in the field in
169 acid-washed polyethylene bottles after filtration through 0.2 μm Sartorius® cellulose acetate
170 filters and then acidified to pH <2, by adding ultra-pure HNO_3 .

171 Lithium isotopic compositions in soil, sediment and water were measured with a
172 Neptune MC-ICP-MS (see Millot et al., 2004, for details) and Li concentrations with a
173 quadrupole ICP-MS. The $^7\text{Li}/^6\text{Li}$ values were normalized to the L-SVEC standard solution
174 (NIST SRM 8545) following the standard-sample bracketing method. Typical in-run precision
175 on $\delta^7\text{Li}$ determination was about 0.1-0.2‰ ($2\sigma_m$). Chemical separation of lithium from the
176 matrix was achieved before mass analysis following a procedure adapted by Millot et al. (2004),
177 using cationic resin (Bio Rad AG® 50W-X12, 200-400 mesh) and HCl (0.2N) for 30 ng of
178 lithium. Blanks for total chemical extraction were less than 20-30 pg of Li, which is negligible
179 since the blank/sample ratio is less than 10^{-3} . Accuracy and reproducibility of the total method
180 (purification procedure plus mass analysis) were tested by repeated measurements of a seawater
181 standard (IRMM BCR-403) after separation of Li from the matrix, for which we obtained a
182 mean value of $\delta^7\text{Li} = +30.8\text{‰} \pm 0.4$ (2σ , $n=15$) over the duration of the analytical period. This
183 mean value agrees with our long-term measurements ($\delta^7\text{Li} = +31.0\text{‰} \pm 0.5$, 2σ , $n=30$, Millot et
184 al. 2004) and with other values from the literature.

185 **4 – Results**

186 The Li data ($\delta^7\text{Li}$ and Li contents) of rock, grit, soil, sediment and separate minerals from the
187 granite and surface and groundwater collected in the catchment are given in Table 1.

188

Sample	Ref.	Li ppm	$\delta^7\text{Li}$	Sample	Ref.	Li $\mu\text{mol L}^{-1}$	$\delta^7\text{Li}$
M1/POU	Whole rock	143.1	-1.9	<i>Spring waters</i>			
ALT1	Mazel grit	104.7	-3.4	Mazel		551	5.0
				FB1		424	4.9
Ap	Apatite	13.3	0.0	Ranc1		158	3.8
Pl	Plagioclase	20.9	-1.7	Ranc2		397	2.6
Bi	Biotite	489.1	0.8	<i>Surface waters</i>			
KF	K-Feldspar	5.3	-2.6	D10'		0.22	12.7
D19-3/A0	A0	56.2	0.1	D8		0.15	9.2
D19-3/A1	A1	68.8	-2.1	D11		0.23	12.1
D19-3/A2	A2	110.9	-3.4	D9bis		0.16	10.0
D17-3/B0	B0	60.6	3.3	D9'		0.21	10.7
D17-3/B1	B1	61.6	0.0	D11'		0.24	13.0
D17-3/B2	B2	66.2	-2.7				

189

190 *Table 1. Results of Li concentration ($\mu\text{g g}^{-1}$) and $\delta^7\text{Li}$ for parent rock, grit, separate minerals,*
191 *sediment and soil, expressed in ppm. Results of Li concentration ($\mu\text{g g}^{-1}$) and $\delta^7\text{Li}$ for thermo-*
192 *mineral waters (e.g., saline waters cold on surface, but linked to a deep hot reservoir) from*
193 *Millot and Négrel, 2007; results of Li concentration ($\mu\text{mol l}^{-1}$) and $\delta^7\text{Li}$ for surface waters.*

194

195

196

For the separate minerals, Li-rich phases decreased in content from biotite ($489 \mu\text{g g}^{-1}$)
197 to K-feldspar ($5 \mu\text{g g}^{-1}$), for an average whole-rock Li content of about $143 \mu\text{g g}^{-1}$. Lithium
198 isotopic compositions in the separate minerals ranged from -2.6‰ in K-feldspar to 0.0‰ in
199 apatite, for a $\delta^7\text{Li}$ of -1.9‰ in bulk rock. Reconstituting the whole rock from the separate
200 minerals led to a Li content of $56 \mu\text{g g}^{-1}$ and a $\delta^7\text{Li}$ of 0.45‰ . These values are inconsistent
201 with the measured ones, implying that the rest of the Li probably occurs in residual minerals
202 with a Li content of around $86.6 \mu\text{g g}^{-1}$ and a $\delta^7\text{Li}$ of -3.43‰ . The Li content in soil and
203 sediment fluctuated from $56 \mu\text{g g}^{-1}$ (surface saprolite A0) to $111 \mu\text{g g}^{-1}$ (soil A2). With the
204 exception of soil A2 (almost twice the content in soil B2), the samples had similar Li contents
205 (surface saprolite 56 vs. $61 \mu\text{g g}^{-1}$; sediment samples 69 vs. $62 \mu\text{g g}^{-1}$). Li isotopes in soil and
206 sediment samples ranged from -3.38‰ (soil A2) to 3.31‰ (surface saprolite B0).

207

208

209

210

211

Surface waters in the catchment had a roughly constant Li content of around 0.14 to
 $0.24 \mu\text{mol L}^{-1}$, corresponding to the lower value observed in streams draining volcanic rocks in
the Massif Central, (Table 1), whose range of variation is from 0.4 to $2.35 \mu\text{mol L}^{-1}$ (Négrel et
al., 2010a). Li-isotope compositions ($\delta^7\text{Li}$) varied in the catchment (Table 1), ranging from $+9$
to $+12\text{‰}$, which is lower than that in other water samples from the Massif Central (Négrel et

212 al., 2010) that range from +12 to +15.1‰. Lithium-isotope compositions and Li concentrations
213 in the surface waters have a linear relationship ($\delta^7\text{Li} = 5.36 \times \text{Li} + 3.73$), with a correlation
214 coefficient $r^2 = 0.81$ ($n=6$). For groundwater, the lithium concentrations and $\delta^7\text{Li}$ were
215 published by Millot et al. (2007): Li concentrations ranged from $157 \mu\text{mol L}^{-1}$ (Ranc 1) to
216 $547 \mu\text{mol L}^{-1}$ (Mazel; their Table 3), which is one order of magnitude higher than in surface
217 water and consistent with their data for thermo-mineral waters in the Massif Central. Lithium-
218 isotope compositions ($\delta^7\text{Li}$) in these groundwaters were less variable (+2.6 to +5.0‰) than in
219 surface waters, with the lowest value observed in Ranc 2 (+2.6‰) and the highest in Mazel
220 (+5‰), a range of variation similar to that in thermo-mineral waters of the Massif Central ($\delta^7\text{Li}$
221 from +2.6 to +5.5‰, Millot et al., 2007).

222 **5 – Discussion**

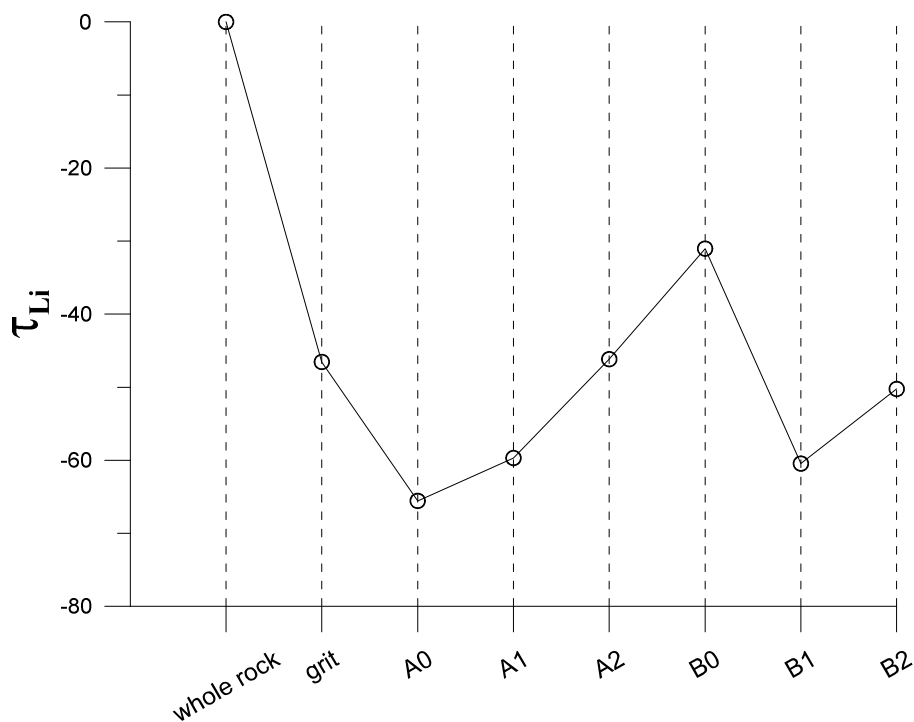
223 ***5.1. Mobility of Li during weathering***

224 In order to evaluate the extent of the chemical mobility of Li during granite weathering, we
225 calculated the weathering intensity with τ , the elemental mass transfer coefficient of Brimhall
226 and Dietrich (1987). This calculation avoids the dilution effect and impact of volume change
227 due to weathering (Nesbitt, 1979). We thus calculated the percentage change for Li relative to
228 the immobile element Ti (Clergue et al., 2015) with equation (1), previously used for other
229 elements in the same catchment (Négrel, 2006) and according to Nesbitt (1979):

$$230 \quad \tau_{\text{Li}} = 100 \times \left(\left[\frac{(\text{Li}/\text{Ti})_{\text{sample}}}{(\text{Li}/\text{Ti})_{\text{granite}}} \right] - 1 \right) \quad (\text{Equation 1})$$

231 Expressed as a percentage, $\tau = 0$ represents the initial unweathered material and $\tau = -$
232 100% means complete removal of Li from the parent material. A positive value reflects Li
233 enrichment by concentration in residual minerals and negative values represent Li depletion,
234 lost from bedrock because of its solubility. However, compared to other soluble elements, less

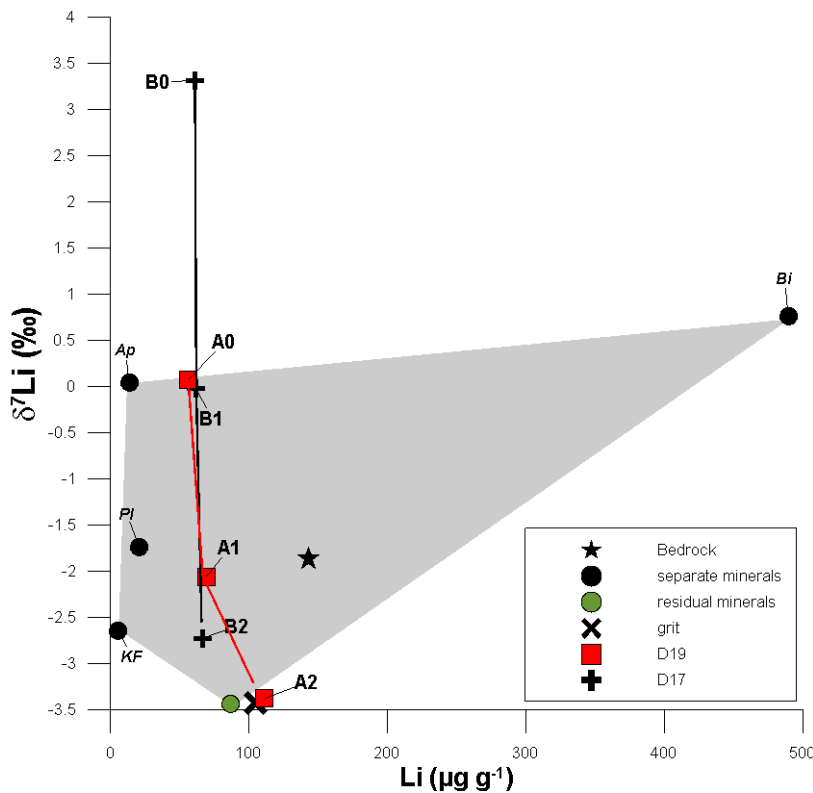
235 depletion of Li may be related to its incorporation into secondary minerals. The percentage
 236 change of Li in the samples, i.e. loss or gain of mobile Li relative to immobile Ti (τ_{Li} , Fig. 2),
 237 ranges from -31 to -66% , the extreme values being for surface-saprolite samples (A0, B0). The
 238 grit is depleted around -47% compared to bedrock, with a decrease of the δ^7Li value and a Li
 239 content from -1.9‰ and 143.1 $\mu g\ g^{-1}$ in granite to -3.4‰ and 104.7 $\mu g\ g^{-1}$ in grit (Fig. 3). The
 240 D19 samples show more Li depletion in surface saprolite (A0, -66%) than in riverbank sediment
 241 (A1, -60%) and soil (A2, -46%). This depletion is marked by a continuous decrease of δ^7Li
 242 values from +0.1‰ in surface saprolite to -3.4‰ in soil. Compared to the decrease in δ^7Li
 243 values, Li concentration remains constant between samples A0 and A1, and shows an increasing
 244 trend in soil sample A2 (Fig. 3), which has the same δ^7Li and Li-concentration values as those
 245 of the grit.



246
 247 *Figure 2. Percentage change of (mobile) Li relative to (immobile) Ti (Equation 1).*
 248

249 The mineralogical composition of the samples was earlier presented in Négrel (2006).
 250 Briefly, surface saprolite A0 is composed of quartz (35%), K-feldspar (~20%), plagioclase

251 (~20%) and illite-micas (~20%). At station D19, riverbank-sediment sample A1 is quite
 252 different, with more quartz (50%), less feldspars (5%) and illite-mica around 20%; it is also
 253 richer in chlorite (20%). Soil sample A2 contains the least quartz (15-20%); with K-feldspar,
 254 illite-micas and plagioclase all around 20%. This variation is accompanied by more negative
 255 $\delta^7\text{Li}$ values, meaning that Li is enriched in soil with a fractionation of Li isotopes and changes
 256 in the mineral abundance of the samples (residual minerals have negative $\delta^7\text{Li}$; Fig. 3). This is
 257 accompanied by a change in the Li concentration, with an 18% increase between A0 and A1,
 258 from 56 to 69 $\mu\text{g g}^{-1}$, and a 38% increase between A1 and A2, from 69 to 112 $\mu\text{g g}^{-1}$. Between
 259 saprolite and soil, the Li concentration increases by 50%.



260

261 *Figure 3. Relationship between $\delta^7\text{Li}$ values (‰) and Li contents ($\mu\text{g g}^{-1}$) for bedrock, grit,*
 262 *surface saprolite (A0, B0), riverbank sediments (A1, B1) and soil (A2, B2). The separate*
 263 *minerals from the granite define the greyed area with the addition of residual minerals.*

264

265 Contrary to station D19, the samples from station D17 show more erratic variations.

266 Surface saprolite B0, depleted around -31%, has a positive $\delta^7\text{Li}$ value of +3.3‰, clearly higher

267 than all mineral values in the granite. Sediment sample B1 is largely depleted (-60%) with a

268 $\delta^7\text{Li}$ value close to 0‰. Soil sample B2 is depleted around -50‰ with a more negative $\delta^7\text{Li}$
269 value of -2.7‰. Compared to the significant variation in $\delta^7\text{Li}$ values, the Li concentration
270 remains largely constant in the three samples with a total variation of around 8% (Fig. 3). Quartz
271 reaches 65% in surface saprolite sample B0, K-feldspar and illite-smectite having a similar
272 abundance (~20%), but plagioclase is only 5%. Riverbank sediment sample B1 contains around
273 25% quartz, and 20% K-feldspar, 20% plagioclase and 20% illite-mica, but only 5% chlorite
274 with 15% as an amorphous phase. Soil sample B2 contains the least quartz (15-20%), but K-
275 feldspar, illite-micas and plagioclase contents are still around 20%. Again, the $\delta^7\text{Li}$ values
276 become more negative from surface saprolite to soil, which can be explained by changes in
277 mineral abundance in the samples, as higher amounts of residual minerals in the soil sample
278 lead to more negative $\delta^7\text{Li}$ values.

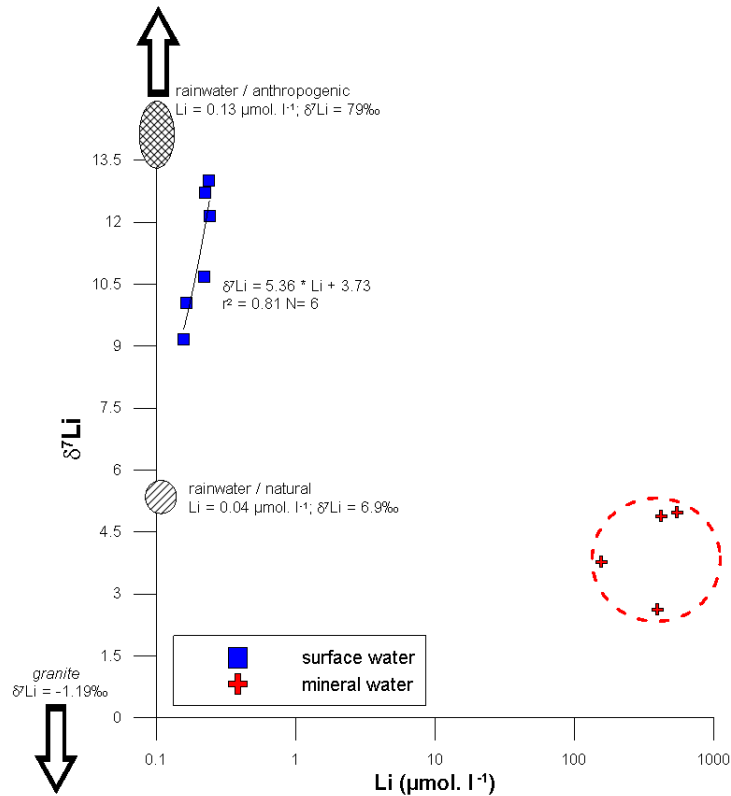
279 **5.2. Atmospheric input correction to surface and groundwater**

280 The need to quantify and subtract the portion of elements contributed by precipitation in the
281 chemical composition of surface- and ground-waters has been apparent for several decades
282 (e.g., Stallard and Edmond, 1981; Meybeck, 1983). Basically, quantifying the precipitation
283 input requires knowledge of its chemical composition (Négrel et al., 1993; Grobois et al., 2000).
284 The classic reference of atmospheric input in unpolluted hydrosystems is chloride, which
285 behaves conservatively throughout the hydrological cycle; the correction for its atmospheric
286 contribution is estimated by reference to the Cl concentration in river water, multiplied by the
287 ratio element/Cl of precipitation (e.g., Meybeck, 1983; Négrel et al., 1993). As stated by Négrel
288 (2006), in the absence of evaporites in the Margeride catchment, Cl ions in the river water can
289 be assumed to originate from wind-blown sea salt and human activity. High Cl contents can be
290 found in (thermo-mineral) groundwater emerging as naturally flowing springs, which are
291 closely related to fractures in the granite that cannot play any role in supplying Cl to the river
292 water. This would have been different in the case of an unexposed basement rock with a cover

293 of sedimentary rock, as described by Négrel et al. (1997). In our mass-balance approach,
294 determining input-output budgets for dissolved constituents in waters similar to Négrel's (2006)
295 work, we used the mean weighted rainfall on the Massif Central over 1.5 years for Cl content
296 (Négrel and Roy, 1998).

297 To determine the highest chloride concentration derived from precipitation input, the
298 standard method (Meybeck, 1983; Négrel et al., 1993) is to multiply the mean weighted Cl
299 value by a concentration factor F resulting from evapotranspiration. With a mean weighted
300 chloride of around $20 \mu\text{mol L}^{-1}$ and an F value of approximately 1.6, around $32 \mu\text{mol L}^{-1}$
301 represent the highest chloride concentration originating from atmospheric input to the river.
302 When the Cl content in water is below $32 \mu\text{mol L}^{-1}$ (Table 1), the entire chloride content of the
303 river is assigned an atmospheric origin; when it is over $32 \mu\text{mol L}^{-1}$, the residual chloride in the
304 river is attributed to human activity (Meybeck, 1983).

305 Using rainwater samples obtained during a rain-input survey over the Massif Central
306 (Négrel and Roy, 1998), Millot et al. (2010b) reported low lithium concentrations, between
307 0.004 and $0.292 \mu\text{mol L}^{-1}$, whereas the $\delta^7\text{Li}$ values varied greatly between $+3.2\text{‰}$ and $+95.6\text{‰}$
308 over the study period. From this observed range, two groups of rainwater with very different Li
309 characteristics were identified (Fig. 4). The first one, named "natural", had a Li concentration
310 of $0.04 \mu\text{mol L}^{-1}$ with a $\delta^7\text{Li}$ value of around $+6.9\text{‰}$; the second one, named "anthropogenic",
311 had a Li concentration of $0.13 \mu\text{mol L}^{-1}$ and a much higher $\delta^7\text{Li}$ value of around $+79\text{‰}$. For the
312 Li isotopes, considering natural and anthropogenic components, the average value over the
313 1.5 year survey was $+26.2\text{‰}$ and the mean concentration-weighted Li isotopes value was
314 $+20.3\text{‰}$ (Millot et al., 2010b). For correcting Li contents and Li isotopes of surface water from
315 rainfall data, we used the average Li content, $0.06 \mu\text{mol L}^{-1}$, and the average $\delta^7\text{Li}$, $+26.20\text{‰}$,
316 of all rainwater samples collected in the Massif Central over 1.5 years (Négrel and Roy, 1998;
317 Millot et al., 2010b; Fig. 4).



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Figure 4. Plot of $\delta^7\text{Li}$ versus Li concentration ($\mu\text{mol L}^{-1}$) for surface water, groundwater and rainwater.

Surface-water samples D8, D9', D9b, D10', D11 and D11' were investigated by Négrel (1999; 2006) for anion contents and now, in this study, for Li (Fig. 4). Applying the atmospheric correction to these surface-water samples showed that D9b and D8 derived their total Cl content from precipitation input and thus reflect no anthropogenic influence, with 35% and 61% of the Li deriving from atmospheric input, respectively. This shows a non-negligible influence of precipitation input on the Li budget in this case, contrary to other observations at very different scales by Ryu et al. (2014) in Hawaii, or by Millot et al. (2010) in the Mackenzie Basin of northern Canada.

Other samples have a residual Cl content that is generally related to anthropogenic input, mainly from agricultural activity. Here, the Li derived from atmospheric input ranged from 40% in sample D11 to 43% in samples D9 and D10. Accordingly, as done by Négrel (1999 and 2006) for the same catchment, we corrected the Li-isotope values observed in the water for

335 atmospheric contribution, which gave a $\delta^7\text{Li}$ ranging from +10.8 (D11') to -2.0‰ (D8). The
336 $\delta^7\text{Li}$ for samples without residual Cl are the lowest, with a $\delta^7\text{Li}$ of -2.0‰ for sample D8 and
337 +0.8‰ for sample D9b. A similar atmospheric correction to mineralized waters has a low
338 impact on Li content (less than 0.06% of the Li being from precipitation input) with no change
339 in the $\delta^7\text{Li}$ value, indicating the dominant influence of water/rock interaction on both Li content
340 and $\delta^7\text{Li}$ value of the mineralized waters.

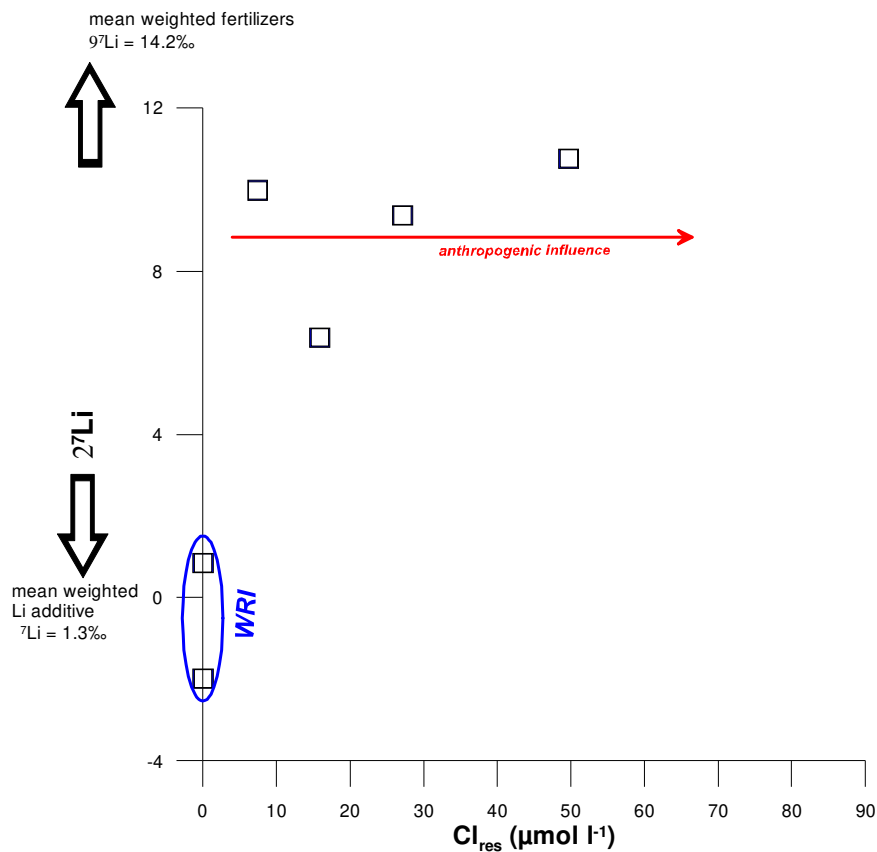
341 However, contrary to previous work on atmospheric and anthropogenic corrections to
342 surface-water chemistry (Négrel, 1999; 2006; Petelet-Giraud et al., 2003), we cannot use the
343 same method for anthropogenic-input correction here. The residual Cl after atmospheric
344 correction derives from anthropogenic input and the correction for such input (e.g. to a zero Cl
345 content) requires knowledge of its Li/Cl ratio. However, this ratio cannot be constrained
346 accurately, which would allow a robust correction for Li content and thus for Li isotopes.

347 Applying the atmospheric correction to the D8, D9, D10 and D11 surface water samples
348 (Négrel, 2006), shows that D8 and D9 derived their total Cl content from atmospheric input,
349 and thus reflect no anthropogenic influence. The Sr content derived from atmospheric input is
350 around 50% in D9 and 57% in D8. The influence of atmospheric input on $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is
351 consistently significant (Négrel, 2006), and, corrected for atmospheric input, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios
352 for water–granite interaction range from 0.72316 (D8) to 0.72511 (D9). Once corrected for
353 atmospheric input, the $\delta^7\text{Li}$ value and Cl concentration are controlled by water–granite
354 interaction and anthropogenic input(s). This is summarized in Fig. 5, where $\delta^7\text{Li}$ is plotted
355 *versus* residual Cl. The two samples with no residual Cl directly yield the value of the $\delta^7\text{Li}$
356 derived from water-rock interaction, with $\delta^7\text{Li}$ values of +0.8‰ (D9) and -2.0‰ (D8)
357 associated with Li concentrations of 0.11 and 0.06 $\mu\text{mol L}^{-1}$, respectively. The other samples
358 have residual Cl values from 7.4 (D10) to 49.7 $\mu\text{mol L}^{-1}$ (D11), $\delta^7\text{Li}$ value from +6.4‰ (D9)
359 to +10.8‰ (D11) and nearly constant Li concentrations of 0.13 to 0.15 $\mu\text{mol L}^{-1}$. This can be

360 related to an increase of the anthropogenic input, with a roughly constant $\delta^7\text{Li}$.

361 Regarding the anthropogenic Li sources, Négrel, et al. (2010) gave a range for the $\delta^7\text{Li}$
362 in fertilizers, such as carbonaceous amendment or NPK, between +2.1‰ and +215‰ and a
363 mean weighted $\delta^7\text{Li}$ value of +14.2‰. For Li used with other trace elements, such as Cu, Fe,
364 Mn, Zn, Co, Mo and B, even though not necessary as an additional nutrient (Négrel et al.,
365 2010a), the $\delta^7\text{Li}$ ranged between -16‰ and + 31‰ with a mean weighted $\delta^7\text{Li}$ value of +1.3‰.
366 These two mean values agree with the range observed in surface waters and thus can explain
367 an anthropogenic input from agricultural activities.

368



369
370 *Figure 5. Plot of $\delta^7\text{Li}$ versus the residual Cl concentration ($\mu\text{mol L}^{-1}$) for surface water, once*
371 *corrected from precipitation input (see text). The mean weighted $\delta^7\text{Li}$ values for the fertilizers*
372 *and Li additives used in agricultural practices are indicated.*
373

374 **5.3 The weathering model for Li**

375

376 **5.3.1 The simple dissolution model**

377 Négrel et al. (2001) developed a weathering model based on dissolution, giving the theoretical
378 (th) isotopic signature (i) of a chemical element (Z) in water being in equilibrium with granite
379 (iZ_{th}), which was initially developed for and applied to strontium. This model considers the
380 congruent dissolution of Sr-bearing phases (mx), their abundance ($\%_{mx}$), isotope ratio (iZ_{mx})
381 and element concentration (Z_{mx}). Each mineral characteristic considered (iZ_{mx} and Z_{mx}) is
382 weighted by the weatherability (W_{mx}) of each (Négrel et al., 2001), summarized in equation 2:

383
$$iZ_{th} = \frac{\sum (iZ_{mx} \times Z_{mx} \times \%_{mx} \times W_{mx})}{\sum (Z_{mx} \times \%_{mx} \times W_{mx})} \quad (\text{Equation 2})$$

384 The theoretical isotopic composition (iZ_{th}) of water in equilibrium with granite was then
385 used for Sr in several environments (Négrel et al., 2001; Petelet-Giraud et al., 2003; Négrel,
386 2006), before being redefined and applied to Nd and Pb in the present watershed (Négrel, 2006;
387 Négrel et al., 2010b). The initial model was based on the hypothesis that the dissolution of
388 plagioclase, K-feldspar and biotite contributes most elemental Sr. The same set of minerals,
389 plus apatite for Nd, and apatite and allanite for Pb, were then considered (Négrel, 2006; Négrel
390 et al., 2010b). For lead-isotope compositions during granite dissolution, we used the concept of
391 Harlavan and Erel (2002) that highlights the role of accessory phases and primary minerals in
392 controlling the isotope composition during water-rock interaction; for the accessory phases, it
393 was suggested that apatite played a major role. Our model thus assumes that only the fluid
394 concentration changes, the isotopic ratio remaining constant, because the secondary minerals
395 are in equilibrium with the parent solution for Sr, Nd and Pb. The relative mineral
396 weatherability W_{mx} , considering that of plagioclase as 1, is 0.25 for biotite and 0.1 for K-
397 feldspar (Négrel et al., 2001). A sensitivity analysis of the model (Petelet-Giraud et al., 2003b;
398 Négrel, 2006), based on testing various mineral-weatherability values from the literature (Blum

399 et al., 1994; Zuddas et al., 1995), consistently showed only minor differences in the isotope
400 values. The model was verified for Sr by comparing the iSr_{th} calculation for given conditions
401 of Sr abundance and the isotopic characteristics of separate minerals, with the $^{87}Sr/^{86}Sr$ ratio of
402 water that has interacted with several granitoids and basalts in France (Petelet-Giraud et al.,
403 2003; Négrel, 2006).

404 For this study, the model was adapted for lithium and applied to the Margeride granite,
405 using data from Table 1. In view of the composition of this granite, we considered K-feldspar,
406 plagioclase and biotite as primary minerals, and apatite as an accessory phase in the model of
407 eq. 2. This was also based on interaction experiments by Millot and Négrel (2013) between a
408 rainwater reference solution (TMRAIN-95) and 1.5 g of powdered granite sample from India
409 at 25 °C (Négrel et al., 2010b). Millot and Négrel (2013) monitored Pb- and Li-isotopic
410 compositions over 12 months of interaction, showing that:

- 411 i) When using Pb isotopes, there is a major contribution of K-feldspar and plagioclase
412 dissolution, and, to a lesser extent, of biotite and apatite dissolution;
- 413 ii) When using Li isotopes, the light lithium isotope (6Li) is preferentially retained during
414 uptake of Li into secondary minerals during weathering.

415 The theoretical δ^7Li signature for water draining this granite is close to -3.3‰. The
416 difference in the isotopic values is always less than 0.1 for Li during sensitivity analysis of the
417 model, done by testing various mineral-weatherability values similar to the Sr, Nd and Pb
418 models (Petelet-Giraud et al., 2003; Négrel, 2006; Négrel et al., 2010b). Our model only
419 provides information on the isotopic value of water after interaction with minerals; it does not
420 assume that the main process associated with isotope fractionation is the formation of secondary
421 precipitates, such as clays, even though the evolution of Li-isotope values is controlled by the
422 precipitation of secondary minerals, as was shown in other environments (Huh et al., 2001;
423 Pistiner and Henderson, 2003; Vigier et al., 2008; Millot et al., 2010).

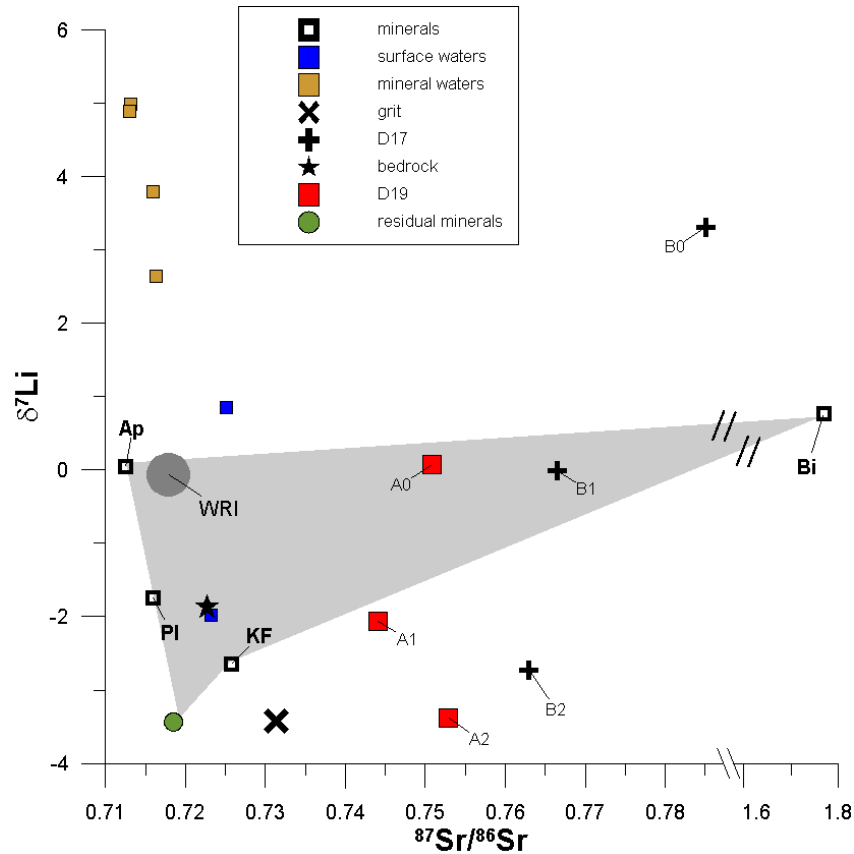
424

425 ***5.3.2. A broader weathering frame using Li and Sr isotopes: Implications for water/rock***
426 ***interaction in the critical zone***

427 Figure 6 is a plot of the $\delta^7\text{Li}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ values, where the results from primary minerals and
428 accessory phases of the granites, the whole rock, the soil and sediment samples, and the mineral-
429 water and surface-water samples, are plotted with the results of the weathering-model
430 computation for the granite. The Sr-isotope systematics for primary minerals and accessory
431 phases of the granites, whole rock, soil and sediment samples, and mineral-water data are from
432 Négrel (2006), and those for surface-water samples are from Négrel (1999).

433 Figure 6 shows several features: 1) For surface waters, the $\delta^7\text{Li}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values
434 disagree with the weathering model, even if Li is not corrected for atmospheric input, the $\delta^7\text{Li}$
435 being either lower or higher than the model value. 2) For thermo-mineral spring waters, there
436 is again no agreement with the results of the weathering model, all springs having a higher $\delta^7\text{Li}$
437 than the weathering model, and a larger influence caused by an increase in weathering of one
438 or more minerals cannot explain the values observed for $\delta^7\text{Li}$ values in the mineralized waters,
439 no minerals in the Margeride granite having such a high $\delta^7\text{Li}$ value. This is particularly true for
440 the residual trace minerals that cannot control the $\delta^7\text{Li}$ values of the water (Figs. 3 and 6). For
441 thermo-mineral spring waters, the $\delta^7\text{Li}$ values thus suggest that other processes lead to the
442 observed signatures because the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio agrees with the results of the weathering model.
443 3) For the residual solids, the $^{87}\text{Sr}/^{86}\text{Sr}$ difference between whole rock (0.72269) and Mazel grit
444 (0.73134) reflects the weathering of low $^{87}\text{Sr}/^{86}\text{Sr}$ - and Rb/Sr-bearing minerals, such as
445 plagioclase and K-feldspar; this is confirmed by the grit mineralogy (~20% of each in this
446 sample; Négrel, 2006), whereas the Mazel grit shows a depleted $\delta^7\text{Li}$ compared to the whole
447 rock. 4) Riverbank sediment A1 at site D19 shows an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.74408 and a $\delta^7\text{Li}$ of
448 0.1‰, both higher than that of the grit. An increase in the Sr-isotope ratio is noted in the

449 sediment from surface saprolite A0 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.75085$) down to soil A2 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.75290$),
 450 accompanied by a large decrease in $\delta^7\text{Li}$ (from +0.1 to -3.4‰). In site D17, soil B2 has the
 451 lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.76296) and $\delta^7\text{Li}$ (-2.7‰), and, as for site D19, the $^{87}\text{Sr}/^{86}\text{Sr}$ (0.76649)
 452 in sediment B1 collected on the river bank increases to 0.78508 in surface saprolite B0,
 453 accompanied by a large increase in the $\delta^7\text{Li}$ (from 0 to +3.3‰).



454

455 *Figure 6. Relationship between the $\delta^7\text{Li}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ for Margeride granite, separate*
 456 *minerals and Mazel grit sample, and surface and mineralized spring waters. $\delta^7\text{Li}$ and $^{87}\text{Sr}/^{86}\text{Sr}$*
 457 *of the remaining trace minerals (titanite, rutile, epidote, zircon) are indicated in the graph (see*
 458 *text). The result of the weathering model is indicated by the grey circle (see text). The separate*
 459 *minerals from the granite define the greyed area with the addition of residual minerals.*

460

461 **5.3.3 Modelling Li isotopic fractionation using a Rayleigh equation: the role of secondary**
 462 **phase precipitation**

463 Here, we apply the batch fractionation model for Li isotopes as developed by Bouchez et al.
 464 (2013) and used by Clergue et al. (2015). This model is based on the non-congruent dissolution
 465 of bedrock leading to a $\delta^7\text{Li}$ in solution ($\delta^7\text{Li}_{\text{solution}}$). As a first approach, this model is only

466 based on (non congruent) dissolution/precipitation reactions. The main process occurring in this
 467 solution is Li-isotope fractionation through the formation of secondary phases that
 468 preferentially incorporate light lithium (⁶Li). This gives a residual solution with a $\delta^7\text{Li}_{\text{diss}}$ and a
 469 $\delta^7\text{Li}_{\text{sec}}$ for the secondary phases. The $\delta^7\text{Li}_{\text{sec}}$ can be expressed as follows:

$$\delta^7\text{Li}_{\text{sec}} = \frac{\alpha \times \delta^7\text{Li}_{\text{rock}} + 1000 f_{\text{Li}} (\alpha - 1)}{\alpha (1 - f_{\text{Li}}) + f_{\text{Li}}} \quad (\text{Equation 3})$$

471 The key parameters are the isotope fractionation factor $\delta^7\text{Li}_{\text{sec}}$ between the different
 472 secondary minerals, and the solution ($\delta^7\text{Li}_{\text{solution}}$) and proportion ($1-f_{\text{Li}}$) of Li in secondary
 473 phases. The f_{Li} can be expressed by the elemental mass transfer coefficient τ calculated with
 474 equation (1), which represents the evolution of the Li/Ti ratio in sediment compared to that of
 475 bedrock.

476 The isotope fractionation factor is calculated from chemical and isotope data measured
 477 on field material; this can be applied to samples from soil, rivers and the sedimentary record,
 478 and does not require prior knowledge of the isotope fractionation factors involved in the detailed
 479 reactions. Weathering products are modelled here with a fractionation factor $\alpha_{\text{sec-dis}}$ ranging
 480 from 0.975 to 0.998, consistent with the range of α values used in the literature (Rudnick et al.,
 481 2004; Clergue et al., 2015). To summarize, the α values in the literature span a range from 0.970
 482 to 1.000 and derive either from laboratory experiments (0.979-0.984, Millot et al., 2010c; Vigier
 483 et al., 2008), or from field data (0.982-0.989, Millot et al., 2010a, 2010c; Tipper et al., 2012;
 484 Dellinger et al., 2013; 2014; 2015).

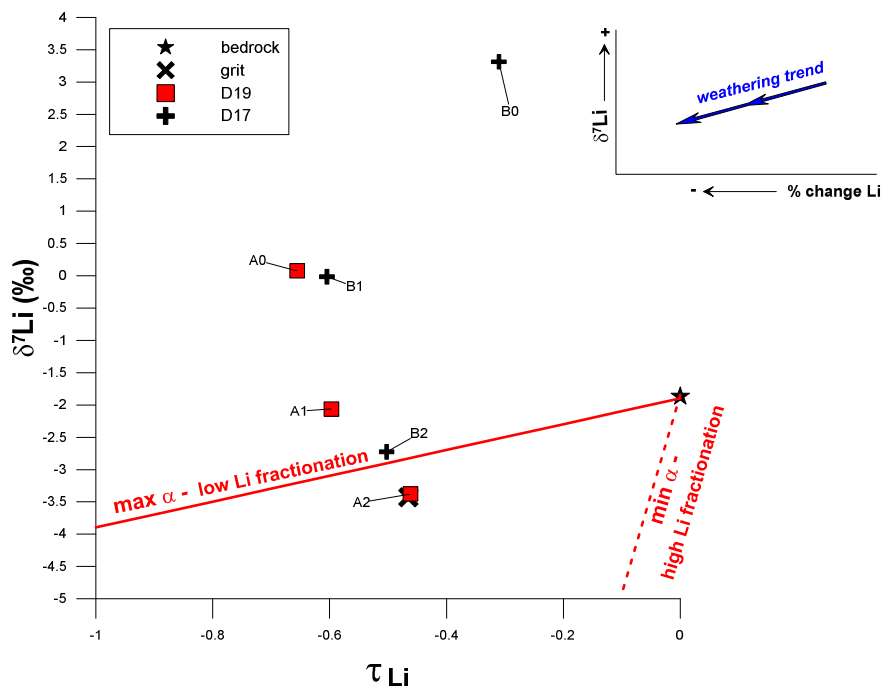
485 We found that the fractionation factor $\alpha_{\text{sec-dis}}$ on Figure 7 can explain some, but not all,
 486 weathering products; the lowest $\delta^7\text{Li}$ observed in the samples fit with the α max (0.998), but
 487 no point is explained by the α min (0.975). Thus, we cannot fit the required fractionation factor

488 $\alpha_{\text{sec-dis}}$ to the soil and sediment data (Fig. 7). Additional processes or inputs should thus be
489 considered and investigated.

490 Facing a broader range of isotopic fractionation for the precipitation of secondary phases
491 than the one defined from experimental clay precipitation, Lemarchand et al. (2010) argued for
492 the precipitation of another possible phase with a higher isotope fractionation. As far as we
493 know, no studies have been carried out on such phases, but oxides could be a good candidate
494 for the fractionation of Li isotopes and can account for the existence of high $\delta^7\text{Li}$ values in
495 weathering products. This argument was already proposed by Millot et al. (2010a) to explain
496 incipient weathering effects on Li isotopes in the Canadian Rocky Mountains. Concerning our
497 samples, only B1 and B2 have an amorphous phase identified by X-ray diffraction (15 and 5%,
498 respectively; Négrel, 2006), agreeing with a $\delta^7\text{Li}$ shift away from the α max line, but only for
499 B1, as sample B2 plots close to the α max line. Conversely, no amorphous phase was identified
500 in samples A0, A1 and B0, though the $\delta^7\text{Li}$ is shifted from the α max line. Thus, the
501 precipitation of secondary clay minerals is not enough to explain the $\delta^7\text{Li}$ shift and the role of
502 other phase-like oxides must be considered.

503 Fe–Mn oxides, one of the main oxides in the non-residue part of soils and river
504 sediments, have an exceptional tendency (particularly Mn oxides) for scavenging trace
505 elements (Cu, Zn, Ni, Pb, etc.; Carpenter et al., 1975), Li not being investigated to our
506 knowledge. One of the few studies describing Li-isotope values in Fe–Mn oxides is that of You
507 and Chan (1996), giving $\delta^7\text{Li}$ values between +22.9 and +33.4‰ for hydrothermal
508 ferromanganese crusts, such values being controlled by post-depositional exchange with
509 seawater. To overcome this lack, we can use data from the labile fraction extracted from soils
510 and river sediments in the same catchment (Négrel and Roy, 2002; Négrel and Petelet-Giraud,
511 2012). These were obtained by leaching with cold and dilute acid, which releases the total
512 inventory of non-residual trace elements, particularly those associated with hydrous Fe–Mn

513 oxides adsorbed on clays, and occurring in carbonates and sulphides in the sediment load, as
 514 well as in natural organic matter. The content of the labile sample fractions from this study is
 515 consistently low, with similar ranges in soil and sediment (0.8–10.1% of total matter content;
 516 mean 6.4%). The Mn contents of this labile fraction range between 50 and 30,000 $\mu\text{g/g}$ (mean
 517 $\pm 6,000 \mu\text{g/g}$). In addition, strong Li-Fe and Li-Mn correlations exist in agricultural soil at a
 518 European scale (GEMAS Project; Négrel et al., 2018). This is strongly related to precipitation of
 519 Fe-Mn oxide/hydroxide coatings, which provides a control over the lithium content within such
 520 phases that encourages investigating the labile fractions in soil and sediment for Li isotopes to
 521 evaluate Li isotope fractionation during the formation of Fe-Mn oxides.



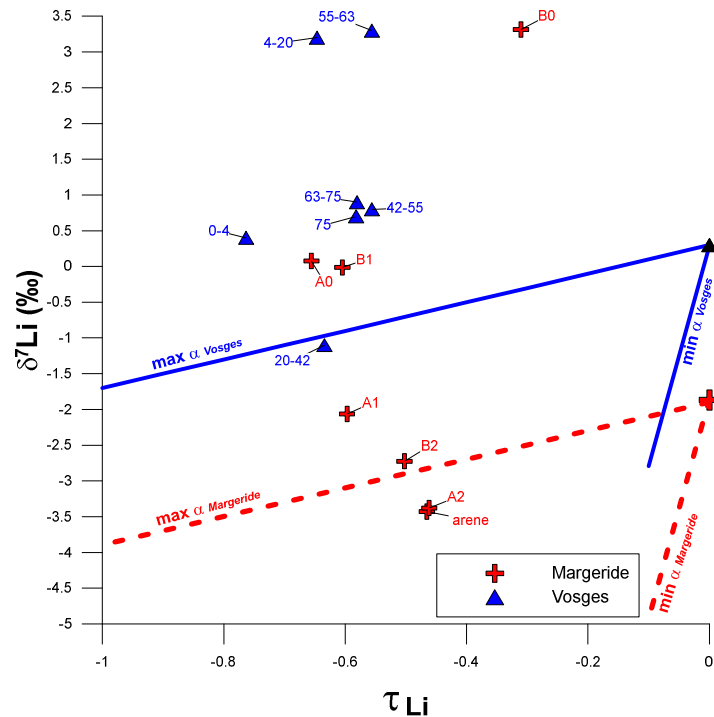
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523 *Figure 7. Li isotopic composition of surface saprolite (A0, B0), riverbank sediments (A1, B1)*
 524 *and soil samples (A2, B2) as a function of τ_{Li} (Equation 1). Straight lines represent the*
 525 *evolution of $\delta^7\text{Li}$ vs. τ_{Li} given by the batch equilibrium model according to Equation 3.*
 526

527

The Margeride data can be compared with other granite areas, but studies on granite and
 528 associated weathering products are relatively rare (Rudnick et al., 2004; Lemarchand et al.,
 529 2010), only the latter concerning the same type of granite as the Margeride. It presents analyses
 530 of Li concentrations and isotopic compositions in rock, soil, vegetation, soil water, rainfall,
 531 springs and stream water of the Strengbach catchment. This forested catchment in the Vosges

532 Mountains (NE France) has been intensively studied and monitored for decades by the
 533 University of Strasbourg. The bedrock is a leucogranite affected by hydrothermal alteration,
 534 the weathering products being saprolite (≤ 10 m thick) and soil overlying the saprolite (± 80 cm
 535 thick). Fractionation factors $\alpha_{\text{sec-dis}}$ are illustrated on Figure 8 for the Strengbach catchment with
 536 the Margeride data (Fig. 7).



537
 538
 539 *Figure 8. Comparison of Li isotopic composition of soil samples as a function of τLi for the*
 540 *Margeride catchment (this study, Fig. 7) and the Strengbach granitic catchment (Vosges*
 541 *Mountains, France; Lemarchand et al., 2010). For the latter, the numbering indicates the depth*
 542 *interval considered in the profile.*

543
 544 Again, the fractionation factor does not explain most Strengbach data. Only one
 545 weathering product can be explained considering the α max of 0.998 (low Li-isotopic
 546 fractionation) and no points are explained by the α min of 0.975 (high fractionation).
 547 Lemarchand et al. (2010) argued that soil is a strongly reactive compartment for Li isotopes,
 548 and that another phase inducing Li-isotope fractionation must be suspected. Identifying the
 549 origin of this fractionation will require more studies at catchment scale for understanding the
 550 processes at the biosphere interface. Anderson et al. (1988) demonstrated that exchangeable Li

551 is an insignificant part of the total Li present in soil, and Reimann et al. (2014a; b) showed a
552 weak affinity of Li for phases like clay and organic matter using Mobile Metal Ion (MMI®)
553 extraction. Combining sequential extraction with Li isotope measurements can help explore
554 how Li is bounded to the different mineral phases and identify the phases that cause the
555 fractionation in soil and sediment.

556 **6 – Conclusions**

557 We carried out a systematic study of lithium-isotope compositions of surface- and ground-
558 waters, and soil and sediment samples collected from a granite catchment in the French Massif
559 Central. This work incorporates many novel aspects, being an integrated investigation of
560 weathering processes by means of lithium isotopes.

561 In water, the lithium isotope composition ($\delta^7\text{Li}$) of a dissolved load is generally higher
562 than corresponding $\delta^7\text{Li}$ values for groundwater, bedrock and sediment. It has been suggested
563 that Li-isotope fractionation in the dissolved load records silicate weathering intensity, as well
564 as fluid-residence time, or exchange processes between water and sediment. In soil and
565 sediment, Li is enriched through fractionation into the lithium-6 and -7 isotopes, leading to less
566 negative $\delta^7\text{Li}$ values and to changes in mineral abundance in the samples.

567 A model for determining the $\delta^7\text{Li}$ of water after interaction with granite was applied,
568 based on the assumption that Li derives from plagioclase, K-feldspar, apatite and biotite. The
569 model calculations showed a relative agreement between the Li isotope composition predicted
570 by the weathering model and that observed in water.

571 The fractionation process during granite weathering was investigated through non-
572 congruent dissolution of the bedrock, leading to a $\delta^7\text{Li}$ in solution. The main process caused by
573 this solution is the fractionation of Li isotopes through the formation of secondary phases that
574 preferentially incorporate light lithium (^6Li). This gives a residual solution with a specific $\delta^7\text{Li}$
575 and another $\delta^7\text{Li}$ value for the secondary phases.

576 We modelled weathering products with a fractionation factor that is consistent with the
577 range of values found in the literature. Our results show that some, but not all, weathering
578 products can be explained by such fractionation. Additional processes or inputs must therefore
579 be investigated, such as the precipitation of another phase with a higher isotope fractionation
580 rate, for which Fe-Mn oxides are a good candidate. Data from the Margeride were compared
581 with those from the Strengbach granite catchment in the Vosges Mountains (NE France); again,
582 the fractionation factor did not explain most Strengbach data and, here too, the role of another
583 phase was suspected.

584 We highlighted the possible role of Li isotopes as tracers of water-rock interaction in a
585 granite catchment. When evaluating regolith (soil and sediment) formation, any additional
586 tracers to the basic ones (major- and trace elements, and Sr isotopes) are important for
587 constraining the whole weathering system.

588 A remaining problem to be solved concerns the distinction between primary effects
589 related to source/origin, and the effects of secondary processes (alteration, dissolution,
590 precipitation) that can modify the isotopic signature, and are key reactions for fractionating Li
591 isotopes. Another approach to understanding and interpreting the isotopic signatures will
592 require Reactive Transport Model (RTM) computer simulations, to arrive at simultaneous
593 solution of the governing equations for solute and geochemical transformations.

594

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605

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818

Sample	Ref.	Li $\mu\text{g g}^{-1}$	$\delta^7\text{Li}$
M1/POU	Whole rock	143.1	-1.9
ALT1	Mazel grit	104.7	-3.4
Ap	Apatite	13.3	0.0
Pl	Plagioclase	20.9	-1.7
Bi	Biotite	489.1	0.8
KF	K-Feldspar	5.3	-2.6
D19-3/A0	A0	56.2	0.1
D19-3/A1	A1	68.8	-2.1
D19-3/A2	A2	110.9	-3.4
D17-3/B0	B0	60.6	3.3
D17-3/B1	B1	61.6	0.0
D17-3/B2	B2	66.2	-2.7

Sample	Li $\mu\text{mol L}^{-1}$	$\delta^7\text{Li}$
<i>Spring waters</i>		
Mazel	551	5.0
FB1	424	4.9
Ranc1	158	3.8
Ranc2	397	2.6
<i>Surface waters</i>		
D10'	0.22	12.7
D8	0.15	9.2
D11	0.23	12.1
D9bis	0.16	10.0
D9'	0.21	10.7
D11'	0.24	13.0