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The influence of hydrothermal activity on the Li isotopic signature of rivers draining volcanic areas

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Abstract

We explore the geochemistry and the isotopic composition of lithium ($\delta^7\text{Li}$) of rivers draining volcanic islands (Guadeloupe, Iceland, Java, Martinique and Sao Miguel) with a specific focus on continental hydrothermal activity. Our preliminary results reveal a global-scale trend between $\delta^7\text{Li}$ and the elemental ratio Li/Na in rivers draining volcanic islands. We suggest that this trend results from a mixture between waters with low $\delta^7\text{Li}$ and high Li/Na, inherited from high-temperature water rock interactions, and waters with low Li/Na and high $\delta^7\text{Li}$, in which Li is controlled by the neoformation of clays during low-temperature chemical weathering in basaltic soils. This latter process can be described by a simple isotope fractionation model, consistent with reported values for isotopic fractionation factors between secondary weathering products and water. These data highlight the important potential role of continental high-temperature weathering processes on the oceanic budget of lithium.

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1. Introduction

The chemical weathering of continental silicate rocks is a major geological process shaping the surface of our planet and playing a crucial role in the long-term evolution of the Earth's climate through the consumption of atmospheric carbon dioxide. Many studies in recent years (see [1] for a review) have shown that lithium (Li) is a

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promising tracer of silicate weathering because: (i) Li is mainly found in silicate minerals and is virtually not affected by biological processes; (ii) Li is a soluble element (an alkali) during water-rock interactions; (iii) the residence time of Li in the oceans is around 3 Myr, higher than the characteristic mixing time of the global ocean (around 1000 years). Consequently, the secular evolution of Li in seawater could be used to constrain global changes in weathering; (iv) Li has two stable isotopes: ^7Li (92.48% of natural Li) and ^6Li (7.52%) reported to be highly fractionated during chemical erosion; as ^6Li is preferentially incorporated into secondary weathering products, the dissolved phase is consequently enriched in ^7Li (e.g. [7], [8]); (v) Li is a light element with a large relative mass difference (around 16%) between its two stable isotopes, making the Li isotopic composition (expressed in per mil deviation from a standard (L-SVEC) as $\delta^7\text{Li} = ((^7\text{Li}/^6\text{Li}) / (^7\text{Li}/^6\text{Li})_{\text{L-SVEC}} - 1) \times 1000$) of natural materials span a very large range. The $\delta^7\text{Li}$ of the riverine dissolved phase is therefore a potential tracer of silicate weathering (e.g. [8], [18], [22]).

Over the Cenozoic, Li and Elderfield (2013) [11] suggested that the relative contribution of felsic rock weathering increased at the cost of volcanic rock weathering. This might have had a major impact on the Li isotope composition of seawater [12]. Even today, chemical weathering of volcanic rocks covering only 5% of the continental area is responsible for 30% of the modern-day global consumption of atmospheric carbon dioxide ([6], [4]), due to their fast dissolution rate. This impact is explained by their petrological characteristics, important orographic precipitations in oceanic islands and by the role of hydrothermal activity which acts as a catalyzer of water-rock interaction by increasing temperature and acidity. However, we still know little about the global Li flux and isotope composition delivered by volcanic areas to the oceans. We also lack insight into the processes controlling the dissolved Li isotope composition of rivers draining volcanic areas at the global scale. To address this issue, here we examine the dissolved geochemistry and Li isotope composition of rivers draining volcanic rocks at the global scale, with a specific focus on the continental contribution of hydrothermal activity.

2. Methodology

2.1. River database

We have measured dissolved $\delta^7\text{Li}$ (Table 1) in rivers draining the islands of Java in Indonesia [14], Réunion [15] and Sao Miguel [16]. The other data were collected from the literature: Sao Miguel in the Azores Archipelago [20], Iceland [19] and [22], Martinique [21], thermal springs from Guadeloupe [17] and Martinique [21].

2.2. Analysis

Concentrations of Na and Li were measured by HPLC Dionex 300, with precision better than 5% ([14], [15] and [16]).

For the lithium isotope measurement, 10 ng to 20 ng of Li (depending on the concentration of Li) were separated from the river water samples by ion-exchange chromatography using resin Bio-Rad AG50-X12 [9]. The volume of the resin was 2.7 mL and Li was eluted in HCl 0.2 N. The elution fraction containing Li was evaporated at a temperature of about 90°C and Li was kept as a salt until the measurement session. Lithium isotope ratios ($^7\text{Li}/^6\text{Li}$) were measured on a MC-ICP-MS (Neptune, Thermo Scientific) at IPGP. The ratios were normalized to the L-SVEC standard [5] using the standard-sample bracketing method. The accuracy of the Li chemical purification procedure was systematically checked using standard materials (seawater NASS 5). The long-term average of $\delta^7\text{Li}$ of these standards leads to an analytical precision of $\pm 0.5\text{‰}$ (2σ).

Table 1. Chemical composition and $\delta^7\text{Li}$ of Sao Miguel, Java, Reunion rivers water samples analyzed for this study

Location		Na	Li	$\delta^7\text{Li}$	2σ
		μM	nM	‰	‰
Sao Miguel					
SM4	R. Grande	2840	9960	5.7	0.5
SM6	Cald. Furnas (thermal spring)	2600	2800	1.2	0.5
Java					
DJava 5	K Ngledole	244	15	27.7	1.1
DJava 9	K Madium	1158	79	40	0.6
DJava 10	Mont Lawu	322	172	19.8	0.5
DJava 13	Solo (Babat)	504	78	45.1	0.5
DJava 15	affl Pabelan	182	48	21.7	0.5
DJava 16	affl Solo (Teras)	399	63	27.2	0.5
DJava 20	Serayu	248	9	42.5	0.5
DJava 21	Manuk	491	38	38	0.5
Reunion					
<i>Main streams (Feb. 95 samples)</i>					
95-DR1	Rivières Langevin	425	32	27.9	0.5
95-DR3	Rivière de l'Est @ outlet	239	9	29.8	0.5
95-DR4	Rivières des Marsouins	241	38	20.8	0.5
<i>Cirque de Salazie</i>					
95-DR5	Rivière des Fleurs Jaunes	936	143	16.1	0.5
95-DR6	Rivière du Mat @ l'Escalier	637	108	19.8	0.5
<i>Cirque de Cilaos</i>					
95-DR7	Bras de Cilaos	1939	237	14.8	0.6
95-DR8	Bras Rouge	1597	426	19.2	0.5
95-DR9	Bras Benjouin	1358	44	27.7	0.5
95-DR10	Rivière St Etienne	357	9	27.2	0.5
<i>Cirque de Mafate</i>					
95-DR11	Rivière des Galets @barrage	919	20	26.8	0.5
95-DR13	Rivière des Galets @Lebot	916	17	24.7	0.5

3. Results

Li isotopic compositions of the volcanic island waters are given in Table 1 and represented in Fig. 1 as a function of their Li/Na ratios. Li/Na ratio is independent of the amount of water in the system (i.e. dilution effects) and can

serve as a proxy for the extent of Li incorporation into secondary minerals [18]. In Fig. 1, rivers impacted by hydrothermal activity (identified based on the chemistry of dissolved elements) were distinguished from those not impacted.

The main result that emerges is the remarkable variability of $\delta^7\text{Li}$ values as well as Li/Na ratios in rivers draining volcanic islands. The $\delta^7\text{Li}$ of rivers draining volcanic areas range from 4.7 ‰ for Carbet Morne Vert in Martinique to 45.1 ‰ for Solo (Babat) in Java. By contrast, the $\delta^7\text{Li}$ of the thermal springs is quite homogeneous, ranging from 1.2 ‰ for the caldeira Furnas in Sao Miguel to 7.1 ‰ for Diamant in Martinique. The Li/Na molar ratio of waters from this study spans 4 orders of magnitude, ranging from $0.01 \cdot 10^{-3}$ for Skovadalvatn river in Iceland to $25 \cdot 10^{-3}$ for the Chaude river in Martinique. The molar ratio Li/Na for thermal springs is generally higher than $1 \cdot 10^{-3}$ and reaches $6.15 \cdot 10^{-3}$ for the thermal spring of Diamant in Martinique. A global negative relationship exists between $\delta^7\text{Li}$ and the molar ratio Li/Na for all water samples as showed in Fig. 1.

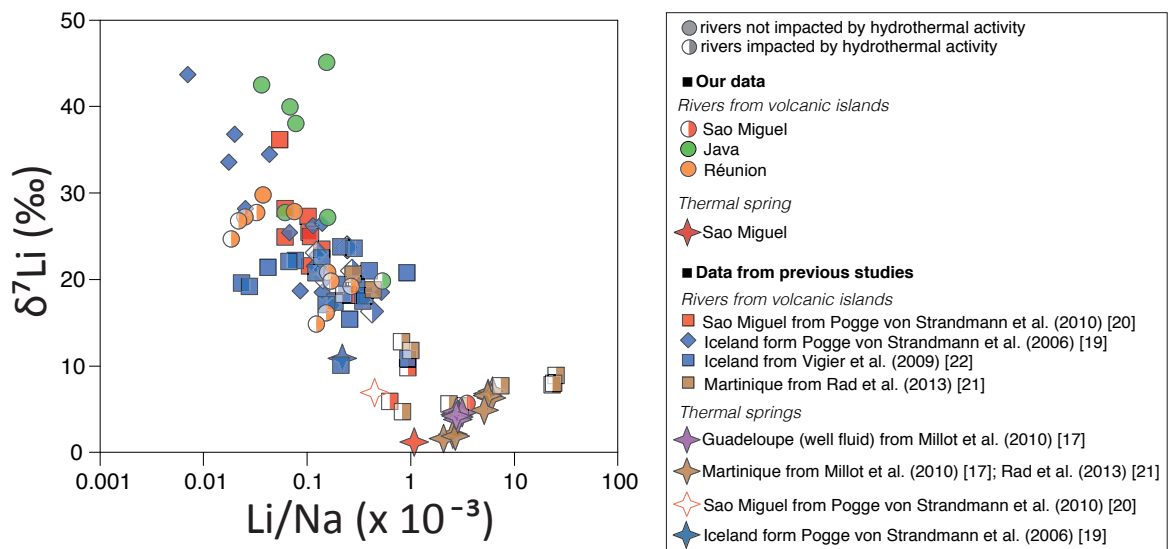


Fig. 1. Relationship between $\delta^7\text{Li}$ and the molar Li/Na ratio of rivers draining volcanic areas and geothermal springs of volcanic islands. Rivers impacted by hydrothermal activity have been distinguished from those draining only low-temperature weathering areas, based on the chemistry of dissolved elements.

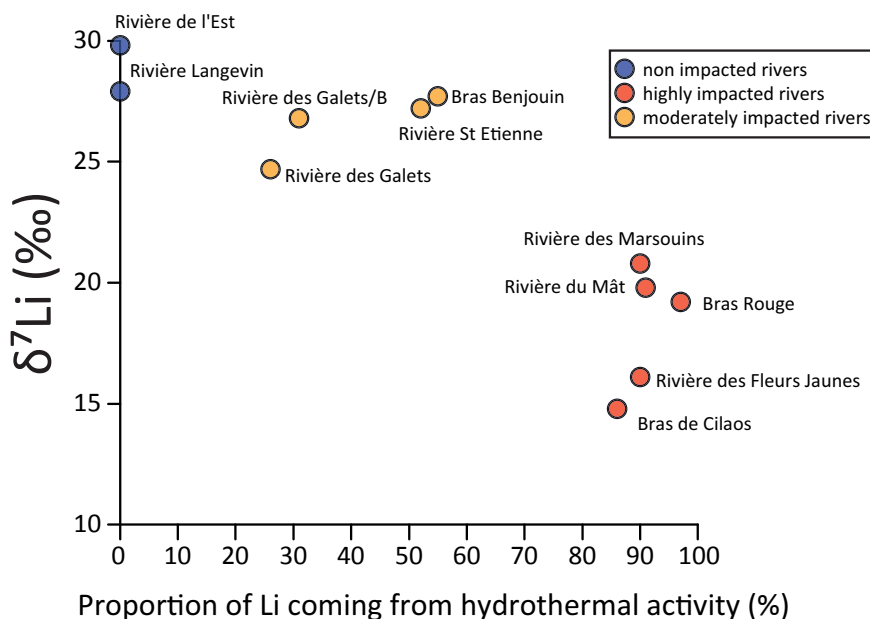


Fig. 2. Relationship between $\delta^7\text{Li}$ of Réunion main streams and the proportion of Li coming from continental hydrothermal activity deduced from a mixing model solved by an inverse method [15].

4. Discussion: a mixture between Li derived from surficial weathering and Li from high-temperature weathering processes

The correlation between river $\delta^7\text{Li}$ and Li/Na ratio in Fig. 1 can be attributed to the mixing between two end-members corresponding to two types of waters of contrasted Li isotopic composition. The main rivers from la Réunion island are particularly interesting as they show an inverse correlation between riverine $\delta^7\text{Li}$ and the proportion of Li coming from hydrothermal inputs (deduced from a mixing model solved by an inverse method [15]) (Fig. 2). This information is not available for the other settings but we hypothesize that the two mixing end-members of Fig. 1 are as follows (mixing curves are represented by dashed curves in Fig. 3):

- one end-member has a low and homogeneous $\delta^7\text{Li}$ (1 - 6‰) and a high Li/Na ratio ($0.45 - 6 \cdot 10^{-3}$), close to those of thermal spring samples (Fig. 1). The range of the $\delta^7\text{Li}$ of this type of water overlaps that of basaltic and andesitic rocks from the literature ($3.6\text{‰} \pm 1.2\text{‰}$ for the arc basalts [13]). The isotopic signature of this end-member can be explained by a congruent dissolution (*i.e.* without isotopic fractionation) of basaltic rocks at high-temperature. The Li/Na ratio of spring water can be explained by the intrinsic variability of the Li/Na ratio of the volcanic rocks. This end-member therefore represents chemical weathering processes occurring at high-temperature when meteoric water infiltrates in active volcanic regions of high heat flow.

- an end-member has a higher $\delta^7\text{Li}$ and a lower Li/Na ratio ($< 0.5 \cdot 10^{-3}$). This signature probably results from low-temperature weathering processes in soils or shallow groundwater. It is now well known that clay formation or more generally the reincorporation of Li in secondary solids result in the preferential incorporation of the light isotope of Li (e.g. [22]). The geochemical signature of this end-member is very heterogeneous (both at large scale and at the scale of one single island) (Fig. 3).

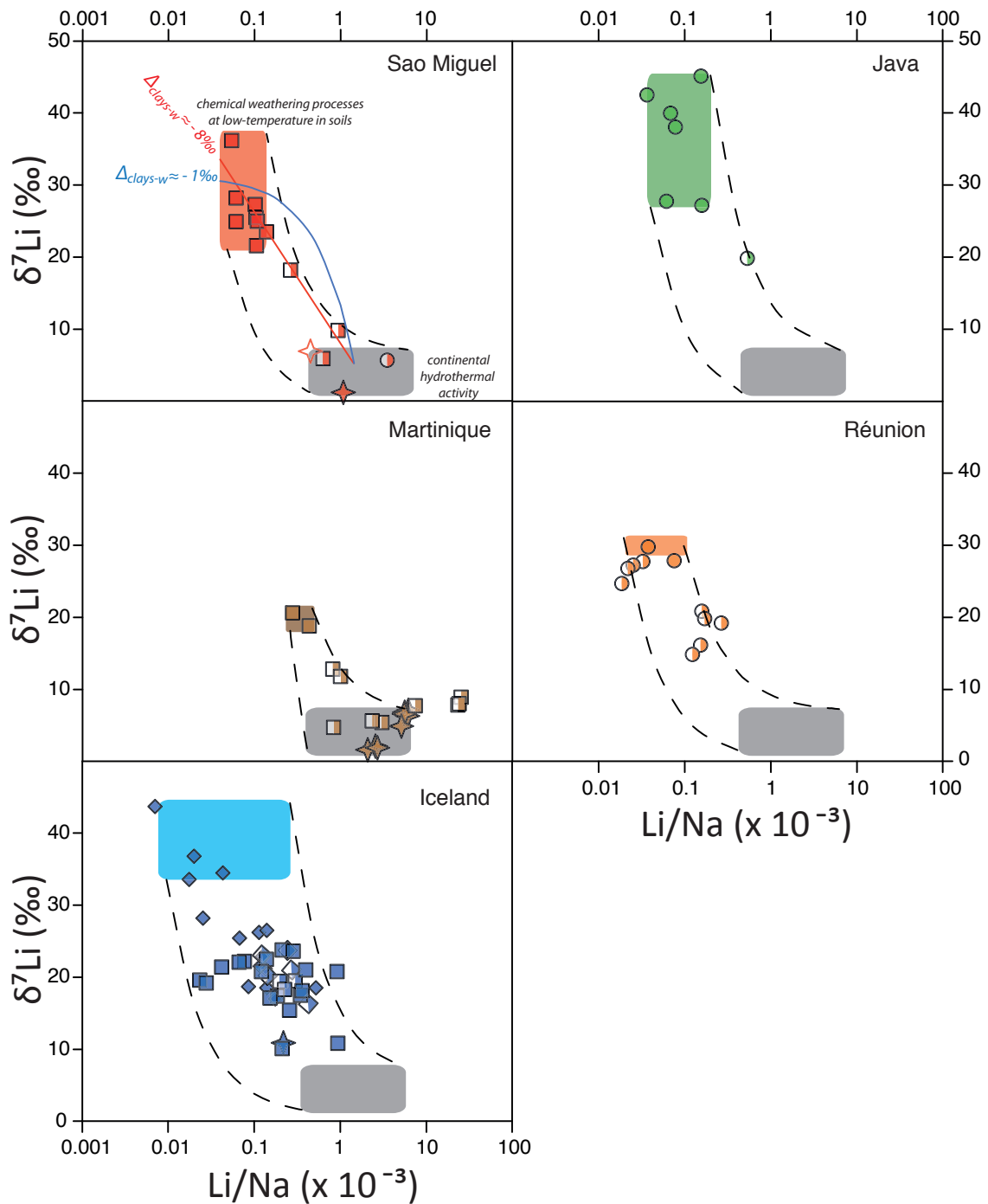


Fig. 3. The relationship showed in Fig.2 can be interpreted as a mixing between two types of waters (see text in section 4) (same symbols as Fig.1). The end-member with high $\delta^7\text{Li}$ and low Li/Na would result from processes in soils (pedogenesis) and can be modeled using a simple Rayleigh isotopic fractionation model (red line, see text 4.). This end-member is very heterogeneous and variable from an island to another. Except for Icelandic rivers, the Li isotopic composition of rivers can be explained by a mixing between Li having experienced pedogenesis and Li from hydrothermal activity.

This second end-member can be predicted by using mass balance models for isotope fractionation during weathering. In these models, Li is dissolved from the basaltic rock without isotopic fractionation, and is then reincorporated in secondary mineral products (i.e. clays, in soils) with an isotope fractionation favoring ^6Li . Such a model relies:

- on isotopic fractionation factors associated with clay formation in basaltic soils, $\Delta_{\text{clays-w}} = \delta^7\text{Li}_{\text{clays}} - \delta^7\text{Li}_w \sim 1000 \cdot \ln(\alpha_{\text{clays-w}})$ (where $\delta^7\text{Li}_w$ and $\delta^7\text{Li}_{\text{clays}}$ are respectively the Li isotope compositions of the water and of the forming clays), which range from -26‰ [10] to -1‰ [22].
- on the fraction of the residual dissolved Li after clay formation, f_{Li} . Assuming that Li and Na have the same mobility during the dissolution of basaltic rocks at low-temperature but that only Li is reincorporated in clays, f_{Li} can be quantified using $(\text{Li}/\text{Na})_w/(\text{Li}/\text{Na})_\beta$, where w denotes the residual dissolved phase and β the basaltic bedrock [18]. In the following we use a molar Li/Na ratio of $1.5 \cdot 10^{-3}$ (basalt from Guadeloupe) for $(\text{Li}/\text{Na})_\beta$.

The most simple type of model is an open through-flow mass balance model (equivalent to a so-called batch model) [2]:

$$\delta^7\text{Li}_w = \delta^7\text{Li}_\beta - (1 - f_{\text{Li}}) \cdot \Delta_{\text{clays-w}} \quad (1)$$

where $\delta^7\text{Li}_\beta$ is the $\delta^7\text{Li}$ of the initial dissolved phase (i.e. that of basaltic rocks, as we assume no fractionation during dissolution, $\delta^7\text{Li}_\beta \sim 5\text{‰}$). The batch model fails to produce a $\delta^7\text{Li}$ for the high- $\delta^7\text{Li}$ end-member higher than around 30‰ (blue curve represented for the case of Sao Miguel in Fig. 3). Such high values can be produced using a Rayleigh distillation model [3] (red line in Fig. 2). In this case,

$$\delta^7\text{Li}_w = \delta^7\text{Li}_\beta - \Delta_{\text{clays-w}} \cdot \ln(f_{\text{Li}}) \quad (2)$$

Using this model, 6% of Li initially dissolved is at the upmost incorporated in secondary solids in the case of Sao Miguel. All river samples from the different volcanic settings investigated here fall into the array formed by the two Rayleigh models relying on the two extreme value of $\Delta_{\text{clays-w}}$. A $\Delta_{\text{clays-w}}$ around -8‰ explains at the first order the geochemical signature of the high $\delta^7\text{Li}$ end-member. It is important to note that the hydrothermally impacted rivers (independently identified based on the chemistry of dissolved elements) fall outside the low-temperature end-member on the theoretical mixing lines with the hydrothermal end-members. The case of Iceland is more difficult to explain. We note the large difference of riverine $\delta^7\text{Li}$ values found by the different studies ([19], [22]). In Iceland, the Li isotopic compositions of the low-temperature end-member span 30 ‰ of $\delta^7\text{Li}$ units.

5. Global implications

Continental hydrothermal activity from volcanic islands produces waters very with high Li concentration (1 – 2 mM) and low $\delta^7\text{Li}$ (the lowest $\delta^7\text{Li}$ observed in riverine dissolved loads). The Li isotopic composition of rivers draining volcanic settings is much influenced by this high-temperature weathering input as shown by the first order mixing models presented here. Therefore, continental hydrothermal activity is likely to strongly impact the global riverine and oceanic Li budgets on geological timescales. These preliminary results open up new horizons for the interpretation of seawater Li isotopic records. Considering the influence of continental hydrothermal activity is needed when interpreting the Li isotopic signature of the global runoff.

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