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

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Abstract

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

Keywords: weathering, isotopes, lithium, groundwater, soil, sediment, granite

1 – Introduction

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

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

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

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

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

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

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

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

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

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

2 - General setting

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

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

3 – Material and methods

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

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

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

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

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

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

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

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

4 – Results

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

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		Spring waters			
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					
KF	K-Feldspar	5.3	-2.6		Surface waters			
					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					

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

For the separate minerals, Li-rich phases decreased in content from biotite (489 $\mu\text{g g}^{-1}$) 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 isotopic compositions in the separate minerals ranged from -2.6‰ in K-feldspar to 0.0‰ in apatite, for a $\delta^7\text{Li}$ of -1.9‰ in bulk rock. Reconstituting the whole rock from the separate 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 with the measured ones, implying that the rest of the Li probably occurs in residual minerals 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 sediment fluctuated from 56 $\mu\text{g g}^{-1}$ (surface saprolite A0) to 111 $\mu\text{g g}^{-1}$ (soil A2). With the exception of soil A2 (almost twice the content in soil B2), the samples had similar Li contents (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 sediment samples ranged from -3.38‰ (soil A2) to 3.31‰ (surface saprolite B0).

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‰, which is lower than that in other water samples from the Massif Central (Négrel et

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

5 – Discussion

5.1. Mobility of Li during weathering

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

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

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

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

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

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

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

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

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

Surface saprolite B0, depleted around -31%, has a positive $\delta^7\text{Li}$ value of +3.3‰, clearly higher than all mineral values in the granite. Sediment sample B1 is largely depleted (-60%) with a

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

5.2. Atmospheric input correction to surface and groundwater

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

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

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

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

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

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

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

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

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

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

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

5.3 The weathering model for Li

5.3.1 The simple dissolution model

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

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

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

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

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

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

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

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

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 accessory phases of the granites, the whole rock, the soil and sediment samples, and the mineral-water and surface-water samples, are plotted with the results of the weathering-model computation for the granite. The Sr-isotope systematics for primary minerals and accessory phases of the granites, whole rock, soil and sediment samples, and mineral-water data are from Négrel (2006), and those for surface-water samples are from Négrel (1999).

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

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

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

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

Here, we apply the batch fractionation model for Li isotopes as developed by Bouchez et al. (2013) and used by Clergue et al. (2015). This model is based on the non-congruent dissolution 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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

6 – Conclusions

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

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

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

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

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

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

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

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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