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# Riverine Li isotope fractionation in the Amazon River basin controlled by the weathering regimes

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# Riverine Li isotope fractionation in the Amazon River basin controlled by the weathering regimes

## Abstract

We report Li isotope composition ( $\delta^7\text{Li}$ ) of river-borne dissolved and solid material in the largest River system on Earth, the Amazon River basin, to characterize Li isotope fractionation at a continental scale. The  $\delta^7\text{Li}$  in the dissolved load (+1.2‰ to +32‰) is fractionated toward heavy values compared to the inferred bedrock (-1‰ to 5‰) and the suspended sediments (-6.8‰ to -0.5‰) as a result of the preferential incorporation of  $^6\text{Li}$  into secondary minerals during weathering. Despite having very contrasted weathering and erosion regimes, both Andean headwaters and lowland rivers share similar ranges of dissolved  $\delta^7\text{Li}$  (+1.2‰ to +18‰). Correlations between dissolved  $\delta^7\text{Li}$  and Li/Na and Li/Mg ratios suggest that the proportion of Li incorporated in secondary minerals during weathering act as the main control on the  $\delta^7\text{Li}_{\text{diss}}$  across the entire Amazon basin. A "batch" steady-state fractionation model for Andean and lowland rivers satisfactorily reproduces these variations, with a fractionation factor between weathering products and dissolved load (a<sub>sec-dis</sub>) of  $0.983 \pm 0.002$ . Two types of supply-limited weathering regimes can be identified for the lowlands: "clearwaters" with dominant incorporation of Li in secondary minerals, and "black waters" (e.g., Rio Negro) where dissolution of secondary minerals enhanced by organic matter produces low  $\delta^7\text{Li}$ . Apart from the black waters, the  $\delta^7\text{Li}$  of Andean and lowland rivers is negatively correlated to the denudation rates with the lowest  $\delta^7\text{Li}$  corresponding to the rivers having the highest denudation rates. In contrast, the main tributaries draining both the Andes and the lowlands have higher  $\delta^7\text{Li}$  compared to other rivers. We propose that part of the dissolved Li derived from weathering in the Andes is re-incorporated in sediments during transfer of water and sediments in floodplains and that this results in an increase of the dissolved  $\delta^7\text{Li}$  along the course of these rivers. Unlike other rivers, the dissolved  $\delta^7\text{Li}$  in the main tributaries is best described by a Rayleigh fractionation model with a fractionation factor a<sub>sec-dis</sub> of 0.991. Altogether, the control imposed by residence time in the weathering zone and floodplain processes results in (i) a non-linear correlation between dissolved  $\delta^7\text{Li}$  and the weathering intensity (defined as W/D) and (ii) a positive relationship between the dissolved Li flux and the denudation rate. These results have important implications for the understanding of past ocean  $\delta^7\text{Li}$  and its use as a paleo weathering proxy.

## Disciplines

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# Riverine Li isotope fractionation in the Amazon River basin controlled by the weathering regimes

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## Abstract

We report Li isotope composition ( $\delta^7\text{Li}$ ) of river-borne dissolved and solid material in the largest River system on Earth, the Amazon River basin, to characterize Li isotope fractionation at a continental scale. The  $\delta^7\text{Li}$  in the dissolved load (+1.2‰ to +32‰) is fractionated toward heavy values compared to the inferred bedrock (-1‰ to 5‰) and the suspended sediments (-6.8 to -0.5‰) as a result of the preferential incorporation of  $^6\text{Li}$  into secondary minerals during weathering. Despite having very contrasted weathering and erosion regimes, both Andean headwaters and lowland rivers share similar ranges of dissolved  $\delta^7\text{Li}$  (+1.2‰ to +18‰). Correlations between dissolved  $\delta^7\text{Li}$  and Li/Na and Li/Mg ratios suggest that the proportion of Li incorporated in secondary minerals during weathering act as the main control on the  $\delta^7\text{Li}_{\text{diss}}$  across the entire Amazon basin. A "batch" steady-state fractionation model for Andean and lowland rivers satisfactorily reproduces these variations, with a fractionation factor between weathering products and dissolved load ( $\alpha_{\text{sec-dis}}$ ) of 0.983. Two types of supply-limited weathering regimes can be identified for the lowlands : "clearwaters" with dominant incorporation of Li in secondary minerals, and "black waters" (e.g. Rio Negro) where dissolution of secondary minerals enhanced by organic matter produces low  $\delta^7\text{Li}$ . Apart from the black waters, the  $\delta^7\text{Li}$  of Andean and lowland rivers is negatively correlated to the denudation rates with the lowest  $\delta^7\text{Li}$  corresponding to the rivers having the highest denudation rates. In contrast, the main tributaries draining both the Andes and the lowlands have higher  $\delta^7\text{Li}$  compared to other rivers. We propose that part of the dissolved Li derived from weathering in the Andes is re-incorporated in sediments during transfer of water and sediments in floodplains and that this results in an increase of the dissolved  $\delta^7\text{Li}$  along the course of these rivers. Unlike other rivers, the dissolved  $\delta^7\text{Li}$  in the main tributaries is best described by a Rayleigh fractionation model with a fractionation factor  $\alpha_{\text{sec-dis}}$  of 0.991. Altogether, the control imposed by residence time in the weathering zone and floodplain processes results in (i) a non-linear correlation between dissolved  $\delta^7\text{Li}$  and the weathering intensity (defined as W/D) and (ii) a positive relationship between the dissolved Li flux and the denudation rate. These results have important implications for the understanding of past ocean  $\delta^7\text{Li}$  and its use as a paleo weathering proxy.

*Keywords:* Lithium isotopes, Amazon River, Weathering, Floodplains, Denudation

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## 1. Introduction

2 Silicate weathering is one of the key geological processes influencing the long-term evolution of climate  
3 through the consumption of atmospheric  $\text{CO}_2$  (Walker et al., 1981; Berner et al., 1983). Identifying how

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4 silicate weathering fluxes relate to potential controlling parameters is thus critical to unravel past climatic  
5 variations (Berner, 1990; Dupré et al., 2003; West et al., 2005). Conflicting results about the respective roles  
6 of climatic, tectonic and lithological parameters in setting chemical weathering fluxes have been reported  
7 (Walker et al., 1981; Raymo and Ruddiman, 1992; Gaillardet et al., 1999; West et al., 2005; Dixon and  
8 von Blanckenburg, 2012; West, 2012; Maher and Chamberlain, 2014). In order to gain insight into the  
9 respective role of these parameters, the direct quantification of paleo-weathering rates and intensities can  
10 be achieved using records of geochemical proxies for chemical weathering (e.g. Sr, Nd, Os, Be isotopes)  
11 (Raymo and Ruddiman, 1992; Willenbring and Von Blanckenburg, 2010; Li and Elderfield, 2013; Torres  
12 et al., 2014; Cogez et al., 2015). However, most of those proxies do not necessarily trace specifically past  
13 silicate weathering fluxes or intensity and a reliable geochemical weathering proxy is still lacking (Raymo  
14 and Ruddiman, 1992; Willenbring and Von Blanckenburg, 2010).

15 Over the last 15 years, numerous studies on soil and river water have shown that Li isotopes is a promising  
16 proxy for silicate weathering reactions (for a recent review see Burton and Vigier (2011)). This is because  
17 Li is mainly hosted in silicate minerals (Kisakurek et al., 2005; Millot et al., 2010c), while not involved  
18 in the biological turnover (Lemarchand et al., 2010) and its isotopes ( $^6\text{Li}$  and  $^7\text{Li}$ ) are fractionated by  
19 chemical weathering (Huh et al., 1998; Pistiner and Henderson, 2003). Laboratory experiments have shown  
20 that mineral dissolution produces no Li isotope fractionation (Pistiner and Henderson, 2003; Wimpenny  
21 et al., 2010a) unlike the precipitation of secondary weathering products (Vigier et al., 2008; Millot et al.,  
22 2010b) and adsorption of Li onto mineral surface phases (Zhang et al., 1998; Pistiner and Henderson, 2003;  
23 Millot and Girard, 2007). In river basins, the lithium isotope composition ( $\delta^7\text{Li}$ ) of the dissolved load is  
24 generally higher (by +6 to +42‰) than corresponding  $\delta^7\text{Li}$  values of bedrock and suspended sediments  
25 (Kisakurek et al., 2005; Pogge von Strandmann et al., 2006, 2008; Vigier et al., 2009; Lemarchand et al.,  
26 2010; Pogge von Strandmann et al., 2010; Millot et al., 2010c; Henchiri et al., 2014). It has been suggested  
27 that the fractionation of Li isotopes in the dissolved load traces either silicate weathering intensity (Huh  
28 et al., 1998, 2001; Kisakurek et al., 2005; Pogge von Strandmann et al., 2006, 2008, 2010; Millot et al.,  
29 2010c), silicate weathering fluxes (Vigier et al., 2009), fluid residence time (Wanner et al., 2014) or exchange  
30 processes between water and sediments (Wimpenny et al., 2010b; Tipper et al., 2012; Pogge von Strandmann  
31 et al., 2012).

32 The recently published Li isotope seawater record over the Cenozoic by Misra and Froelich (2012) reveals  
33 a 9‰ increase of the ocean  $\delta^7\text{Li}$  over the last 60 Myr. This has been interpreted as reflecting an increase  
34 of the  $\delta^7\text{Li}$  of continental riverine input implying a large shift of the continental weathering regime (from  
35 "supply-limited" to "weathering-limited") as a result of increased uplift and denudation rates from early  
36 Cenozoic up to now (Misra and Froelich, 2012; Li and West, 2014; Froelich and Misra, 2014; Wanner et al.,  
37 2014). However, the parameters controlling Li isotope fractionation during chemical weathering and the link  
38 between Li isotope composition in river water and weathering regime are still poorly understood, especially  
39 at the continental scale.

40 Herein, we investigate the Li isotope composition of the riverine products (water and sediments) transpor-  
41 ted by the largest river system on Earth, the Amazon River. This allows us to study Li isotope fractionation  
42 by chemical weathering at a continental scale, in a relatively unpolluted area with various climatic regimes  
43 ranging from wet tropical to cold conditions, and spanning a very large range of runoffs, altitudes, bedrock  
44 types and denudation regimes. We show in particular how the weathering regime (supply vs. kinetic limi-  
45 tation) and the geomorphic setting (hillslopes vs. floodplains) influence the Li mass balance and therefore  
46 Li isotope fractionation. Based on these findings, we provide clues on how to interpret the Li isotope sedi-

47 mentary record archived in carbonates and terrigenous sediments in terms of past variations in continental  
48 weathering intensity and style.

## 49 2. Settings

50 The Amazon River basin is the largest river basin on Earth in terms of discharge, basin area, and one  
51 of the largest in terms of total denudation (Meade et al., 1979; Gaillardet et al., 1999). We define 4 main  
52 geomorphic areas in the Amazon Basin :

53 1. The Andes correspond to the Andean Cordillera where the relief ranges from about 6700 m to 500 m  
54 with steep slopes and high erosion rates. The northern part of the Andes (Peru and Ecuador) is drained by  
55 the tributaries of the Solimões River (Napo, Tigre, Morona, Pastaza, Marañon, Huallaga and Ucayali rivers)  
56 while the main tributaries of the Madeira River (Madre de Dios, Beni and Mamore rivers) drain the southern  
57 part of the Andes (Bolivia). In the Madeira basin, the lithology is relatively uniform and corresponds almost  
58 exclusively to low-grade uplifted Paleozoic silicate sedimentary rocks with a few Tertiary and Quaternary  
59 sedimentary deposits (e.g. in the Alto Beni river basin) (Stallard and Edmond, 1983; Dosseto et al., 2006b;  
60 Moquet et al., 2011). In the Solimões basin, the lithology comprises both sedimentary and igneous rocks of  
61 intermediate composition, essentially andesites in the active volcanic belt in Ecuador (Stallard and Edmond,  
62 1983). The runoff increases from 150 mm/yr in the south (Mamore River basin) to 3400 mm/yr in the north  
63 (Moquet et al., 2011). Rivers draining the Andes are typically called the "white waters" (Gibbs, 1967) with  
64 high suspended sediment concentrations ([SPM]) from 500 to 5000 mg/L (Guyot et al., 1996; Aalto et al.,  
65 2006; Wittmann et al., 2011). The silicate weathering rates (referred here as "W") in these river basins range  
66 from 7 to 75 t.km<sup>-2</sup>.y<sup>-1</sup> with a mean value at 22 t.km<sup>-2</sup>.y<sup>-1</sup> for the Andean area (Moquet et al., 2011).  
67 In the Andes, the weathering regime is said to be "weathering-limited" or almost equivalently "kinetically-  
68 limited" (Stallard and Edmond, 1983), meaning that the primary minerals are not completely weathered  
69 before being eroded away (West et al., 2005).

70 2. The lowlands and forelands, with a relief below 500 m, have lower slopes than the Andean part and  
71 are formed by Tertiary and Quaternary sediments eroded from the Andes. Those sediments have typical  
72 PAAS-like ("Post Archean Australian Shales") composition except for some formations in the Solimões basin  
73 which have andesitic provenance signature (Roddaz et al., 2005). Rivers draining exclusively the lowlands  
74 are more diluted and have lower suspended sediment content than Andean rivers (< 100 mg/L). The silicate  
75 weathering rates of lowland rivers are generally lower than 12 t.km<sup>-2</sup>.y<sup>-1</sup> (Moquet et al., 2011).

76 3. The Guyana and Brazilian shields (500-3000 m altitude) lithology corresponds essentially to the  
77 Precambrian basement formed by intermediate to acid igneous and metamorphic rocks and a few sedimentary  
78 rock outcrops. Those areas are covered by very thick soils and have very low denudation rates (Stallard and  
79 Edmond, 1983; Gaillardet et al., 1997). The [SPM] is generally no greater than 20-30 mg/L (Gaillardet et al.,  
80 1997; Moreira-Turcq et al., 2003; Wittmann et al., 2011). Two types of river water draining the shield terrains  
81 have been described by Stallard and Edmond (1983) : "clear waters" that drain lateritic (kaolinite-rich) soils  
82 and have low dissolved organic carbon content (DOC) and "black waters" draining forest areas with podzolic  
83 soils composed almost exclusively of quartz and having very high DOC content. Silicate weathering rates  
84 are very low ranging from 1 to 10 t.km<sup>-1</sup>.y<sup>-1</sup> (Gaillardet et al., 1997; Bouchez et al., 2014).

85 4. Floodplains correspond to low relief environments adjacent to a stream where sediments and water  
86 deriving from the high elevation Andes are continuously deposited and exchanged with the main channel  
87 (Dunne et al., 1998; Bourgoïn et al., 2007; Bouchez et al., 2012). As a result, river sediments can have a

88 residence time in the basin much longer than their residence time in soils (Dosseto et al., 2006a,b) and  
89 therefore be the locus of significant weathering reactions (West et al., 2002; Lupker et al., 2012; Bouchez  
90 et al., 2012; Frings et al., 2014).

91 River discharge and sediment fluxes of Amazon rivers are monitored by the HyBAm (Hydrology of the  
92 Amazon Basin, <http://www.ore-hybam.org>) international program since more than two decade. In addition,  
93 mid-term and long-term sediment fluxes have been determined using cosmogenic radionuclides ( $10^3$  year time  
94 scale) and fission track analyses ( $10^6$  year time scale) (Safran et al., 2005; Wittmann et al., 2011).

### 95 3. Sampling and analytical methods

#### 96 3.1. Sampling and major, trace elements concentration measurements

97 Water, suspended sediments and river bed sand samples were collected during several sampling cruises  
98 between 1989 and 2008. This sample set includes rivers sampled during both low and high water stages. These  
99 samples have been already characterized for major, trace element and isotope composition (Sr, Nd, U) and  
100 detailed information about analytical methods are available elsewhere (Gaillardet et al., 1997; Dosseto et al.,  
101 2006a,b; Bouchez et al., 2011, 2012). Briefly, river water samples were collected in acid-washed polypropylene  
102 containers and then filtered on site using Teflon filtration units ( $0.2 \mu\text{m}$  porosity). Before the analysis,  
103 the aliquots for cations, trace elements and isotope analyses were acidified with ultrapure  $\text{HNO}_3$  to pH 2.  
104 Major anions, cations, silica and Li concentrations were measured by ion chromatography, and trace element  
105 concentrations by quadrupole ICP-MS. All samples were stored in a cold room at  $4^\circ\text{C}$ .

#### 106 3.2. Li isotope measurements

107 For the dissolved load, a sample volume of 5 to 100 mL was evaporated in Teflon beakers at a temperature  
108 of about  $90^\circ\text{C}$ . The residue was then dissolved in 16 N distilled  $\text{HNO}_3$  and heated at  $100^\circ\text{C}$  during at least  
109 24 h to oxidise organic matter, and dried down again at  $90^\circ\text{C}$ . For the sediments, the acid digestion method  
110 used is described in Dellinger et al. (2014) and Li was then separated from the matrix by ion-exchange  
111 chromatography using a method modified from James and Palmer (2000) and described in Dellinger et al.  
112 (2014). Purified samples were kept until measurement as solid salts in Teflon beakers in order to avoid  
113 "ageing" of the solutions through Li adsorption or leaching of organic matter from container walls. Li isotope  
114 composition was measured using a MC-ICP-MS Neptune (Thermo Scientific, Bremen) at the laboratory  
115 of Geochemistry and Cosmochemistry at IPG Paris. Details on the analytical procedure are available in  
116 Dellinger et al. (2014). Accuracy and reproducibility of the isotopic measurements were checked through  
117 reported analyses of the IRMM-016 international standard solution, SRM rock standards, and seawater.  
118 Repeated measurements of the basalt reference materials JB-2 yielded  $\delta^7\text{Li} = +4.47 \pm 0.53\text{‰}$  ( $\pm 2\sigma$ ,  $n = 30$   
119 separations and 15 digestions) and for BHVO-2,  $\delta^7\text{Li} = +4.34 \pm 0.41\text{‰}$  ( $\pm 2\sigma$ ,  $n = 6$  digestions). Repeated  
120 measurements of the seawater NASS-5 reference material yielded  $\delta^7\text{Li} = +30.91 \pm 0.26\text{‰}$  ( $\pm 2\sigma$ ,  $n = 7$   
121 separations). Seven samples were duplicated and these duplicates agree within less than  $0.60\text{‰}$ .

122 The Li concentration and isotope composition of Amazon river sediment depth-profiles have been pu-  
123 blished and discussed elsewhere (Dellinger et al., 2014). In the present study, the existing dataset has been  
124 extended to include Li concentration and isotope composition of surface SPM samples from small Beni river  
125 tributaries and shield/lowland rivers. It should be mentioned that for a few rivers, the SPM and waters  
126 analysed here have not been collected at the same time. When it is the case, it is notified in the main text  
127 or in the figures.

## 128 4. Results

### 129 4.1. Major elements in the dissolved load

130 Major and trace elements data are given in table (1) and agree (within 30%) with monthly time-series  
131 reported by Moquet et al. (2011). Major and trace element variability in the Amazon River has been  
132 extensively discussed elsewhere (Stallard and Edmond, 1981, 1983, 1987; Gaillardet et al., 1997; Elbaz-  
133 Poulichet et al., 1999; Mortatti and Probst, 2003; Moquet et al., 2011). Briefly, river TDS (Total Dissolved  
134 Solid) range from 2 to 200 mg/L with the lowest values for the shield rivers and some Andean catchments.  
135 Solimões tributaries draining outcrops of halite and evaporites have the highest TDS values (Stallard and  
136 Edmond, 1983; Moquet et al., 2011). Calcium (Ca) and magnesium (Mg) are always the dominant cations  
137 compared to sodium (Na) and potassium (K) except in some sodium-rich tributaries of the Solimões draining  
138 saline formations. Magnesium concentration is generally higher in the Madeira River basin (up to 350  
139  $\mu\text{mol/L}$ ) compared to the Solimões River basin (maximum 100  $\mu\text{mol/L}$ ). Shield rivers (black and clear  
140 waters) have very low cation concentration (except for K) compared to other rivers.

### 141 4.2. Lithium concentration and isotope ratios

142 Dissolved lithium concentrations ( $[\text{Li}]_{\text{diss}}$ ) in the Amazon River basin span two orders of magnitude  
143 ranging from 0.03 to 1.7  $\mu\text{mol/L}$ , with a mean concentration of 0.32  $\mu\text{mol/L}$  ( $\text{SD}=0.37$ ,  $n=54$ ) close to the  
144 worldwide riverine average of 0.27  $\mu\text{mol/L}$  (Gaillardet et al., 2014; Misra and Froelich, 2012) and the original  
145 estimate of Huh et al. (1998). Our values are in good agreement with data on some Amazon tributaries  
146 published by Huh et al. (1998). The rivers draining the Amazonian shield and the Lowlands have the lowest  
147  $[\text{Li}]_{\text{diss}}$ , between 0.03 and 0.12  $\mu\text{mol/L}$  (Fig. 3). The major tributaries of Solimões and Madeira rivers have  
148 intermediate Li content between 0.06 and 0.60  $\mu\text{mol/L}$  while the Andean rivers from the Beni River basin  
149 have the highest Li concentration (0.5 to 1.7  $\mu\text{mol/L}$ ).

150 The dissolved Li isotope composition ( $\delta^7\text{Li}_{\text{diss}}$ ) displays a large range of variation from +1.2 to +32.9‰  
151 and is fractionated toward high values compared to source rocks (Fig. 2). The suspended sediments have  
152 more homogeneous  $\delta^7\text{Li}$  values and are slightly enriched in  $^6\text{Li}$  compared to source rocks (Fig. 2). The range  
153 of dissolved  $\delta^7\text{Li}$  values is comparable to the range defined by other rivers (Li and West, 2014). The  $\delta^7\text{Li}$  of  
154 the Amazon River mainstream at Óbidos ranges between +16.2 and +19.3‰ depending on the hydrological  
155 conditions. The maximum difference in  $\delta^7\text{Li}$  between two samples of the same river at different times is 9.2‰  
156 for the Negro River and 6.5‰ for the Madeira River (if we include samples from the study of Huh et al.  
157 (1998) for both rivers), 4.6‰ for the Beni River at Rurrenabaque, 3.2‰ for the Amazon River and less than  
158 2‰ for other rivers (Tapajós, Trombetas, Madre de Dios, Mamore and Beni at Riberalta). Therefore, only  
159 the Negro and Madeira rivers show some seasonality, most likely relating to relative contributions of their  
160 tributaries. The homogeneity of the dissolved  $\delta^7\text{Li}$  in the water column has been checked by measuring 3  
161 samples collected at different depths at Óbidos, which yields similar results within analytical uncertainty  
162 ( $\pm 0.5$  to 1‰). Andean rivers have lower  $\delta^7\text{Li}_{\text{diss}}$  (+3.8 to +16‰) than other mountainous river (Kisakurek  
163 et al., 2005; Millot et al., 2010c). The  $\delta^7\text{Li}$  of the Negro River are the lowest ever measured in running  
164 surface waters (Li and West, 2014; Wanner et al., 2014). The Mamore River has the highest  $\delta^7\text{Li}_{\text{diss}}$  value  
165 of the sample set measured here (around 31‰).

166 A bell-shaped relationship is observed between  $\delta^7\text{Li}_{\text{diss}}$  and Li concentration (Fig. 3). For rivers having  
167  $[\text{Li}]_{\text{diss}}$  lower than 0.20  $\mu\text{mol.L}^{-1}$ , Li concentration is positively correlated with  $\delta^7\text{Li}_{\text{diss}}$  values, while for  
168 rivers having  $[\text{Li}]_{\text{diss}}$  higher than 0.20  $\mu\text{mol.L}^{-1}$ , Li concentration is negatively correlated with  $\delta^7\text{Li}_{\text{diss}}$ . A



169 clear regional distribution can be observed with rivers having common geomorphological features also sharing  
 170 similar Li concentration and isotope composition. Rivers having  $[\text{Li}]_{\text{diss}}$  higher than  $0.4 \mu\text{mol.L}^{-1}$  correspond  
 171 to the Beni River and its tributaries with  $\delta^7\text{Li}_{\text{diss}}$  values systematically lower than 16‰. Shield and lowland  
 172 rivers have the lowest Li concentration and display  $\delta^7\text{Li}$  values from +2 to +16‰. Therefore, Andean  
 173 and shield rivers, which are characterized by drastically distinct erosion and weathering conditions, display  
 174 similar ranges of Li isotope composition. Finally, rivers having intermediate  $[\text{Li}]_{\text{diss}}$  ( $0.06\text{-}0.60 \mu\text{mol.L}^{-1}$ )  
 175 correspond to major tributaries of Solimões and Madeira rivers, which drain both the Andes and the lowland  
 176 areas (Madre de dios, Mamore and Madeira rivers) and to the Amazon River at Óbidos. Compared to rivers  
 177 draining only the Andes or the Amazonian plain, they have a much higher  $\delta^7\text{Li}_{\text{diss}}$ , generally higher than  
 178 16‰.

## 179 5. Sources and isotope fractionation of Li in the Amazon River and tributaries

### 180 5.1. Partitioning of Li between dissolved and suspended loads

181 Following Gaillardet et al. (2014) and Bouchez et al. (2013), the proportion of lithium transported in  
 182 the suspended load ( $e^{\text{Li}}$  in %) can be calculated by the Eq. (1) :

$$e^{\text{Li}} = \frac{[\text{SPM}] \times [\text{Li}]_{\text{sed}}}{[\text{SPM}] \times [\text{Li}]_{\text{sed}} + [\text{Li}]_{\text{diss}}} \times 100 \quad (1)$$

183 with  $[\text{SPM}]$  being the concentration of suspended sediments (in g/L),  $[\text{Li}]_{\text{sed}}$  and  $[\text{Li}]_{\text{diss}}$  the Li concen-  
 184 tration in sediments (in ppm) and water (in ppb) from Dellinger et al. (2014) and Tables (1 and 2). Here we  
 185 use the long-term average of sediment fluxes derived from both sediment gauging (Meade et al., 1979; Guyot  
 186 et al., 1996; Wittmann et al., 2011) and comogenic nuclides (Wittmann et al., 2011) when available (values  
 187 are reported in Table S1) rather than the instantaneous sediment flux measured the day of the sampling  
 188 because daily SPM concentration can vary over three orders of magnitude depending on the hydrological  
 189 stage (e.g. Armijos et al., 2013). Between  $\sim 40$  and 97% of Li is transported in the solid form in the Amazon  
 190 rivers (Fig. 4). For most of the river samples, this proportion is higher than 95%. The lowland rivers, es-  
 191 pecially those draining the shields have the highest proportion of Li transported in the dissolved load, (e.g.  
 192 Tapajós and Trombetas rivers). This difference between lowland and Andean rivers is consistent with the  
 193 results for the Orinoco River (Huh et al., 2001). It should be noted that this calculation does not take into  
 194 account the variability in  $[\text{Li}]_{\text{sed}}$  with depth and especially the decrease of Li concentration in suspended  
 195 sediments toward the bottom of the river due to the dilution with quartz minerals (Dellinger et al., 2014).  
 196 The predominant form of Li transported in the Amazon River basin is thus the solid phase in agreement  
 197 with what was found at the global scale (Misra and Froelich, 2012; Li and West, 2014).

### 198 5.2. Source of dissolved lithium

199 In the Amazon basin, potential sources of dissolved Li include rainwater, dissolution of evaporites, car-  
 200 bonates and silicates. As Li is not a nutrient, vegetation is not expected to be a significant sink or source  
 201 of Li. In the following we estimate the proportion of Li deriving from each source and demonstrate that  
 202 dissolved Li in Amazon rivers is mostly sourced from silicate weathering.

203 *5.2.1. Atmospheric inputs*

204 Only few data on Li concentration and isotope composition of rainwater have been reported so far (Pis-  
 205 tiner and Henderson, 2003; Pogge von Strandmann et al., 2006, 2010; Lemarchand et al., 2010; Millot et al.,  
 206 2010a). These studies have shown that Li in rainwater derives from both marine aerosol and silicate mineral  
 207 dust. Following Gaillardet et al. (1997), we assume that dust-derived trace elements in rainwater are sourced  
 208 from the Amazon Basin itself and perform a correction only for marine aerosols using the characteristics of  
 209 modern seawater. The seawater Li/Cl ratio is on average equal to  $5.10^{-5}$  (Millot et al., 2010c) and its  $\delta^7\text{Li}$   
 210 = +31‰ (Millot et al., 2007). The concentration of the element X deriving from atmospheric input is :

$$[\text{X}]_{\text{rain}} = [\text{Cl}]_{\text{rain}} \times \left( \frac{\text{X}}{\text{Cl}} \right)_{\text{ocean}} \quad (2)$$

211 The maximum estimated chlorine concentration deriving from marine inputs ( $[\text{Cl}]_{\text{rain}}$ ) has been assumed  
 212 to be  $20 \mu\text{mol.L}^{-1}$  for large Amazon tributaries (Gaillardet et al., 1997) and 3 to  $8 \mu\text{mol.L}^{-1}$  for the eastern  
 213 river basins in Bolivia, Peru and Ecuador (Stallard and Edmond, 1981; Moquet et al., 2011). The calculated  
 214  $[\text{Li}]_{\text{rain}}$  is low, with a maximum estimated contribution of rainwater-derived Li of  $\sim 2\%$  for the shield rivers,  
 215 0.5-1% for the main tributaries (Solimões, Madeira and Amazon at Obidos) and less than 0.1% for Andean  
 216 rivers. The dissolved  $\delta^7\text{Li}$  is therefore not corrected for atmospheric input because the estimated shift of Li  
 217 isotope composition associated with this marine contribution is less than 0.3‰ which we consider as a very  
 218 minor.

219 *5.2.2. Evaporites*

220 Some rivers have Cl concentrations exceeding  $[\text{Cl}]_{\text{rain}}$ , which suggests that they are influenced by halite  
 221 dissolution. Marine evaporites deposits have been reported (salt domes) essentially in the Ucayali and Ma-  
 222 rañón basins (Huallaga River). Chlorine concentration derived from evaporite dissolution is estimated by  
 223 subtracting  $[\text{Cl}]_{\text{rain}}$  to the river Cl concentration ( $[\text{Cl}]_{\text{ev}} = [\text{Cl}]_{\text{diss}} - [\text{Cl}]_{\text{rain}}$ ), and the concentration of Li  
 224 derived from halite dissolution is :

$$[\text{Li}]_{\text{ev}} = [\text{Cl}]_{\text{ev}} \times \left( \frac{\text{Li}}{\text{Na}} \right)_{\text{ev}} \quad (3)$$

225 Assuming congruent dissolution of halite and using a mean Li/Na value of  $3 \times 10^{-5}$  for marine evaporites  
 226 (Reeder et al., 1972; Kloppmann et al., 2001; Imahashi et al., 1993), we calculate a maximum contribution  
 227 of Li deriving from evaporite dissolution of 11% for the Huallaga River and less than 1% for most of the  
 228 other rivers. The contribution of evaporites to the dissolved Li load is thus relatively minor. In the following,  
 229 the concentration of the element X corrected from rainwater and evaporite input is referred to  $[\text{X}]^*$  ( $[\text{X}]^* =$   
 230  $[\text{X}]_{\text{diss}} - [\text{X}]_{\text{rain}} - [\text{X}]_{\text{ev}}$ ).

231 *5.2.3. Carbonates and silicates*

232 Several studies on rivers draining mixed lithologies show that the input of Li from the weathering of  
 233 carbonates is generally negligible compared to silicate weathering inputs (Kisakurek et al., 2005; Millot  
 234 et al., 2010c). Following Millot et al. (2010c), we can use the typical Li/Ca molar ratio in carbonates ( $\sim 1.5$   
 235  $\pm 0.5 \times 10^{-5}$ ) (Hathorne and James, 2006; Pogge von Strandmann et al., 2013), and by assuming that all  
 236 the dissolved calcium derives from carbonate weathering, estimate the maximum proportion of Li deriving  
 237 from carbonate weathering.

$$[\text{Li}]_{\text{carb}} = [\text{Ca}]^* \times \left( \frac{\text{Li}}{\text{Ca}} \right)_{\text{carb}} \quad (4)$$

238 Altogether, our calculation shows that more than 95% of the dissolved Li is derived from silicate wea-  
 239 thering, confirming the previous studies on large river basins with mixed lithologies and the negligible input  
 240 of Li from carbonate weathering (Huh et al., 2001; Kisakurek et al., 2005; Millot et al., 2010c). Therefore,  
 241 it is not necessary to correct the  $\delta^7\text{Li}_{\text{diss}}$  from non-silicated sources.

### 242 5.3. Lithium isotope fractionation during continental weathering

243 The dissolved load of the Amazon rivers is strongly fractionated toward high  $\delta^7\text{Li}$  values compared to  
 244 the source rock (Fig. 2). This result is entirely consistent with Dellinger et al. (2014) who showed that the  
 245  $\delta^7\text{Li}$  values of river sands from Amazon rivers cover a range comparable to that of bedrocks while suspended  
 246 sediments are slightly enriched in  $^6\text{Li}$ . Dissolved load and suspended load appear thus to be complementary  
 247 reservoirs (Fig. 2). As none of the various non-silicates sources (rain, evaporites, carbonates), nor the  $\delta^7\text{Li}$   
 248 variability in the silicate bedrock can account for the range of dissolved  $\delta^7\text{Li}$ , we concluded that most of  
 249 the fractionation of Li isotopes is produced by silicate weathering processes and sorting, consistently with  
 250 previous studies on small and large basins (Huh et al., 1998; Pogge von Strandmann et al., 2006; Vigier  
 251 et al., 2009; Millot et al., 2010c).

#### 252 5.3.1. Evidence for Li incorporation in secondary minerals

253 Both experimental and field-based studies (*e.g.* Huh et al., 1998; Pistiner and Henderson, 2003; Vigier  
 254 et al., 2008; Verney-Carron et al., 2011) have shown that incorporation or adsorption of Li into secondary  
 255 weathering products (clays and iron hydroxides) is accompanied by large Li isotope fractionation. According  
 256 to Millot et al. (2010c), the Li incorporation into secondary minerals can be revealed by comparing the  
 257 concentration of Li with an element that is much less sensitive to this process (a conservative element) such  
 258 as Na or Mg. Indeed, both Na and Mg are most likely released in solution at the same rate as Li during  
 259 mineral dissolution (Verney-Carron et al., 2011). Yet, unlike Li which has a strong affinity for clay minerals  
 260 and oxyhydroxides, Na and Mg are in most cases not significantly incorporated into secondary weathering  
 261 products (Sawhney, 1972) We note however that significant incorporation or adsorption of Mg can occur  
 262 (depending of the clay mineral phase) as indicated by studies on Mg isotopes (Tipper et al., 2006, 2012;  
 263 Huang et al., 2012; Wimpenny et al., 2014, *e.g.*). Another complication for the use of Mg is the influence  
 264 or carbonates. These issue are addressed in the appendix A.

265 The  $\delta^7\text{Li}_{\text{diss}}$  of Amazon rivers is negatively correlated with the dissolved  $(\text{Li}/\text{Na})^*$  and  $(\text{Li}/\text{Mg})^*$  (Fig.  
 266 5). The most Li-depleted rivers (relative to Na and Mg) have the highest  $\delta^7\text{Li}$  values, and vice-versa. The  
 267 correlation between  $(\text{Li}/\text{Na})^*$  and  $\delta^7\text{Li}_{\text{diss}}$  is weaker than that with  $(\text{Li}/\text{Mg})^*$ , with the rivers draining the  
 268 shield being shifted toward lower  $(\text{Li}/\text{Na})^*$  values compared to other rivers. These correlations suggest that  
 269 in the Amazon basin, Li isotope fractionation in the dissolved load is linked to Li incorporation in solid  
 270 weathering products. Whether Li in secondary minerals is incorporated into the mineral structure or is  
 271 adsorbed at the mineral surface cannot be further constrained with the present dataset and in the following  
 272 we do not distinguish between these two processes. Following Gislason et al. (1996), Georg et al. (2007) and  
 273 Millot et al. (2010c), the proportion of Li initially dissolved remaining in solution after secondary mineral  
 274 formation ( $f_{\text{diss}}^{\text{Li}}$ ), can be calculated as :

$$f_{\text{diss}}^{\text{Li}} = \frac{(\text{Li}/\text{X})_{\text{diss}}}{(\text{Li}/\text{X})_0} \quad (5)$$

275 Where X is Na or Mg and  $(\text{Li}/\text{X})_0$  corresponds to the initially dissolved Li/X ratio before incorporation  
 276 of Li in secondary minerals. A  $f_{\text{diss}}^{\text{Li}}$  value of 1 means that Li is not re-incorporated in secondary minerals  
 277 after its initial dissolution (congruent dissolution) while a value of 0 indicates that all the lithium initially  
 278 dissolved has been re-incorporated into secondary weathering products. Within the assumption that Li, Na  
 279 and Mg are congruently dissolved from the rock sources, the  $(\text{Li}/\text{X})_0$  ratio can be calculated by the following  
 280 equation :

$$\left(\frac{\text{Li}}{\text{X}}\right)_0 = \sum_i \left(\frac{\text{Li}}{\text{X}}\right)_i^{\text{rock}} \gamma_i^{\text{X}} \quad (6)$$

281 Where  $\gamma_i^{\text{X}}$  are the mixing proportions of the element X of each rock source i contributing to the dissolved  
 282 load and  $(\text{Li}/\text{X})_i^{\text{rock}}$  are the (Li/X) ratio of each rock source i. In the Amazon basin, estimation of the  $(\text{Li}/\text{X})_0$   
 283 values is critical because the range of Li/Na and Li/Mg values in the silicate source rocks and river sands is  
 284 very large and could at least partly explain the scatter of river data (Fig. 5). Shales are Li-rich (60-80 ppm)  
 285 compared to granitic rocks (10-45 ppm) and volcanic rocks (5-20 ppm) (Holland, 1984; Teng et al., 2008;  
 286 Burton and Vigier, 2011). In the next section, we discuss the different methods used to correct for source  
 287 rock variability and calculate the  $(\text{Li}/\text{X})_0$  ratio for each river.

### 288 5.3.2. Determination of the $(\text{Li}/\text{X})_0$ ratio of each river basin

289 For the Madeira and Solimões rivers, we use the riverine dissolved strontium isotope composition  
 290 ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) to determine the  $(\text{Li}/\text{X})_0$  of each river. Sr isotope have been extensively used as a source tracer  
 291 in rivers (e.g. Palmer and Edmond, 1992) because (i) Sr is generally conservative in river water and (ii) the  
 292  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is "insensitive" to weathering processes (dissolution and precipitation of new mineral phases).  
 293 In the Amazon basin, the silicate source rock comprises both igneous (mostly andesites and granodiorites)  
 294 and sedimentary rocks (Stallard and Edmond, 1983) that have distinct  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio values (Petford and  
 295 Atherton, 1996; Roddaz et al., 2005; Bryant et al., 2006). The  $(\text{Sr}/\text{Na})^*$  and  $(^{87}\text{Sr}/^{86}\text{Sr})^*$  ratios of the rivers  
 296 of the Madeira basin can be explained by a mixture between carbonate and shale weathering (Fig. 6), which  
 297 is consistent with the geology of the Madeira Basin composed exclusively of sedimentary rocks. Rivers of  
 298 the Solimões basin plot closer to the igneous rocks - carbonates mixing line, with a variable contribution  
 299 of shale weathering (Fig. 6). This is again in good agreement with the lithology of those basins where both  
 300 sedimentary and igneous rocks are present in the bedrock. Collectively, it shows that the respective input of  
 301 shales and igneous rock weathering to the dissolved load can be estimated using the dissolved  $^{87}\text{Sr}/^{86}\text{Sr}$ . A  
 302 mixing model between five end-members (atmospheric, evaporite, shale, igneous rocks and carbonate) can  
 303 be solved using an inverse method in order to determine, for each river, the contribution of the different  
 304 sources (Gaillardet et al., 1997). The determination of the compositional range of each end-member, as well  
 305 as the mixing proportion of Na ( $\gamma_i^{\text{Na}}$ ) are detailed in appendix A.

306 Results of the mixing model show that in the Madeira basin, the contribution of igneous rock weathering  
 307 is negligible (except in the Orthon River), consistently with the scarcity of igneous rocks in the Madeira  
 308 watershed. In the Solimões basin, we find that  $\text{Na}_{\text{sil}}$  (i.e. dissolved Na deriving from silicate weathering) is  
 309 mostly sourced from igneous rocks weathering for the Morona, Pastaza and Marañon at Borja (> 70%),  
 310 while essentially derived from shale weathering for others tributaries (> 50 to 80%). Using Eq. (12) with  
 311 the mixing proportions ( $\gamma_i^{\text{Na}}$ ) and the mean Li/Na ratio of the source rocks, we calculate the  $(\text{Li}/\text{Na})_0$  for  
 312 each river (see Appendix B).

313 For the rivers draining the Brazilian and Guiana shields, the source rock corresponds essentially to shield

314 rocks which have a granodioritic composition similar to Upper Continental Crust (UCC) (Gaillardet et al.,  
 315 1997). Because the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of shield rocks is similar to that of shales, the  $^{87}\text{Sr}/^{86}\text{Sr}$  cannot be used  
 316 to calculate the respective contribution of granitic and shale rocks weathering and estimate the  $(\text{Li}/\text{X})_0$  of  
 317 shield rivers. We rather use the trends between  $\delta^7\text{Li}$ ,  $(\text{Li}/\text{Mg})$  and  $(\text{Li}/\text{Na})$  defined by shield rivers in Fig.  
 318 (5) to estimate the  $(\text{Li}/\text{X})_0$  of shield rivers (see Appendix B).

### 319 5.3.3. Calculation of the $f_{\text{diss}}^{\text{Li}}$ values and covariation with $\delta^7\text{Li}$

320 With the  $(\text{Li}/\text{X})_0$  of each river estimated in the previous section, it is possible using Eq. (5) to calculate  
 321 the  $f_{\text{diss}}^{\text{Li}}$  value for the different rivers (Table 3). For the Madeira and Solimões river basins, the  $f_{\text{Li}}$  are  
 322 calculated using only Na and not Mg in Eq. (5) because in those basin, a large part of the Mg is derived  
 323 from carbonate weathering. For the rivers draining the Brazilian and Guiana shields,  $f_{\text{diss}}^{\text{Li}}$  are calculated  
 324 using both Na and Mg because (i) the contribution of carbonate weathering is low (Gaillardet et al., 1997),  
 325 or negligible (Edmond et al., 1995) and (ii)  $[\text{Na}]^*$  concentrations are very dilute and have a larger uncertainty  
 326 than  $[\text{Mg}]_{\text{diss}}^*$  (see Appendix B for more details).

327 In the Madeira basin, the calculated  $f_{\text{Li}}$  values range from as low as 0.04 for the Mamore River to 0.69 in  
 328 the Challana River (Table 3). In the Solimões River basin, the  $f_{\text{diss}}^{\text{Li}}$  values range from 0.06 in the Huallaga  
 329 River to 0.32 in the Ucayali River (Table 3). Finally, in the rivers draining the Amazonian shield,  $f_{\text{diss}}^{\text{Li}}$  range  
 330 from 0.17 for the Jaciparana River to 0.80 in the Negro River. No systematic variation of  $f_{\text{diss}}^{\text{Li}}$  with the  
 331 geomorphic and weathering regime is observed. The Beni River tributaries characterized by a "weathering-  
 332 limited" regime (Moquet et al., 2011; Bouchez et al., 2014) display the same range of  $f_{\text{diss}}^{\text{Li}}$  variation than  
 333 "supply-limited" rivers draining the Amazonian plain and shield areas. These values are high indicating  
 334 little net Li re-incorporation. The main tributaries of the Madeira River basin are characterized by a high  
 335 proportion of Li incorporated into secondary minerals ( $f_{\text{Li}} < 0.20$ ), with the Mamore River having the  
 336 lowest  $f_{\text{diss}}^{\text{Li}}$  from all rivers studied here. In the Beni River basin, the variability of the  $f_{\text{diss}}^{\text{Li}}$  values is also  
 337 very large. The rivers draining the Eastern Cordillera with the highest relief (Tipuani, Challana, Mapiri,  
 338 Coroico) have generally lower  $f_{\text{diss}}^{\text{Li}}$  values than the rivers of the subandean zone (Alto Beni, Chepete and  
 339 Quiquibey) indicating more net Li incorporation in the Andean zones with low relief.

340 By combining the mixing proportion of sodium ( $\gamma_i^{\text{Na}}$ ) and the  $(\text{Li}/\text{Na})$  ratio of the source rocks, it  
 341 is possible to calculate the proportion of dissolved Li initially released in solution (before incorporation in  
 342 secondary minerals) from the various sources (Table 3). Because shales are enriched in Li compared to igneous  
 343 rocks, we find that in the Solimões River basin, the maximum proportion of Li initially dissolved from igneous  
 344 rocks is only 20% (for the Morona and Pastaza rivers) despite the fact that the majority of the sodium in  
 345 these rivers derives from the weathering of igneous rock. This shows that even in catchments dominantly  
 346 underlain by igneous rocks, most of the lithium derives from the dissolution of silicate sedimentary rocks.  
 347 In the Amazon basin, weathering of silicate sedimentary rocks exerts a significant control on the dissolved  
 348 Li flux.

349 Overall, the  $\delta^7\text{Li}_{\text{diss}}$  values are well correlated to  $f_{\text{diss}}^{\text{Li}}$  at the scale of the whole Amazon River basin (Fig.  
 350 7). The rivers that have the lowest proportion of Li incorporated into secondary minerals ( $f_{\text{diss}}^{\text{Li}} > 0.6$  for the  
 351 Challana, Tipuani and Negro rivers) also have the lowest Li isotope composition while the highest  $\delta^7\text{Li}_{\text{diss}}$   
 352 values are associated with high proportion of Li incorporated into the solid ( $f_{\text{diss}}^{\text{Li}} < 0.1$ ). This demonstrates  
 353 unambiguously that the first-order control on the  $\delta^7\text{Li}_{\text{diss}}$  in the Amazon basin is the proportion of Li  
 354 incorporated in present-day products of silicate weathering. The comparison between Fig. (5) and Fig.  
 355 (7) also emphasises the importance of considering source rock variability to quantify Li incorporation in

356 secondary minerals. An interesting observation is that major tributaries of the Madeira and Solimões rivers  
 357 (green and red squares in Fig. 7) all lie above (higher  $\delta^7\text{Li}_{\text{diss}}$ ) the trend defined by the Andean, clear and  
 358 black waters in Fig. (7) although their waters are a mixture of waters from these different zones. This, in  
 359 particular, shows that the  $\delta^7\text{Li}_{\text{diss}}$  of main tributaries of Madeira and Solimões basins cannot be explained  
 360 only by the mixing of lowland and Andean tributaries. In other words, either the  $\delta^7\text{Li}$  is not conservative or  
 361 a Li source is missing (see section 6.3 for further discussion).

#### 362 5.4. Modeling the Li isotope fractionation during Li incorporation in secondary minerals

##### 363 5.4.1. Dissolved load

364 To assess the influence of the weathering regime on the dissolved  $\delta^7\text{Li}$ , the trends of the Fig. (7) can  
 365 be modelled using a mass balance model (Johnson et al., 2004; Georg et al., 2007; Bouchez et al., 2013).  
 366 Such a simple approach allows for the determination of field-based fractionation factors associated with  
 367 the incorporation of Li into secondary minerals. Conceptually, we first consider the weathering zone as an  
 368 open flow-through system in which Li is released in a dissolved form by dissolution of primary minerals  
 369 and removed from solution by incorporation into secondary minerals. At steady state, all dissolution and  
 370 precipitation input and output fluxes and isotope composition are balanced, and the Li isotope composition  
 371 can be modelled as (Bouchez et al., 2013) :

$$\delta^7\text{Li}_{\text{diss}} = \delta^7\text{Li}_0 - \Delta_{\text{sec-diss}} \times (1 - f_{\text{Li}}) \quad (7)$$

$$\delta^7\text{Li}_{\text{sec}} = \Delta_{\text{sec-diss}} + \delta^7\text{Li}_{\text{diss}} \quad (8)$$

372 Where  $\delta^7\text{Li}_0$ ,  $\delta^7\text{Li}_{\text{diss}}$  and  $\delta^7\text{Li}_{\text{sec}}$  correspond to the Li isotope composition of the initial solution after  
 373 dissolution, the dissolved load and the solid weathering products, respectively. With no fractionation during  
 374 dissolution (Pistiner and Henderson, 2003), the term  $\delta^7\text{Li}_0$  corresponds to the mean  $\delta^7\text{Li}_{\text{rock}}$  of the weathered  
 375 rocks. The term  $\Delta_{\text{sec-diss}}$  is the isotope fractionation factor between secondary products and the dissolved  
 376 load ( $\Delta_{\text{sec-diss}} = \delta^7\text{Li}_{\text{sec}} - \delta^7\text{Li}_{\text{diss}} = 1000 \ln(\alpha_{\text{sec-diss}})$ ). The assumptions behind this steady-state model  
 377 are extensively discussed in Bouchez et al. (2013). Large river systems have the advantage to integrate the  
 378 spatial variability in isotope signatures and processes, and to "smooth" the temporal variability, such that  
 379 the assumption of steady-state is most valid at this scale. For the sake of simplicity in the following we refer  
 380 to this mass balance model as the "batch" system although it should be emphasized that the mass transfer  
 381 underlying this model is different from that of a true batch model.

382 Another fractionation model is the Rayleigh distillation model, where secondary products do not re-  
 383 dissolve. In this model, the isotope composition of the dissolved load can evolve toward higher Li isotope  
 384 composition than in the batch model.

$$\delta^7\text{Li}_{\text{diss}} = \delta^7\text{Li}_0 + \Delta_{\text{sec-diss}} \times \ln(f_{\text{Li}}) \quad (9)$$

385 The exceptionally large range of  $f_{\text{diss}}^{\text{Li}}$  values in the Amazon rivers allows us to discriminate between  
 386 these two models. At first order, both models are able to explain the variability in  $\delta^7\text{Li}_{\text{diss}}$  of Amazon basin  
 387 rivers (Fig. 7). However, the data are better explained by two separate trends : (i) a "batch" fractionation  
 388 curve for the Beni Andean rivers, lowlands rivers and shield tributaries and (ii) a Rayleigh distillation curve  
 389 for the main tributaries of Madeira and Solimões basins. This difference of fractionation behaviours have

390 also been reported for the silicon isotopes in Iceland (Georg et al., 2007) and in the Amazon (Hughes et al.,  
391 2013).

392 For the first set of rivers, the linear trend (Fig. 7) shows that as a whole, each river basin can be  
393 reasonably described as a single “batch” reactor (Eq. 7) with its own characteristic  $f_{\text{diss}}^{\text{Li}}$  value. Therefore,  
394 the variability in  $\delta^7\text{Li}_{\text{diss}}$  across these rivers stems from a similar process (same  $\alpha_{\text{sec-diss}}$ ) and type of mass  
395 exchange between compartments (“batch” model), but characterised by a different extent of reaction ( $f_{\text{diss}}^{\text{Li}}$ ).  
396 A linear trend as observed in Fig. (7) does not result from a mixture between end members (such mixing  
397 trend would be an hyperbola).

398 The slope of the correlation (Fig. 7) yields a fractionation factor between dissolved and secondary pro-  
399 ducts  $\alpha_{\text{sec-diss}} = 0.983 \pm 0.002$  ( $n = 22$ ,  $r^2 = 0.86$ ), or  $\Delta_{\text{sec-diss}} = -17\text{‰}$ . This fractionation factor value  
400 is in very good agreement with experimental data (precipitation of smectite and basalt alteration phases at  
401 various temperatures) (Vigier et al., 2008; Millot et al., 2010b) and the global Li isotope fractionation trend  
402 compiled by Li and West (2014). We also note that a single fractionation factor is needed to explain the data  
403 of Andean, lowlands and shield rivers. This means that the fractionation factor is independent of the type of  
404 the secondary minerals phases as lowland and shield rivers transport high amounts of kaolinite and smectite  
405 whereas the Andean rivers sediments clay-sized are mostly composed by an illite-chlorite clay assemblage  
406 (Guyot et al., 2007). This observation is in good agreement with recent experimental data (Vigier et al.,  
407 2011).

408 The second set of rivers define a specific Rayleigh trend with a fractionation factor  $\alpha_{\text{sec-dis}}$  of  $0.991 \pm$   
409  $0.002$ . The two different isotope fractionation factors suggest that different processes generate Li isotope  
410 fractionation in the Andes/shield and along the course of the Madeira River. Furthermore, the fact that the  
411 data along the Madeira and Solimões large tributaries are better fitted by a different mass balance model  
412 would suggest that the way water and sediments interact is different there from the rest of the basin (see  
413 section 6.3). However, unlike the rivers fitting the batch fractionation model, the Solimões and Madeira main  
414 tributaries Li isotope composition and  $f_{\text{diss}}^{\text{Li}}$  variability could also be explained by a mixing trend between  
415 two end members (for example, between two end members having signature of the Mamore and Beni rivers).  
416 This issue is addressed in the section 6.3 of this paper.

#### 417 5.4.2. *Suspended load*

418 The  $\delta^7\text{Li}$  of the suspended load can be used to test the batch fractionation model previously defined.  
419 For simplicity, we focus only on rivers fitting the batch fractionation model. Using the fractionation factor  
420 ( $\alpha_{\text{sec-diss}}$ ) previously determined from the dissolved load, we can predict the  $\delta^7\text{Li}$  of the modern-day wea-  
421 thering products (clays and oxides) using Eq. (8) and compare them to the  $\delta^7\text{Li}$  measured in the suspended  
422 loads (Fig. 8). For a given fractionation factor, Eq. (8) predicts that  $\delta^7\text{Li}_{\text{sec}} - \delta^7\text{Li}_{\text{rock}}$  is linearly related to  
423  $f_{\text{Li}}$ . In this study and for most of the rivers, only surface sediments have been sampled and thus are plotted  
424 in Fig (8) although a large variability of sediment Li concentration and isotope composition with depth has  
425 been reported (Dellinger et al., 2014).

426 Two different trends can be identified in Fig. (8). The first one corresponds to the lowland and shield  
427 rivers (except for the Rio Negro). In these rivers, the  $\delta^7\text{Li}$  of surface sediments plot within uncertainty on  
428 the predicted isotope composition of modern weathering products and are therefore in good agreement with  
429 the fractionation factor ( $\alpha_{\text{sec-diss}}$ ) and  $f_{\text{diss}}^{\text{Li}}$  values deduced from the study of the dissolved load. This is  
430 consistent with a supply-limited weathering regime where SPM is formed of secondary weathering products  
431 because primary minerals are completely weathered before being transported away from the weathering zone

432 (West et al., 2005). For Andean rivers, surface sediment  $\delta^7\text{Li}$  is systematically higher than the expected value  
433 for secondary minerals. Two hypotheses can explain this discrepancy (i) the batch fractionation model does  
434 not satisfactorily explain those data or (ii) the suspended sediments of Andean rivers is not composed only  
435 by the complementary phase of the dissolved load but also contains an unweathered rock component having  
436 Li isotope composition similar to that of shales. This conclusion is in perfect agreement with Dellinger et al.  
437 (2014) that showed that in the Andean rivers, the proportion of unweathered bedrock fragments in the  
438 suspended load of these rivers can reach 70 %.

439 Finally, although it could be expected that the Rio Negro transports only secondary weathering products,  
440 its sediment  $\delta^7\text{Li}$  is different from  $\delta^7\text{Li}_{\text{sec}}$  predicted by Eq. (8). The Negro River is characterized by very  
441 high  $f_{\text{diss}}^{\text{Li}}$  values, indicating that the proportion of Li incorporated into secondary minerals is rather small  
442 compared to other rivers. Therefore even very small amounts of unweathered sediments transported by the  
443 Rio Negro could significantly increase the  $\delta^7\text{Li}$  of its sediments. This result would be in good agreement  
444 with mineralogical data showing that the Rio Negro suspended load contains only 10 to 20% clay minerals,  
445 with the remaining being quartz minerals and organic colloids (Brinkmann, 1986). However, we cannot  
446 exclude that the high  $\delta^7\text{Li}_{\text{sed}}$  of the Rio Negro is influenced by atmospheric dusts having higher Li isotope  
447 composition than secondary clays.

## 448 6. What controls the incorporation of Li in secondary phases and the dissolved Li isotope 449 composition ?

450 As shown above,  $\delta^7\text{Li}_{\text{diss}}$  is controlled by the proportion of Li incorporated into secondary minerals. In  
451 this section we discuss the parameters which control the proportion of Li incorporated in secondary minerals,  
452 and thereby river dissolved  $\delta^7\text{Li}$ .

### 453 6.1. Control by denudation rate and residence time in the weathering zone

454 We focus in this section only on the rivers fitting the "batch" fractionation model in Fig. (9.a), i.e.  
455 lowland and Andean rivers. Other rivers (main tributaries of the Madeira and Solimoes rivers) will be  
456 discussed separately in the section 6.3. Fluid flow (e.g. Maher and Chamberlain, 2014; Wanner et al., 2014)  
457 and mineral residence time (Ferrier and Kirchner, 2008; Bouchez et al., 2013) are two main controls on the  
458 transfer of elements during weathering. We explore here the links between  $\delta^7\text{Li}_{\text{diss}}$ , the dissolved flux of Li  
459 and the denudation rate, as proposed by Bouchez et al. (2013). The total denudation rate (D) used here  
460 corresponds to the sum of the silicate chemical weathering rate (as defined by Bouchez and Gaillardet, 2014)  
461 and physical denudation rate. Total denudation rates are based on either long-term sediment and solute data  
462 (Guyot et al., 1996; Laraque et al., 2009; Filizola and Guyot, 2009; Mortatti and Probst, 2003; Moquet et al.,  
463 2011) or from cosmogenic nuclide concentrations in river sands (Safran et al., 2005; Wittmann et al., 2009,  
464 2011).

465 At first order, the dissolved Li flux of the different river basins is positively correlated ( $r^2 = 0.84$ ) to  
466 both sediment gauging and cosmogenic-nuclide derived denudation rates (Fig. 9.c), while showing only a  
467 weak correlation to the silicate weathering rate ( $r^2 = 0.37$ ) and no global correlation with runoff. Rivers  
468 having the highest denudation rates (Beni rivers) have the highest Li fluxes while the shield rivers have the  
469 lowest dissolved Li flux. This correlation reflects the first-order control on the dissolved Li flux by denudation  
470 and show that mineral residence time rather than fluid residence time controls the dissolved Li flux in the  
471 Amazon basin.



472 In the Andes, high denudation rates prevail, which lead to short residence times of solid in soils and rivers.  
473 Under these conditions, weathering regime is said to be "weathering-limited". The  $\delta^7\text{Li}$  of rivers draining the  
474 Bolivian Andes defines a negative correlation with cosmogenic nuclide-derived denudation rates, on which  
475 also fit the lowland "clear water" rivers (Fig. 9.a). On one hand, the Challana River, which has the lowest  
476  $\delta^7\text{Li}$  among Andean rivers, also has the highest cosmogenic denudation rate. At the other end, the Tapajós  
477 and Orthon rivers have very low denudation rates and high  $\delta^7\text{Li}$  value. A similar correlation has also been  
478 recently observed by Pogge von Strandmann and Henderson (2015) for rivers in New Zealand. As suggested  
479 by Bouchez et al. (2013) on the basis of the model of Ferrier and Kirchner (2008), this correlation can be  
480 attributed to the kinetic limitation (resulting from high erosion rates) on secondary products precipitation.  
481 Very high erosion rates limit the formation of soils and the precipitation of clay minerals (high  $f_{\text{diss}}^{\text{Li}}$ , Fig.  
482 9.b) as the residence time of solids at the Earth surface is too short (Bouchez et al., 2013). If the kinetics of  
483 clay mineral precipitation is too slow compared to the rate of sediment export within the basin, only small  
484 amounts of Li will be incorporated into secondary minerals (Fig. 9.B). As a result, weathering will appear  
485 to be congruent with  $\delta^7\text{Li}_{\text{diss}} \approx \delta^7\text{Li}_{\text{rock}}$ . At lower denudation rates ( $< 100 \text{ t.km}^{-2}.\text{y}^{-1}$ ), particle residence  
486 time becomes longer and mineral precipitation take place, leading to higher  $f_{\text{diss}}^{\text{Li}}$  and hence Li isotope  
487 fractionation with  $\delta^7\text{Li}_{\text{diss}} > \delta^7\text{Li}_{\text{rock}}$ . It is worth noting that the correlation between  $\delta^7\text{Li}$  and the sediment  
488 gauging derived denudation rate is less significant than the cosmogenic nuclide derived denudation rate,  
489 although the rivers having the highest "sediment gauging derived" denudation rates (except the Alto Beni  
490 river) have generally lower  $\delta^7\text{Li}$  than lowland "clear waters". This could indicate that the Li isotopes reflect  
491 processes occurring on the millennium time scale (corresponding to the cosmogenic-derived denudation rate)  
492 rather than on the decadal time scale. In this regard, the fact that the Alto Beni river does not plot on the  
493 correlation defined by other rivers might be due to the recent mobilization of Plio-Quaternary sediments  
494 (Dosseto et al., 2006b) resulting in much higher short-term denudation rates than the long-term average.

495 At very low denudation rate, some rivers (Trombetas and Rio Negro rivers) also have very low  $\delta^7\text{Li}$   
496 values (Fig. 9.a). Indeed, at these low denudation rates, clays reside in the weathering zone for a very long  
497 time (Mathieu et al., 1995; Dosseto et al., 2006a) and may be re-dissolved which hence results in "congruent  
498 weathering" conditions (Misra and Froelich, 2012; Froelich and Misra, 2014; Ryu et al., 2014) in a way that  
499 there is no export of isotopically fractionated Li in the solid load (Bouchez et al., 2013). The variability of  
500 the  $\delta^7\text{Li}$  values of these rivers is explored in the next section. In summary, for rivers fitting the "batch"  
501 fractionation model, both very high and very low denudation rates produce congruent weathering and similar  
502 Li isotope composition.

### 503 6.2. *Supply-limited weathering regime in the lowlands*

504 Lowland areas are characterized by a "supply-limited" or ("transport-limited") weathering regime (Stal-  
505 lard and Edmond, 1983), with some river waters having low pH and high dissolved Al, Fe and organic matter  
506 concentrations. In such environments, organic acids enhance dissolution rates and weathering intensity of  
507 silicates (Viers et al., 1997, 2000). The DOC (Dissolved Organic Carbon) concentrations were not measured  
508 on those samples so we use the dissolved Al concentration as a proxy for the DOC concentrations. Indeed,  
509 in those rivers, the dissolved Al content and pH are controlled by the amount of dissolved organic matter  
510 (Viers et al., 1997; Deberdt et al., 2002). The dissolved  $\delta^7\text{Li}$  of shield rivers is well correlated to both the  
511 dissolved Al/Li ratio and pH (Fig. 10). The most Al-depleted rivers correspond to the "clear water" rivers  
512 and have relatively high  $\delta^7\text{Li}$  compositions while the most Al-rich rivers have low pH values and  $\delta^7\text{Li}$ , and  
513 correspond to the "black water" rivers like the Negro River.

514 The "clear water" rivers (e.g. Tapajós River) contain lower levels of dissolved organic carbon and drain  
515 lateritic soils, rich in kaolinite and iron-oxides, and developed on the shield and tertiary sediments (Stallard  
516 and Edmond, 1983; Fritsch et al., 2011). In such environments, the formation of kaolinite during present-day  
517 dissolution-precipitation processes results in a limited loss of Al and Fe compared to Si (Fritsch et al., 2011).  
518 We suggest, similarly to the study of Ryu et al. (2014) that Li is also retained in the solid residue, and that  
519 this process drives the  $\delta^7\text{Li}_{\text{diss}}$  toward heavy values as a result of isotope fractionation during the formation  
520 of kaolinite and iron oxide. On the opposite, the "black waters" such as the Negro River are associated with  
521 acidic and reducing waterlogged podzolic soils where dissolution of iron oxides and clay minerals predominate  
522 compared to precipitation reactions (Fritsch et al., 2011). Those soils are clay-depleted and dominated by  
523 coarse quartz minerals (Brinkmann, 1986; Do Nascimento et al., 2004), where water is well-drained. This  
524 results in a net export of aluminium and iron to the river waters through the formation of organo-metallic  
525 complexes (Allard et al., 2011; Fritsch et al., 2011). As a result we suggest that in these areas, there is the  
526 net dissolution of  $^7\text{Li}$ -depleted secondary minerals (near the surface of the weathering profile) along with  
527 the net formation of secondary minerals (at depth). If both reactions occur at the same rate (i.e. steady-  
528 state), rock-like dissolved  $\delta^7\text{Li}$  are obtained in water draining the profile. Podzolisation in the Amazon  
529 basin occurs in flat and swampy areas where organic matter accumulate. There is thus an indirect control  
530 between topography and Li isotope composition in the plains of the Amazon basin. Such interpretation is  
531 in good agreement with the conclusions of Hughes et al. (2013) on the Si isotope composition of the Rio  
532 Negro. Furthermore, the correlation of the  $\delta^7\text{Li}$  with dissolved Al content is very similar to that described  
533 by Cardinal et al. (2010) for silicon isotopes in the Congo River basin and is interpreted in the same manner.

534 To summarize, the lowlands are characterized by two distinct weathering regimes, as proposed by Bouchez  
535 et al. (2013) for low denudation rates setting : (i) lateritisation processes resulting in a high proportion of Li  
536 incorporated in secondary minerals ; (ii) podzolisation, where clay minerals previously formed are dissolved  
537 by organic matter, equivalent to congruent weathering of the silicate crust and leading to rock-like  $\delta^7\text{Li}$   
538 values. The difference between these two types of weathering regimes is probably related to large contrasts  
539 in runoff and topographic features. Other examples of congruent weathering with no fractionation in the  
540 dissolved load compared to the bedrock have been reported in some other extreme weathering environments  
541 (Cardinal et al., 2010; Ryu et al., 2014). Supply-limited weathering regimes can produce a large range of  
542  $\delta^7\text{Li}$  values depending of the proportion of Li incorporated in secondary products and therefore do not  
543 necessarily result in congruent weathering and low dissolved  $\delta^7\text{Li}$  as proposed by Huh et al. (2001) and  
544 Misra and Froelich (2012).

### 545 6.3. The role of floodplains in setting large rivers $\delta^7\text{Li}$

546 The large tributaries, that are not well described by a "batch" fractionation model in Fig. (7), do not plot  
547 on the correlation between denudation rates and  $\delta^7\text{Li}$ . Therefore their isotope composition is not controlled  
548 only by the mineral residence time in the soil weathering zone and another mechanism must be considered.  
549 These main tributaries of the Madeira and Solimões (draining both the Andes and the lowlands areas) at  
550 lowland locations have the highest  $\delta^7\text{Li}$  signatures with a proportion of Li incorporated in secondary minerals  
551 of more than 80-90%. The  $\delta^7\text{Li}$  of the Beni river increases from 8-12‰ at the outlet of the Andes to 16‰ at  
552 the lowland location. This is unexpected because (i) the contribution of dissolved matter from the lowland  
553 is small compared to that from the Andes (Gaillardet et al., 1997; Moquet et al., 2011) and (ii) the pure  
554 lowland rivers from the Madeira basin have lower  $\delta^7\text{Li}$  values (11.5 to 15.5‰) than the Beni sampled in  
555 the lowland. Accordingly, the main tributaries of Madeira and Solimões basins either follow (a) a Rayleigh

556 mass-balance with a fractionation factor of -9‰, or (b) plot on a mixing trend between an end member  
557 having a high  $f_{\text{diss}}^{\text{Li}}$  and a low  $\delta^7\text{Li}$  and another end member having a low  $f_{\text{diss}}^{\text{Li}}$  and a high  $\delta^7\text{Li}$  (Section  
558 5.4.1). These two observations are consistent, with respectively either (a) a process of Li removal associated  
559 with isotope fractionation during transfer through the floodplains or (b) an addition of high dissolved  $\delta^7\text{Li}$   
560 source from floodplains areas in the main tributaries. Such influence of floodplains on the dissolved  $\delta^7\text{Li}$  has  
561 also been proposed by Pogge von Strandmann and Henderson (2015) to explain the high  $\delta^7\text{Li}$  of eastern  
562 rivers from New Zealand.

563 These two hypotheses can be tested by comparing the net dissolved lithium fluxes transported by the  
564 river systems upstream and downstream the floodplain reaches. Such comparison is difficult because only  
565 the Andean dissolved Li flux for the Beni river basin is known. However, a first-order estimate of the Andean  
566 dissolved Li flux can be determined for each river by multiplying the Li/Na ratio by the dissolved Na flux  
567 both derived from the Andes. For this we assume that the  $f_{\text{diss}}^{\text{Li}}$  value of Andean rivers is the same as  
568 for the Beni River upstream the floodplain, ranging between 0.2 and 0.4, and we use the mean annual  
569 dissolved Na flux deriving from the weathering of silicate rocks from the study of Moquet et al. (2011). This  
570 calculation shows that for the main tributaries there is no increase of the net Li flux downstream but rather  
571 a decrease, especially for the Mamoré and Huallaga rivers. These two rivers have the highest dissolved Li  
572 isotope composition at their mouth.

573 Another approach is to use the correlation between the denudation rate and the dissolved Li flux (Fig.  
574 9c). At first order, the dissolved Li flux is related to the denudation rate as described in the section 6.1.  
575 However, as lowland reaches have low denudation rate, if there is an additional process of supply or removal  
576 of dissolved Li in the floodplain, the dissolved Li flux of the main tributaries should be offset (as observed for  
577 the Mamore and Huallaga River) compared to the global trend defined by the lowland and Andean rivers.  
578 Interestingly, on this figure, the Mamore and Huallaga rivers (that have the highest  $\delta^7\text{Li}$ ) are slightly offset  
579 compared to the global correlation. Using the equation of the correlation of the Fig. (9c), it is possible to  
580 calculate the theoretical dissolved Li flux of the main tributaries and compare it with the actual measured  
581 flux as shown on the Fig. (11). On this figure, addition of high  $\delta^7\text{Li}$  lithium in the floodplain should result  
582 in a positive correlation. On the contrary, removal of dissolved Li should produce a negative correlation. We  
583 observe that all the main tributaries, except the Ucayali river, plot on the negative trend showing that the  
584 Amazon floodplain seems to act as a net sink of dissolved Li. This suggest a process-related fractionation  
585 of Li isotope rather than mixing with additional source of Li, to explain the very high  $\delta^7\text{Li}$  values. This  
586 conclusion is consistent with the observation of dissolved silicon removal inferred from changes in Si isotope  
587 fractionation in the seasonal floodplains of the Okavango Delta (Frings et al., 2014).

588 The exact mechanism responsible for Li uptake in the floodplains can only be speculated at this stage  
589 but some hypotheses can be discussed. Downstream from the Andes-lowland transition, river sediments and  
590 waters from the main channel are temporally stored in alluvial plains (Guyot et al., 1996; Bouchez et al.,  
591 2012). In these environments, water and sediments interact and authigenic secondary minerals might form  
592 (Frings et al., 2014) and incorporate part of the dissolved Li. Floodplain lakes and groundwater systems  
593 isolated from the main channel during a sufficiently long period of time become closed systems, in which  
594 Li could evolve along a Rayleigh fractionation path if a significant amount of Li is incorporated into clay  
595 minerals or oxides. Water from floodplain lakes and groundwater returning to the main channel during annual  
596 high water stage would then contribute to the increase in  $\delta^7\text{Li}$ -signature of the river. Reactive-transport  
597 modelling have shown that subsurface residence time of water (Wanner et al., 2014) and small changes in  
598 aquifer conditions (Pogge von Strandmann et al., 2014) can strongly influence the Li isotope composition

599 of groundwater systems. Although there is no clear correlation between runoff and Li isotope fractionation  
600 in the Amazon floodplains, it is interesting to note that the Mamore River (having the highest  $\delta^7\text{Li}$  value)  
601 is characterized by the lowest runoff and higher weathering intensity among the main tributaries. This may  
602 indicate increasing fractionation along the course of the river, as the contact time between the water and  
603 the sediment increases as proposed by Wanner et al. (2014), but validation of this hypothesis would require  
604 further investigation of the links between fluid travel time and the evolution of the  $\delta^7\text{Li}$  in the floodplain.  
605 Altogether, this shows that Li does not behave conservatively in rivers draining both mountain ranges and  
606 floodplains. We estimate that for these rivers, 75 to 90% of the Li removal in secondary minerals takes place  
607 in the weathering zone uplands and 10 to 25% in the floodplains. For the Mamore and Huallaga Rivers, up  
608 to 90% of the dissolved lithium entering the floodplain reaches is removed in solid weathering products in  
609 the floodplain (Fig. 11). Therefore, the dissolved flux of Li is significantly reduced by incorporation of Li  
610 into secondary products when water travels through in the floodplains.

#### 611 *6.4. Relation between $\delta^7\text{Li}$ and weathering intensity*

612 In the Amazon basin, "white", "clear" and "black" waters corresponding to very different weathering  
613 regime have distinct Li isotope signatures. The Solimões, Madeira and Amazon rivers correspond to the  
614 mixture of these 3 types of waters. Thus, we can calculate that the  $\delta^7\text{Li}$  of the Amazon River at its mouth  
615 results from the mixture of 76% of Li deriving from the Andes/floodplains (white waters), 15% from the  
616 laterite-lowlands (clear waters) and 9% from the podzol (black waters). About 60% of the dissolved Li  
617 derived from the Andes is removed from the dissolved load in floodplains.

618 We found no clear relationship between  $\delta^7\text{Li}_{\text{diss}}$ , dissolved Li fluxes and silicate weathering rates or runoff.  
619 Rather, the control imposed by denudation rates, floodplain processes and residence time in the weathering  
620 zone observed at the scale of the whole Amazon River basin results in an equivocal bell-curved relationship  
621 (Fig. 12) between dissolved  $\delta^7\text{Li}$  and the weathering intensity. The latter is defined here as W/D (Bouchez  
622 et al., 2014), the ratio between the chemical silicate weathering rates W (as defined by Bouchez and Gaillardet  
623 (2014)) and the total denudation rates D. It corresponds to the fraction of material dissolved from a given  
624 mass of rock and is similar to the "CDF" (Chemical Depletion Factor, i.e. Riebe et al., 2001), the "CIA"  
625 (Chemical Index of Alteration, i.e. Nesbitt and Young, 1982) or element-specific weathering indexes (i.e.  
626 Gaillardet et al., 1997). In the Amazon basin, high weathering intensity ( $W/D > 0.1$ ) which characterize  
627 supply-limited weathering regimes produce low values of  $\delta^7\text{Li}$  (1-15‰) and dissolved Li fluxes (Fig. 9).  
628 Weathering-limited regimes in the Andes having very low weathering intensity ( $W/D < 0.01$ ) have also  
629 relatively low  $\delta^7\text{Li}$  similar to supply-limited settings (Fig. 12) but much higher dissolved Li fluxes (Fig. 9).  
630 Therefore, both high and low weathering intensity produce low  $\delta^7\text{Li}$  values, but at very different Li fluxes.  
631 Finally, main tributaries which integrate both highland and lowland area have intermediate weathering  
632 intensities ( $W/D = 0.01-0.10$ ) with high  $\delta^7\text{Li}$  values (14-32‰) due to secondary processes occurring in the  
633 floodplains.

634 Other river systems for which the  $\delta^7\text{Li}_{\text{diss}}$ , along with a reliable estimate of both  $\delta^7\text{Li}_{\text{rock}}$  and time-  
635 integrated W/D data are available (see table S2), also plot on the same bell-curved relationship as the  
636 Amazon rivers (Fig. 12). In this regard, apparent contradictory interpretations from past studies (Huh  
637 et al., 2001; Vigier et al., 2009; Pogge von Strandmann et al., 2010; Misra and Froelich, 2012; Pogge von  
638 Strandmann and Henderson, 2015) can be reconciled by this non-linear relationship between  $\delta^7\text{Li}_{\text{diss}}$  and  
639 the weathering intensity. Indeed, rivers from Iceland studied by Vigier et al. (2009) have low W/D and plot  
640 on the positive trend between  $\delta^7\text{Li}_{\text{diss}}$  and W/D whereas rivers from the Orinoco River from Huh et al.

641 (2001) have intermediate to high W/D (Edmond et al., 1995, 1996), and therefore plot on the negative trend  
642 between  $\delta^7\text{Li}_{\text{diss}}$  and W/D. We note that Andean rivers from the study of Huh et al. (2001) have been  
643 sampled downstream the floodplain, which may explains their very high  $\delta^7\text{Li}_{\text{diss}}$  value.

644 Altogether, these relationships between  $\delta^7\text{Li}$ , dissolved Li flux, weathering intensity and denudation can  
645 be used to constrain paleo weathering and erosion conditions from past Li isotope composition records  
646 (Hathorne and James, 2006; Misra and Froelich, 2012; Pogge von Strandmann et al., 2013).

## 647 7. Conclusions and global implications

648 The Li isotope composition of the Amazon River dissolved load displays a large range of variation from  
649  $+1\text{‰}$  to  $+32\text{‰}$ , in relation with the geomorphic regime. We show that the partitioning of Li between the  
650 dissolved load and solid weathering products ( $f_{\text{diss}}^{\text{Li}}$  values) governs the Li isotope composition of the dissolved  
651 load. Congruent release of Li results in rock-like  $\delta^7\text{Li}$  values, while extensive Li incorporation (and associated  
652 Li isotope fractionation) in secondary weathering products drives dissolved Li isotope composition toward  
653 higher values. We calculate a single isotope fractionation factor  $\alpha_{\text{sec-dis}}$  associated with secondary mineral  
654 precipitation in soils of  $0.983 \pm 0.002$ . This isotope fractionation factor value does not depend on the type  
655 of secondary minerals formed and is in good agreement with the values from the experimental studies of  
656 Vigier et al. (2008) and Millot et al. (2010b).

657 These conclusions are consistent with previous interpretation of the Li isotope composition in rivers and  
658 sedimentary archives (Misra and Froelich, 2012; Bouchez et al., 2013; Li and West, 2014). However, although  
659 a seawater record of Li isotope composition can be interpreted in a relatively straightforward way in terms  
660 of Li mass balance, we show how its translation in terms of (present or past) weathering regime is equivocal :

661 – First, in the Amazon Basin, lowland rivers characterized by "supply-" or "transport-limited" regimes  
662 do not necessarily show congruent Li release, and hence display a large range of dissolved  $\delta^7\text{Li}$  values  
663 (from  $+1.2$  to  $+16\text{‰}$  ). Relatedly, rock-like  $\delta^7\text{Li}$  values are observed at both ends of the weathering  
664 regime spectrum, *i.e.* in lowland settings (*e.g.* Negro River) and in high mountain belts (*e.g.* Beni  
665 headwaters). This is because these radically different weathering regimes can lead to similar Li mass  
666 balance ("congruent weathering") from the perspective of the dissolved load. Therefore, low  $\delta^7\text{Li}$  values  
667 in sedimentary archives (as observed for the early Cenozoic ; Misra and Froelich, 2012) can in principle  
668 be interpreted as reflecting the predominance of supply-limited regimes or of high-erosion settings.  
669 In such cases, additional constraints (*e.g.* geological arguments or other stable isotope systems with  
670 different sensitivity along the spectrum of weathering regimes) are needed to distinguish between  
671 these two interpretations. We propose here that the dissolved Li flux can also serve for a better  
672 reconstruction of past denudation rates (Li and West, 2014) as high Li dissolved fluxes correspond  
673 only to high denudation rates.

674 – Second, dissolved  $\delta^7\text{Li}$  signatures at the outlet of large rivers are influenced by lowland processes that  
675 differ drastically from those prevailing on hillslopes of eroding upland areas. Dissolved Li released by  
676 weathering reactions in high-erosion settings is significantly retained in floodplains through interaction  
677 with solid particles, resulting in Li isotope fractionation. As this process (1) traps a large fraction of  
678 the river dissolved Li flux and (2) obeys a Rayleigh mass balance model with a fractionation factor  
679  $\alpha_{\text{sec-dis}}$  of 0.991, it can drive the residual dissolved  $\delta^7\text{Li}$  toward extremely high values. Therefore, Li  
680 isotope composition of large rivers at their mouth, and hence past variations in the ocean  $\delta^7\text{Li}$ , are  
681 not simply the conservative mixture of the various tributaries but might well also reflect variations

682 in the global extent and style of weathering processes affecting Li in river floodplains. The relative  
 683 influence of hillslope and floodplain processes on the global riverine dissolved  $\delta^7\text{Li}$  and weathering  
 684 rates in general remains to be quantified, for both present-day conditions and past variations.

685 **Appendix A : the inversion mixing model between rain, evaporites, carbonates, shales and**  
 686 **igneous rocks**

687 The inverse mixing model used here is similar to one by Gaillardet et al. (1997) applied to the Amazon  
 688 Basin. The main difference is that in the Madeira and Solimões tributaries, we consider two silicate end-  
 689 members (igneous rocks and shales) instead of one as in Gaillardet et al. (1997). For each dissolved species  
 690 (X) of a river, the following mixing equations are :

$$\left(\frac{X}{\text{Na}}\right)^{\text{diss}} = \sum_i \left(\frac{X}{\text{Na}}\right)_i^{\text{diss}} \gamma_i^{\text{Na}} \quad (10)$$

$$\left(\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}\right)^{\text{diss}} \left(\frac{\text{Sr}}{\text{Na}}\right)^{\text{diss}} = \sum_i \left(\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}\right)_i^{\text{diss}} \left(\frac{\text{Sr}}{\text{Na}}\right)_i^{\text{diss}} \gamma_i^{\text{Na}} \quad (11)$$

691 with  $X = \text{Sr}, \text{Ca}, \text{Mg}, \text{HCO}_3$ ;  $i = \text{rain, evaporite, shale, igneous rock and carbonate}$  and  $\gamma_i^{\text{Na}}$  is the  
 692 proportion of dissolved sodium deriving from the end-member  $i$ . For example,  $(\text{Sr}/\text{Na})_{\text{sha}}$  is the Sr/Na ratio  
 693 of water interacting only with shale lithology. The mixing model is solved by an inverse method similar  
 694 to the one used by Gaillardet et al. (1997). This inverse method requires defining "a priori" values for all  
 695 parameters and yields "a posteriori" values as a best fit between the model and parameters.

696 For the rain, carbonate and evaporite end-member, we use the same Na-normalized ratios as Gaillardet  
 697 et al. (1997) except for  $(\text{Sr}/\text{Na})_{\text{ev}}$ . Indeed, we note that the Huallaga River, which chemistry is dominated  
 698 by evaporite input ( $\text{Cl}/\text{Na} = 1$ ) has a Sr/Na ratio of  $1 \times 10^{-3}$ , lower than the Sr/Na of the evaporite  
 699 end-member of  $3 \times 10^{-3}$  reported by Gaillardet et al. (1997) and based on salt springs from Stallard and  
 700 Edmond (1983). Therefore, here we use an intermediate mean  $(\text{Sr}/\text{Na})_{\text{ev}}$  value of  $2 \pm 1 \times 10^{-3}$  to correct  
 701 for Sr deriving from evaporite dissolution.

702 The shale weathering end-member can be constrained using the chemical composition of the Challana  
 703 and Chepete rivers, which only drain shales. We estimate the respective values for the shale end-member  
 704 from the chemical composition of these two rivers, corrected from atmospheric inputs :  $(\text{Ca}/\text{Na})_{\text{sha}} = 0.4 \pm$   
 705  $0.2$ ,  $(\text{Mg}/\text{Na})_{\text{sha}} = 0.5 \pm 0.3$ ,  $(\text{HCO}_3/\text{Na})_{\text{sha}} = 1.5 \pm 1.0$ ,  $(\text{Sr}/\text{Na})_{\text{sha}} = 1.5 \pm 0.5$ ,  $({}^{87}\text{Sr}/{}^{86}\text{Sr})_{\text{sha}} = 0.732 \pm$   
 706  $0.005$ . The error bar reflects our knowledge of the parameters.

707 The igneous rocks in the Solimões basin are andesites in the north (Napo, Pastaza and Morona rivers) and  
 708 both andesites and granodiorites in the south (Maronon, Huallaga and Ucayali). The  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  of andesites  
 709 in Ecuador display a very narrow range of values with a mean value of  $0.7042 \pm 0.0003$  (Bryant et al., 2006).  
 710 Similarly, the  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  of Andean granodiorites (in the Solimões river Basin) has a narrow range of value  
 711 of  $0.7050 \pm 0.0005$  (Petford and Atherton, 1996). Therefore, we can estimate that the Sr isotope ratio of  
 712 the igneous rock weathering end-member is  $({}^{87}\text{Sr}/{}^{86}\text{Sr})_{\text{ign}} = 0.7050 \pm 0.0005$ . Our dataset does not include  
 713 any river draining only igneous rocks, but the chemical composition of this end-member can be constrained  
 714 of the Coca River (Santos et al., 2014), which drains predominantly igneous rocks. Its  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  is as low  
 715 as  $0.7055$  (Santos et al., 2014), lower than any other published data from the Solimões basin (including our  
 716 dataset) and very close to the value of the  $({}^{87}\text{Sr}/{}^{86}\text{Sr})_{\text{ign}}$  end-member. According to Moquet et al. (2011) the  
 717 contribution of evaporites and carbonate weathering to the Coca River is low but not negligible. Using the

718 results of Moquet et al. (2011), we can correct the data for the Coca river (Santos et al., 2014) from carbonate  
 719 and evaporite inputs to estimate the composition of the pure igneous rock end-member :  $(\text{Ca}/\text{Na})_{\text{ign}} = 0.8$   
 720  $\pm 0.3$ ,  $(\text{Mg}/\text{Na})_{\text{ign}} = 0.3 \pm 0.2$ ,  $(\text{HCO}_3/\text{Na})_{\text{ign}} = 3.7 \pm 0.7$  and  $(\text{Sr}/\text{Na})_{\text{ign}} = 4.8 \pm 0.6$ .

## 721 Appendix B : determination of the $(\text{Li}/\text{X})_0$ and $f_{\text{diss}}^{\text{Li}}$ values

722 The fraction of Li left in solution after secondary solids formation can be calculated using Eq. (5). With  
 723 the example of sodium, the  $(\text{Li}/\text{Na})_0$  can be calculated by the following Equation (12) :

$$\left(\frac{\text{Li}}{\text{Na}}\right)_0 = \sum_i \left(\frac{\text{Li}}{\text{Na}}\right)_i^{\text{rock}} \gamma_i^{\text{Na}} \quad (12)$$

724 Where  $\gamma_i^{\text{Na}}$  are the mixing proportions of each source i calculated by the equations (10) and (11) and  
 725  $(\text{Li}/\text{Na})_i^{\text{rock}}$  the ratio  $(\text{Li}/\text{Na})$  of the rock source i.

726 Na and Mg can both be used as conservative tracers, each of them presenting advantages and caveats.  
 727 In some contexts Mg can be incorporated significantly in secondary minerals like smectite. In addition, part  
 728 of the dissolved Mg derives from carbonate weathering (Gaillardet et al., 1997; Moquet et al., 2011) or in  
 729 the case of some Solimões catchments from the weathering of gypsum (Moquet et al., 2011). Therefore,  
 730 an additional correction is needed to obtain silicate-derived Mg whereas  $\text{Na}^*$  can be directly used as  $\text{Na}_{\text{sil}}$ .  
 731 However, Li and Mg are contained in the same primary minerals phases because they have a similar ionic  
 732 radius, and hence are most likely released stoichiometrically into solution (Huh et al., 1998). Moreover, Mg  
 733 concentrations are weakly influenced by rainwater and evaporite contribution compared to sodium. This can  
 734 be critical in the case of very dilute waters like in rivers draining Amazonian shield where cyclic sodium  
 735 correction results in large uncertainties in the determination of  $\text{Na}^*$  (Gaillardet et al., 1997). In this study,  
 736 we use Li/Na ratios for Anean rivers and both Li/Na and Li/Mg ratios for shield rivers.

### 737 Estimation of the $(\text{Li}/\text{Na})_0$ ratio in the Madeira and Solimões river basins

738 In the Madeira river basin, the lithology is uniform and corresponds almost exclusively to Paleozoic (in  
 739 the Andes) and Tertiary (in the lowlands) sedimentary rocks having a shale-type composition (Stallard and  
 740 Edmond, 1983; Roddaz et al., 2005). The largest database of Li concentrations in shales is from Ronov et al.  
 741 (1970). According to Holland (1984) and based on the database of Ronov et al. (1970), the mean Li and  
 742 sodium ( $[\text{Na}_2\text{O}]$ ) concentrations of the shales of the Russian Platform are respectively 80 ppm and 0.081% (N  
 743  $\sim 500$ ) so the mean molar Li/Na ratio is  $0.040 \pm 0.05$ . This value is similar to the mean chemical composition  
 744 of the Beni river bed sands ( $\text{Li}/\text{Na} = 0.041$ ,  $n = 3$ ), that integrate the bedrock variability at the scale of the  
 745 Beni watershed (Dellinger et al., 2014). In the Solimões river basin, igneous rocks contributes significantly  
 746 to the weathering budget. For the igneous rock end-member, the andesite median Li/Na compiled from the  
 747 Georoc database (<http://georoc.mpch-mainz.gwdg.de/georoc/>; Sarbas and Nohl, 2008) is  $0.0014 \pm 0.0003$   
 748 ( $2\sigma/\sqrt{N}$ ,  $N = 1600$ ), and the granodiorite median Li/Na is  $0.0049 \pm 0.0013$  ( $2\sigma/\sqrt{N}$ ,  $N = 60$ ). Therefore  
 749 we use an intermediate value of  $0.0030 \pm 0.0015$  for the igneous rock end-member.

### 750 Estimation of the $(\text{Li}/\text{Na})_0$ and $(\text{Li}/\text{Mg})_0$ ratio in the shield river basins

751 According to Gaillardet et al. (1997), weathering of Brazilian and Guiana shields operate at steady state  
 752 over a bedrock having a mean chemical composition similar to UCC (Taylor and McLennan, 1985) which  
 753 has typically the composition of a granodiorite. We can use the correlations defined by the rivers draining

754 the shield rocks in the Fig. (5) to infer the  $(\text{Li}/\text{Na})_0$ ,  $(\text{Li}/\text{Mg})_0$  and  $\delta^7\text{Li}$  of shield rivers source rocks. The  
755 best correlation is obtained for the Li/Mg ratio, uncorrected for carbonate input despite evidence from the  
756 inversion of river chemistry that carbonates are contributing to the dissolved load (Gaillardet et al., 1997).  
757 However, more recent studies stated that the Mg/Na variability of rivers draining shield rock in tropical area  
758 is inherited from bedrock variability rather than due to mixing with Mg deriving from limestone weathering  
759 (Viers et al., 2000; Gurumurthy et al., 2012). Therefore, here we consider that all the Mg derives from silicate  
760 weathering. In the Fig. (5), the intercept between the river trend and the mixing trend between granodiorites  
761 and shales should give the mean composition of the source rocks. We calculate an intercept source rock  $\delta^7\text{Li}$   
762 value of  $+1 \pm 1\%$ , and a Li/Mg and Li/Na values of  $0.014 \pm 0.003$  and  $0.061 \pm 0.010$  respectively. This  
763 intercept has a Li/Mg and Li/Na ratio slightly higher than the mean value for the granodiorite (Fig. 5).  
764 We propose that this is due to a slight input of shales weathering as some outcrops of sedimentary rocks  
765 has been described in the shield and the Amazon trough (Brinkmann, 1986; Stallard and Edmond, 1983).  
766 This corresponds to a input of 5 to 15% of total  $(\text{Na})_{\text{sil}}$  and  $(\text{Mg})_{\text{sil}}$  deriving from the weathering of shales.  
767 The  $f_{\text{diss}}^{\text{Li}}$  values calculated with sodium ranges from 0.25 to 0.76 and with Mg from 0.16 to 1.00. There is  
768 generally less than 20% difference between the two estimate and therefore we use the mean value between  
769 the  $f_{\text{diss}}^{\text{Li}}$  determined with Na and Mg.

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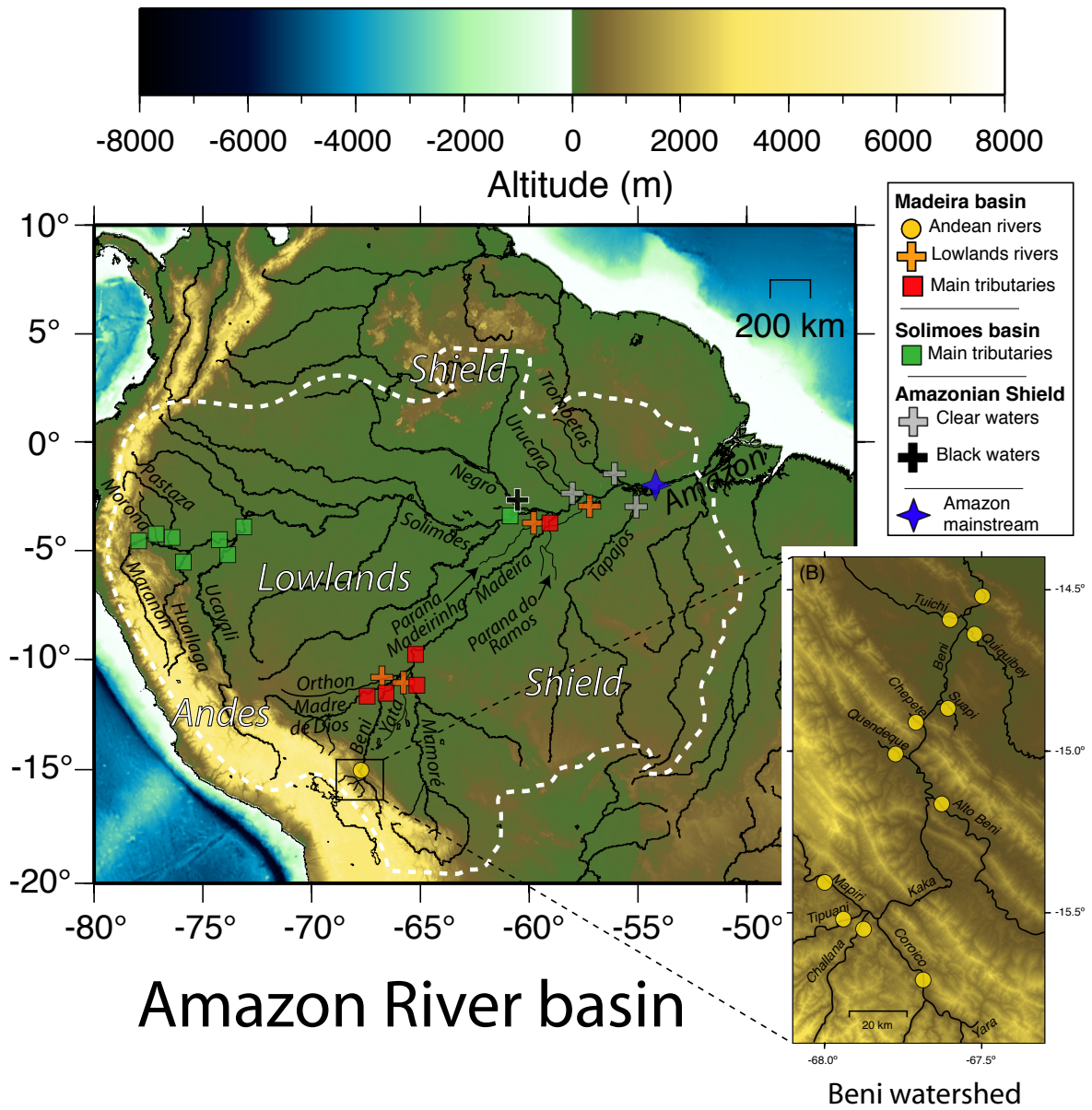


FIGURE 1: Map of the Amazon River basin with the location of river samples.

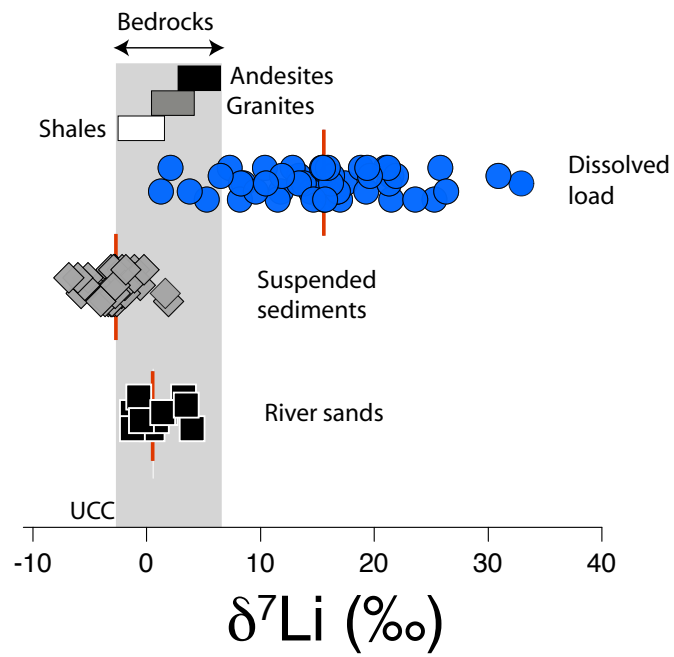


FIGURE 2: Li isotope composition in Amazon river-borne material. The red marker indicates the mean isotope composition in each component. Suspended sediment and sands data are from Dellinger et al. (2014). Reported bedrock data are global mean  $\delta^7\text{Li}$  of shales ( $-0.5 \pm 1.9\text{‰}$ ), andesites ( $+4.8 \pm 1.4\text{‰}$ ) and granodiorites ( $+2.0 \pm 2.2\text{‰}$ ) from the literature compiled in Dellinger et al. (2014).

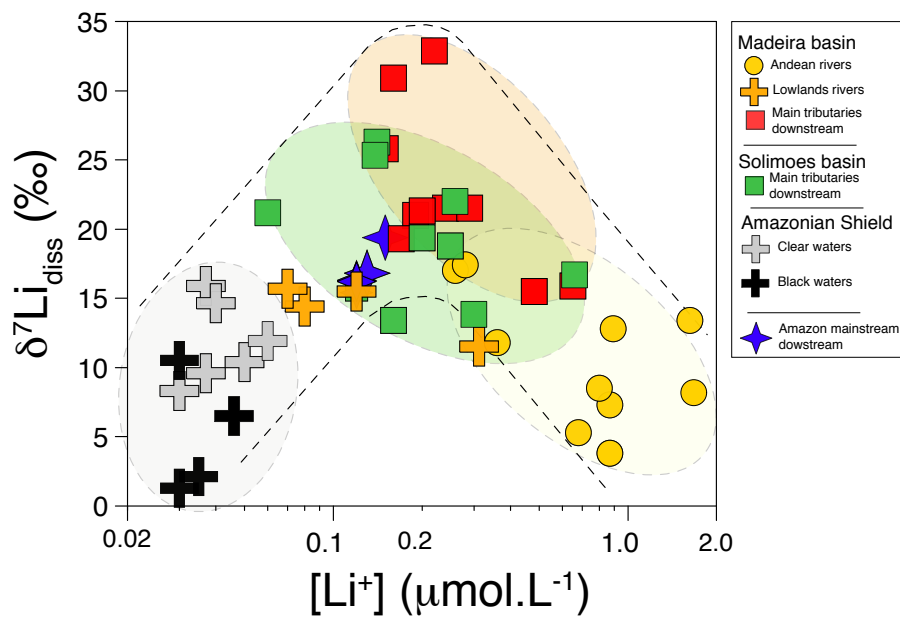


FIGURE 3: Li isotope composition ( $\delta^7\text{Li}_{\text{diss}}$ ) as a function of the Li concentration in the dissolved load. Data from Huh et al. (1998) of Amazon tributaries (Negro, Solimões, Madeira and Amazon) are also displayed on this figure and the following figures of this publication.

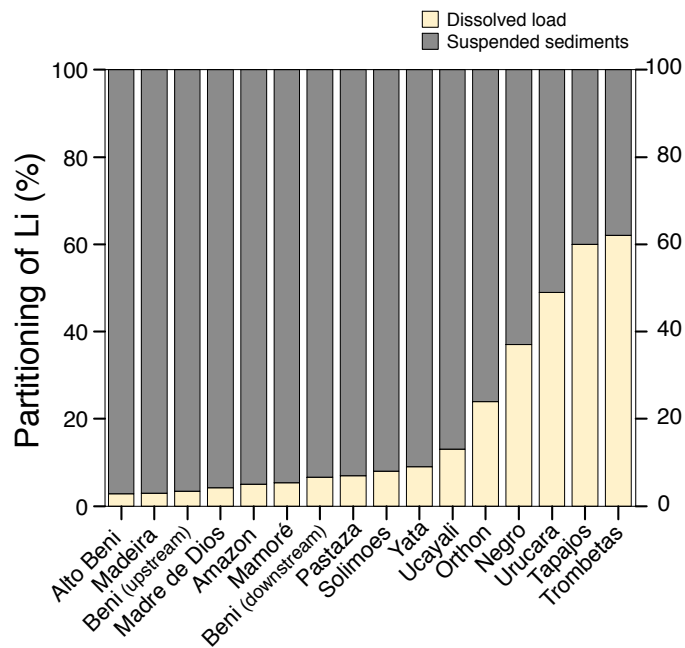


FIGURE 4: Partitioning of Li between the dissolved and particulate load. Only Li concentration measured in surface suspended sediments was used in Eq. (1).



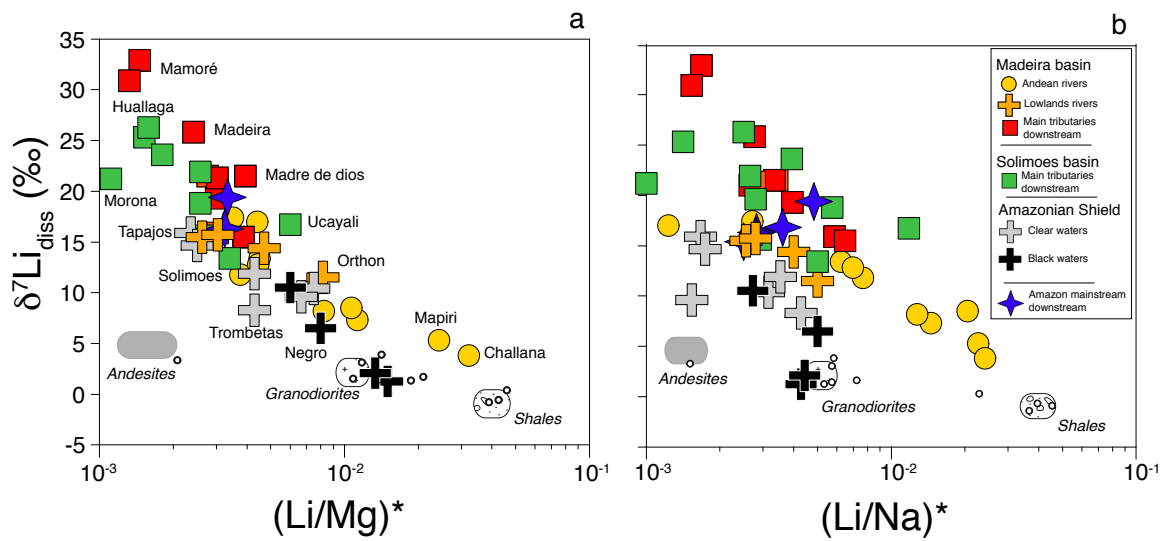


FIGURE 5: Dissolved Li isotope composition ( $\delta^7\text{Li}$ ) vs a)  $(\text{Li}/\text{Mg})^*$  and b)  $(\text{Li}/\text{Na})^*$  molar ratios. The superscript "\*" indicates that molar ratios are corrected for rainwater and evaporite inputs. Typical bedrock ratios and Amazon river sands are added for comparison.

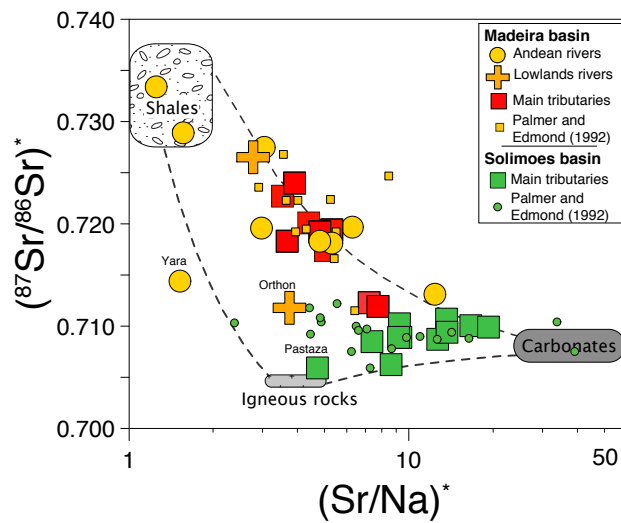


FIGURE 6: Dissolved  $(^{87}\text{Sr}/^{86}\text{Sr})^*$  versus  $(\text{Sr}/\text{Na})^*$  in the Amazon River system. The superscript "\*" means that the data are corrected for rainwater and evaporite inputs. "Igneous rocks" refers to Andean andesites and granodiorites in the Amazon Basin

. Data from Palmer and Edmond (1992) are also represented while rivers draining only the Brazilian and Guiana shield are not displayed. The endmembers (shale, igneous rocks and carbonates) correspond to the chemical composition of water masses draining each type of rock and defined in Appendix A.

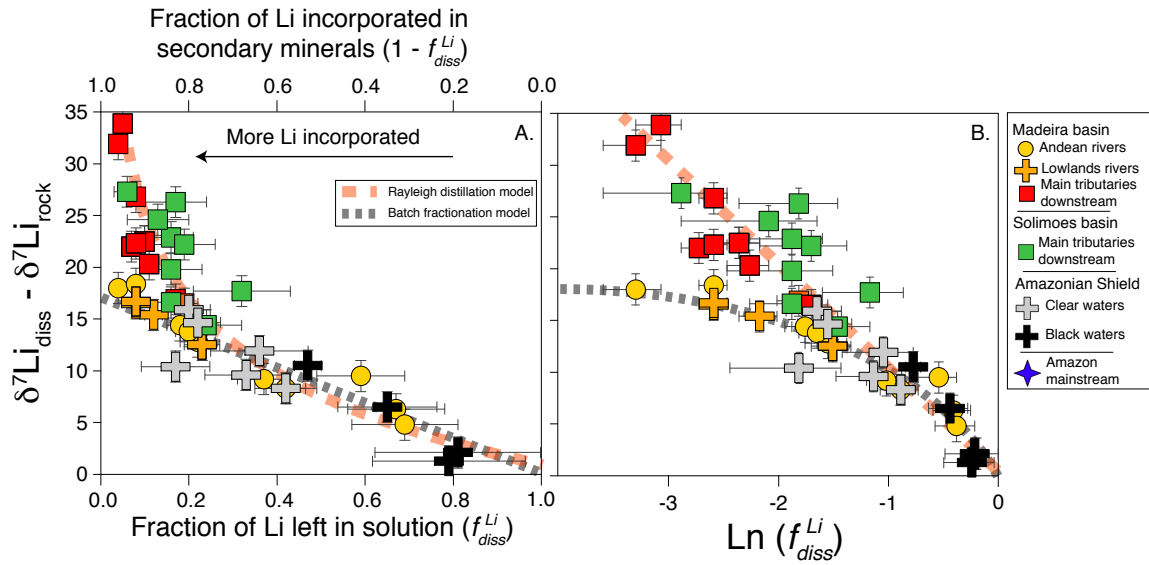


FIGURE 7: Li isotope composition of the dissolved load corrected from the composition of the bedrock ( $\delta^7\text{Li}_{\text{diss}} - \delta^7\text{Li}_{\text{rock}}$ ) vs. a) the fraction of Li remaining in solution ( $f_{\text{diss}}^{\text{Li}}$ ) and b) the natural logarithm of  $(1 - f_{\text{diss}}^{\text{Li}})$ . The fitted expected Rayleigh distillation and "batch" trends are represented in red and black dotted lines respectively. The  $\delta^7\text{Li}_{\text{rock}}$  corresponds to the  $\delta^7\text{Li}_0$  calculated for each river using the mixing proportion of Li given in the Table (7) and the mean Li isotope composition of each bedrock. For rivers draining only shales, the right Y-intercept of the line in the  $\delta^7\text{Li}_{\text{diss}} - f_{\text{diss}}^{\text{Li}}$  space gives an accurate estimate of the source shale bedrock of  $-1.0 \pm 0.3\text{‰}$ .

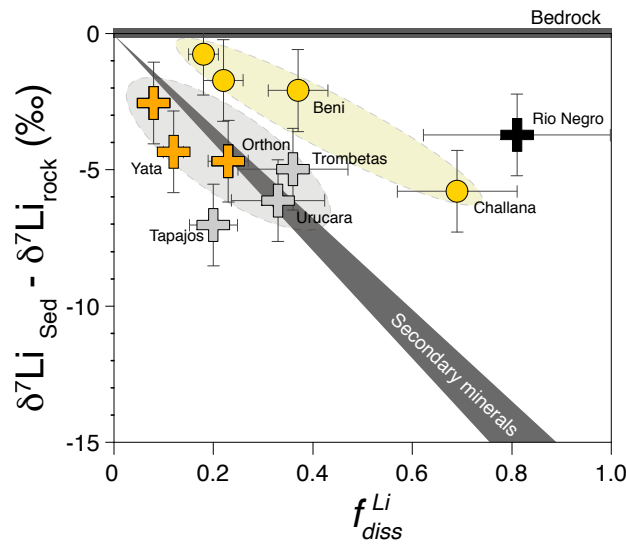


FIGURE 8: The  $(\delta^7\text{Li}_{\text{sed}} - \delta^7\text{Li}_{\text{rock}})$  as a function of the fraction of Li remaining in solution ( $f_{\text{diss}}^{\text{Li}}$ ). Here "sed" refers only to surface suspended sediments. The grey envelope corresponds to the theoretical Li isotope composition predicted by a "batch" fractionation model with a fractionation factor of  $0.983 \pm 0.002$ . The black line corresponds to the isotope composition of the bedrock.

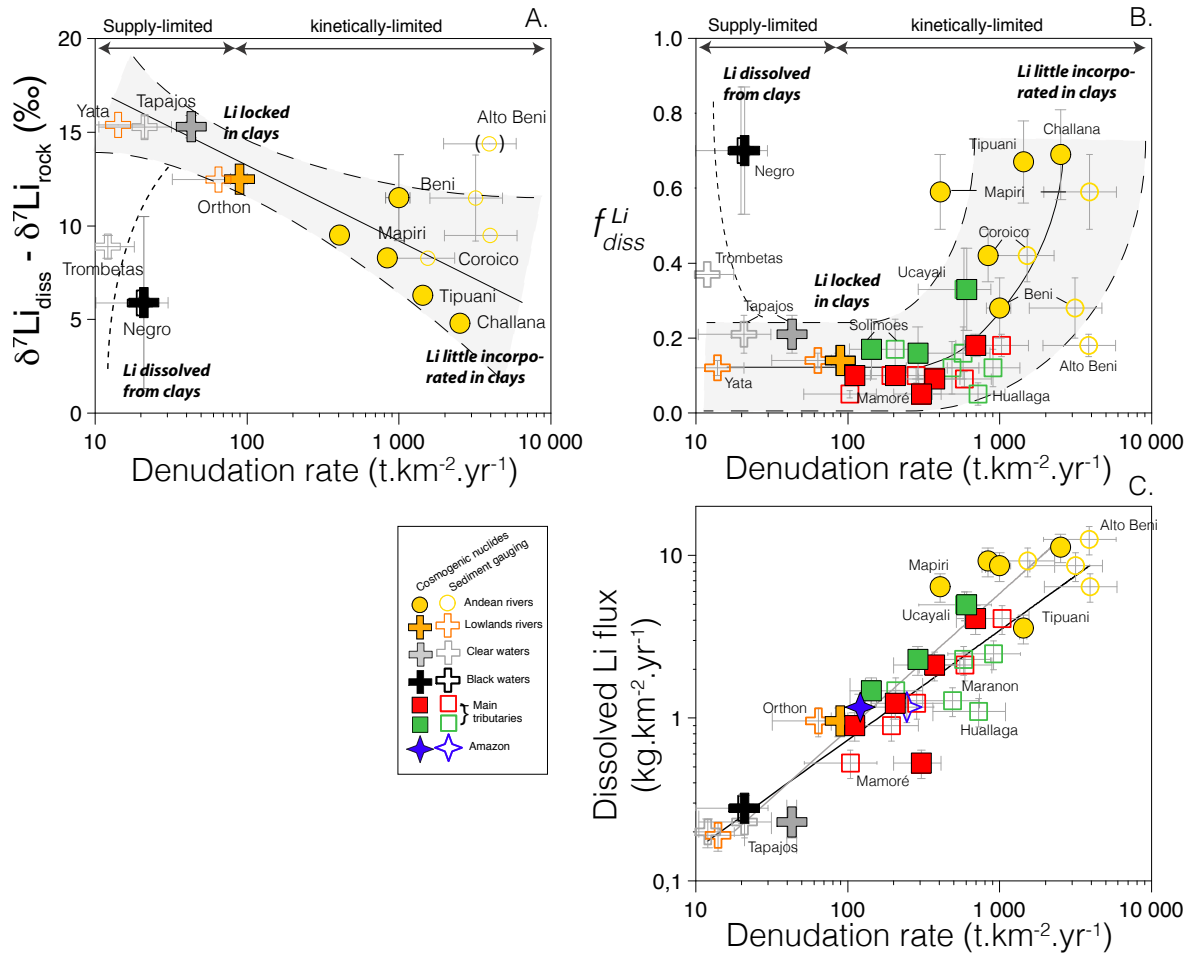


FIGURE 9: a) Li isotope composition of the dissolved load corrected from the composition of the bedrock ( $\delta^7Li_{diss} - \delta^7Li_{rock}$ ) as a function of denudation rates for rivers fitting the "batch" fractionation model. The other rivers are not represented on this diagram. Both cosmogenic nuclide-derived (closed symbols) and sediment gauging-derived (open symbols) denudation rates are represented. The black line represents the correlation between  $\delta^7Li_{diss} - \delta^7Li_{rock}$  and the denudation rate and is similar to the trend modelled by Bouchez et al. (2013). The Alto Beni river does not plot on the correlation defined by other rivers, its present-day denudation flux might be too high because of recent mobilization of plio-quaternary sediments (Dosseto et al., 2006b). (b) fraction of Li left in solution ( $f_{diss}^{Li}$ ) as the function of the denudation rate.  $f_{diss}^{Li}$  values are less than 0.2 for denudation rates inferior to  $1000 t \cdot km^{-2} \cdot yr^{-1}$  and increase for higher denudation rates (c) Specific dissolved flux of lithium as a function of the denudation rate. The black line represents the best fit for the sediment-gauging derived denudation rate ( $r^2 = 0.91$ ), the grey line represents the best fit for the cosmogenic derived denudation rate ( $r^2 = 0.78$ )

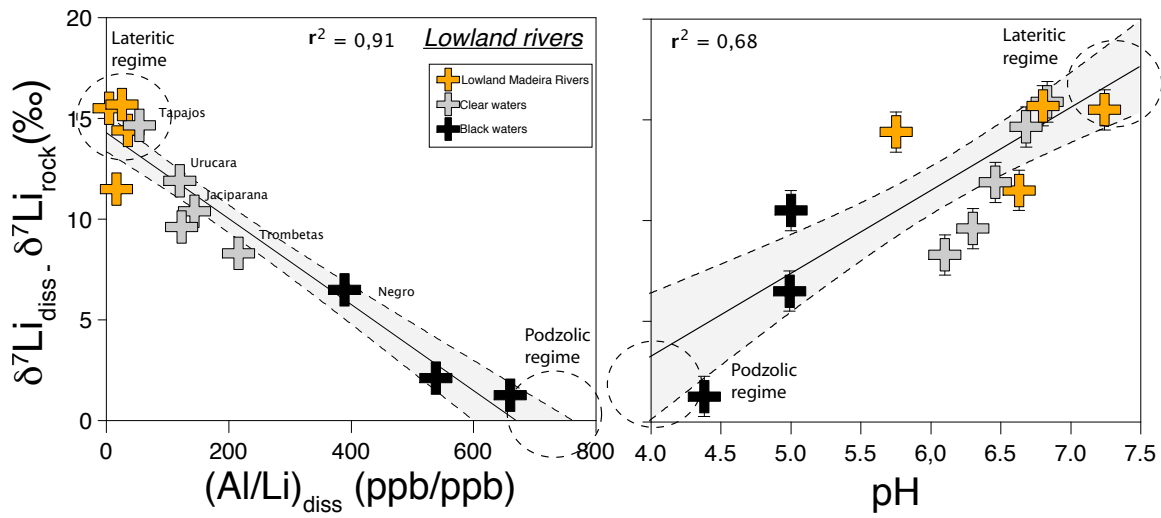


FIGURE 10: Dissolved Li isotope composition corrected from the composition of the bedrock ( $\delta^7\text{Li}_{\text{diss}} - \delta^7\text{Li}_{\text{rock}}$ ) of the lowland rivers vs. the dissolved Al/Li ratio and pH. River samples can be interpreted as mixture of two types of waters derived from podzolic and lateritic regimes of weathering.

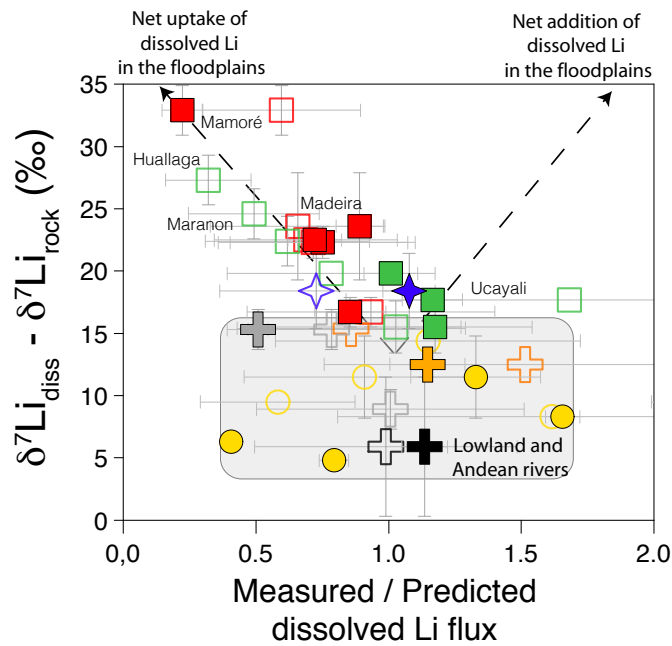


FIGURE 11: Dissolved Li isotope composition corrected from the composition of the bedrock  $\delta^7\text{Li}_{\text{diss}} - \delta^7\text{Li}_{\text{rock}}$  vs. the ratio between the predicted and measured dissolved Li flux. The predicted dissolved Li flux is calculated using the equation of the correlation of Fig. (9c) for both cosmogenic nuclides and sediment gauging-derived denudation rates.

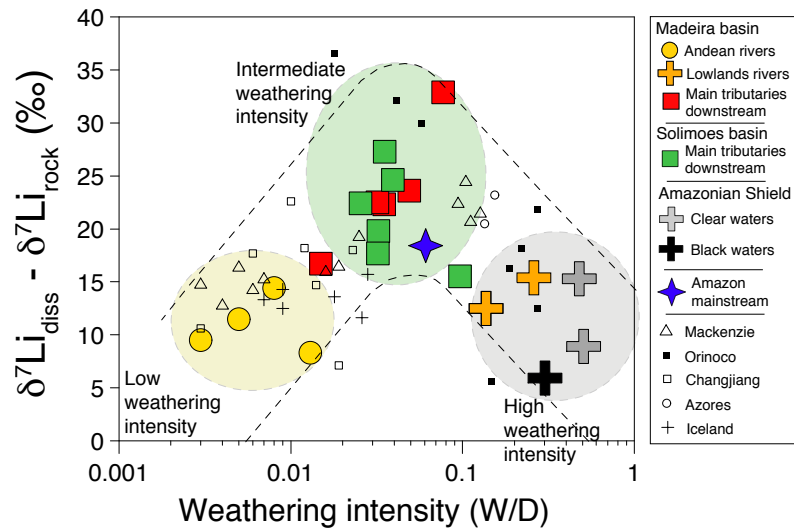


FIGURE 12: Dissolved Li isotope composition corrected from the composition of the bedrock  $\delta^7\text{Li}_{\text{diss}} - \delta^7\text{Li}_{\text{Rock}}$  vs. silicate weathering intensity, calculated as the ratio between silicate chemical weathering rates and total denudation rate (inferred from decadal sediment gauging measurements). Lithium isotope data for other river systems are from Huh et al. (2001); Pogge von Strandmann et al. (2006, 2010); Vigier et al. (2009); Millot et al. (2010c); Wang et al. (2015) Rivers influenced by hydrothermal weathering are not plotted on this figure because their Li isotope composition is controlled by the input from hot springs (Henchiri et al., 2014) rather than the weathering intensity. References for the compiled or calculated weathering intensity data are given in supplementary materials (table S3).

1027 **List of captions**

1028 Table 1 : Dissolved major and trace element concentrations and Li-Sr isotope composition of rivers. All  
1029 concentrations are in  $\mu\text{mol.L}^{-1}$  except Al concentrations (in ppb)

1030 Table 2 : Li concentration and isotope composition of Amazon tributaries surface sediments

1031 Table 3 : Proportion of lithium initially dissolved from each source, and fraction of silicate-derived Li  
1032 incorporated in secondary minerals

Table 1

Sample	Rivers	Location	pH	Surface SPM (mg/L)	$\delta^7\text{Li}$ (‰)	Li	Na	K	Mg	Ca	HCO <sub>3</sub>	Cl	NO <sub>3</sub>	SO <sub>4</sub>	NICB	SiO <sub>2</sub>	<sup>87</sup> Sr/ <sup>86</sup> Sr	Sr	Al (ppb)
<i>Madeira Basin</i>																			
AM01-01	Huarinilla	-	-	-	11.8	0.36	51	8	97	41	207	4	15	49	2.6	117	0.72740	0.14	17
AM01-02	Yara	-	-	-	-	0.56	44	3	34	17	-	1	16	44	-	-	0.71442	0.07	15
AM01-03	Yara	-	-	-	-	0.82	90	16	120	90	197	7	24	143	2.5	149	-	0.24	22
AM01-04	Coroico	Guanay	6.5	387	7.3	0.87	62	12	78	55	116	2	14	95	5.1	136	-	0.14	14
AM01-05	Tipuani	Guanay	5.7	1518	5.3	0.68	31	16	28	14	9	2	5	57	0.1	101	-	0.05	4
AM01-06	Challana	Guanay	6.4	1610	3.8	0.87	37	12	28	12	16	1	15	48	1.5	114	0.73331	0.05	15
AM01-07	Mapiri	Guanay	7.2	1620	8.5	0.80	44	16	75	119	-	6	-	6	-	107	0.71969	0.25	10
AM01-08	Alto Beni	Mouth	7.8	8399	13.4	1.62	282	57	359	416	875	25	7	443	5.1	124	0.71921	0.80	20
AM01-09	Quendeque	Mouth	7.4	-	-	0.10	34	24	59	228	484	2	12	67	0.2	89	0.71311	0.41	32
AM01-10	Chepete	Mouth	7.2	1111	17.0	0.26	222	32	60	105	461	12	5	53	0.0	-	0.72847	0.34	8
AM01-11	Suapi	Mouth	7.2	141	-	0.15	39	36	45	202	415	3	12	52	6.3	128	-	-	14
AM01-12	Quiquibey	Mouth	7.5	1895	17.4	0.28	106	43	80	324	821	3	10	54	1.6	-	-	-	11
AM01-13	Tuichi	Mouth	6.4	3590	-	0.53	44	25	54	106	100	2	3	142	0.1	87	0.72103	-	8
AM01-14	Beni	Rurrenabaque	7.4	5265	12.8	0.89	138	38	199	328	575	13	12	310	0.8	-	0.71816	0.61	21
AM07-04	Beni	Rurrenabaque	6.4	109	8.2	1.67	164	25	204	286	520	34	7	283	3.2	159	0.71759	0.74	-
AM01-16	Beni	Riberalta	7.0	1036	15.9	0.65	119	48	212	290	640	11	14	231	3.6	137	0.71932	0.58	28
AM07-09	Beni	Riberalta	6.7	1003	15.5	0.48	87	33	125	197	442	15	9	104	11.2	129	0.71911	0.40	-
AM01-15	Madre de Dios	Riberalta	6.9	950	21.5	0.24	72	30	61	171	435	3	11	57	0.6	139	0.71233	0.51	3
AM07-14	Madre de Dios	Riberalta	5.9	437	21.0	0.19	77	28	63	190	451	6	10	43	9.3	130	0.71191	0.56	-
AM01-17	Orthon	Mouth	6.6	460	11.5	0.31	66	41	39	62	256	4	4	3	12.9	-	0.71180	0.23	36
AM01-18	Yata	Mouth	5.8	56	14.4	0.08	22	15	18	12	63	2	4	1	24.6	91	0.72643	0.06	20
AM01-19	Mamoré	Guayaramerin	6.7	507	32.9	0.22	155	48	146	202	497	32	11	162	3.8	153	0.72157	0.48	8
AM07-19	Mamoré	Guayaramerin	6.5	156	30.9	0.16	137	71	122	162	484	35	7	77	11.9	197	0.72258	0.45	-
AM6/1-6	Parana Madeirinha	Mouth	7.2	-	15.5	0.12	108	23	45	205	510	68	-	25	0.2	-	-	-	4
AM6/1-11	Parana do Ramos	Mouth	6.8	-	15.7	0.07	40	15	25	61	179	18	1	15	0.5	-	-	-	13
AM01-20	Jaciparana	Mouth	-	-	10.4	0.06	23	28	8	12	76	4	7	2	1.5	112	0.75620	0.04	60
AM01-21	Madeira	Porto Velho	-	-	21.5	0.29	99	38	106	173	438	14	12	123	-2.2	139	0.71718	0.45	7
AM06-35	Madeira	Foz Madeira	6.9	219	19.3	0.17	58	32	58	101	274	17	12	49	1.8	125	-	0.30	5
AM05-16	Madeira	Foz Madeira	-	85	21.3	0.20	90	29	68	115	275	21	8	60	12.4	151	0.71816	0.27	3
<i>Solimoès Basin</i>																			
AM08-33	Maranon	Borja	8.1	845	21.9	0.26	185	25	100	455	773	92	11	120	15.4	176	-	-	-
AM08-34	Morona	Mouth	-	174	21.2	0.06	84	21	56	182	381	21	13	20	21.6	226	0.70629	0.58	-

Sample	Rivers	Location	pH	Surface SPM	$\delta^7\text{Li}$	Li	Na	K	Mg	Ca	HCO <sub>3</sub>	Cl	NO <sub>3</sub>	SO <sub>4</sub>	NICB	SiO <sub>2</sub>	<sup>87</sup> Sr/ <sup>86</sup> Sr	Sr	Al
AM08-36	Pastaza	Mouth	-	102	25.3	0.14	168	28	94	117	364	70	9	31	18.3	293	0.70629	0.56	-
AM08-38	Huallaga	Mouth	-	335	26.3	0.14	1660	32	96	653	986	1621	7	187	6.4	180	0.70904	1.52	-
AM08-40	Tigre	Nueva York	-	25	13.8	0.30	498	16	33	81	90	666	8	9	-5.3	159	0.71671	1.14	-
AM08-05	Amazonas	Tamshiyacu	7.4	344	18.8	0.25	397	36	97	607	1010	358	8	98	14.7	176	0.70917	1.20	-
AM08-24	Maranon	San Regis	7.4	177	23.6	0.12	477	29	82	502	803	445	-	76	16.3	182	0.70878	0.97	-
AM08-13	Ucayali	Jenaro Herrera	-	490	16.7	0.66	308	40	114	683	1109	254	16	128	15.8	153	0.70943	1.43	-
AM05-4	Solimoes	Manacapuru	6.8	283	15.6	0.12	125	25	48	213	-	86	13	27	-	180	-	-	-
AM06-15	Solimoes	Manacapuru	-	333	13.4	0.16	101	20	50	188	443	71	12	34	0.4	158	0.70918	0.53	-
<i>Amazon river mainstream</i>																			
AM05-13	Amazonas	Iracema	-	47	16.3	0.12	85	21	37	136	240	49	10	22	23.6	141	-	0.38	-
AM06-63	Amazonas	Obidos	6.8	127	15.4	0.12	105	21	39	165	355	64	10	22	11.6	146	-	0.44	-
AM05-37	Amazonas	Obidos	-	175	16.8	0.13	81	20	36	131	242	49	1	20	23.2	140	-	0.32	-
AM05-35	Amazonas	Obidos	-	318	16.2	0.12	86	21	38	138	241	49	4	21	26.2	144	-	0.33	-
AM05-39	Amazonas	Obidos	-	250	19.4	0.15	85	23	48	158	352	56	9	35	5.9	135	-	0.32	-
<i>Shield rivers</i>																			
AM6/1-20	Tapajós	Mouth	6.8	-	15.9	0.037	33	22	17.9	23.5	114	10.5	9.7	1.6	0.3	-	-	-	-
Tapajos 19	Tapajós	Mouth	6.7	6	14.7	0.039	33	21	17.0	21.0	114	12.0	-	3.0	-1.5	160	0.73317	0.10	15
AM6/1-13	Trombetas	Mouth	6.3	-	9.6	0.037	39	17	7.7	11.1	71	14.9	3.3	2.2	0.6	-	-	-	34
Trombetas 16	Trombetas	Mouth	6.1	13	8.3	0.037	31	23	9.0	11.0	39	21.0	-	4.0	27.7	103	0.73230	0.08	45
Urucara 10	Urucara	Mouth	6.5	8	11.9	0.049	35	36	16.0	35.0	140	21.0	-	6.0	0.0	105	0.72358	0.15	50
AM6/1-2	Rio Negro	Paricatuba	4.4	-	1.3	0.027	12	6	2.5	4.1	13	5.7	8.8	1.6	0.6	-	-	-	137
AM06-20	Rio Negro	Paricatuba	5.0	4	6.5	0.037	19	7	6.1	-	21	12.7	6.8	3.7	-	84	-	0.08	108
AM01-22	Rio Negro	Paricatuba	-	-	2.1	0.035	14	5	3.1	4.5	20	6.1	6.2	1.0	1.1	-	-	0.03	149



Table 2

Sample	Rivers	Li	$\delta^7\text{Li}$ MES
<i>Lowland and shield rivers</i>		ppm	
AM6/1-11	Parana dos Ramos	27	-3.6
AM01-17	Orthon	59	-5.7
AM01-18	Yata	100	-5.3
AM01-27	Trombetas	20	-5.1
AM01-22 MES Negro	Negro	44	-2.7
AM6/1-09 MES	Urucara	43	-4.0
AM6/1-20 Tapajos	Tapajos	24	-5.4
AM01-29	Tapajos	27	-6.0
<i>Madeira basin</i>			
AM01-01	Huarinilla	89	-2.7
AM01-06	Challana	91	-6.8
AM01-08	Alto Beni	79	-1.8

Table 3

Samples	Rivers	Location	fLi	Proportion of Li dissolved from each source (%)					$\delta^7\text{Li}_0$
				rain	eva	car	sha	ign	
<i>Madeira Basin</i>									
AM01-01	Huarinilla	-	0.22 ± 0.04	0.1	0.0	0.2	99.8	0.0	-1.0
AM01-02	Yara	-	0.38 ± 0.06	0.0	0.0	0.0	99.9	0.0	-1.0
AM01-03	Yara	-	0.28 ± 0.05	0.0	0.0	0.2	99.8	0.0	-1.0
AM01-04	Coroico	Guanay	0.42 ± 0.07	0.0	0.0	0.1	99.9	0.0	-1.0
AM01-05	Tipuani	Guanay	0.67 ± 0.11	0.0	0.0	0.0	100.0	0.0	-1.0
AM01-06	Challana	Guanay	0.69 ± 0.12	0.0	0.0	0.0	100.0	0.0	-1.0
AM01-07	Mapiri	Guanay	0.59 ± 0.10	0.0	0.0	0.2	99.7	0.0	-0.9
AM01-08	Alto Beni	Mouth	0.18 ± 0.03	0.0	0.0	0.4	99.6	0.0	-0.9
AM01-09	Quendeque	Mouth	0.09 ± 0.01	0.1	0.0	3.4	96.5	0.0	-0.1
AM01-10	Chepete	Mouth	0.04 ± 0.01	0.2	0.0	0.6	99.2	0.0	-0.8
AM01-11	Suapi	Mouth	0.12 ± 0.02	0.1	0.0	2.0	97.9	0.0	-0.5
AM01-12	Quiquibey	Mouth	0.08 ± 0.01	0.1	0.0	1.7	98.2	0.0	-0.5
AM01-13	Tiuchi	Mouth	0.36 ± 0.06	0.0	0.0	0.3	99.7	0.0	-0.9
AM01-14	Beni	Rurrenabaque	0.20 ± 0.03	0.0	0.0	0.6	99.4	0.0	-0.9
AM07-04	Beni	Rurrenabaque	0.37 ± 0.06	0.0	0.0	0.3	99.7	0.0	-0.9
AM01-16	Beni	Riberalta	0.17 ± 0.03	0.1	0.0	0.7	99.3	0.0	-0.8
AM07-09	Beni	Riberalta	0.19 ± 0.03	0.1	0.0	0.6	99.3	0.0	-0.8
AM01-15	Madre de Dios	Riberalta	0.10 ± 0.02	0.1	0.0	1.0	98.9	0.0	-0.7
AM07-14	Madre de Dios	Riberalta	0.07 ± 0.01	0.1	0.0	1.5	98.4	0.0	-0.6
AM01-17	Orthon	Mouth	0.23 ± 0.04	0.0	0.0	0.0	93.3	6.7	-0.6
AM01-18	Yata	Mouth	0.12 ± 0.02	0.1	0.0	0.2	99.7	0.0	-0.9
AM01-19	Mamoré	Guayaramerin	0.05 ± 0.01	0.0	0.0	0.1	99.9	0.1	-1.0
AM07-19	Mamoré	Guayaramerin	0.04 ± 0.01	0.0	0.0	0.1	99.9	0.1	-1.0
AM6/1-6	Parana Madeirinha	Mouth	0.08 ± 0.01	0.9	0.8	2.3	96.0	0.0	-0.4
AM6/1-11	Parana do Ramos	Mouth	0.08 ± 0.01	1.3	0.0	1.2	97.5	0.0	-0.7
AM01-21	Madeira	Porto Velho	0.10 ± 0.02	0.1	0.0	0.9	98.9	0.0	-0.8
AM06-35	Madeira	Foz Madeira	0.11 ± 0.02	0.5	0.0	0.9	98.6	0.0	-0.8
AM05-16	Madeira	Foz Madeira	0.08 ± 0.01	0.5	0.0	0.8	98.7	0.0	-0.8
Madeira (Huh et al.)	Madeira	Foz Madeira	0.08 ± 0.01	0.4	0.0	1.1	98.5	0.0	-0.7
<i>Solimoes Basin</i>									
AM08-33	Maranon	Borja	0.12 ± 0.04	0.0	0.0	0.2	85.1	14.6	-0.1
AM08-34	Morona	Mouth	0.17 ± 0.06	0.1	0.0	0.6	79.5	19.9	0.3
AM08-36	Pastaza	Mouth	0.17 ± 0.07	0.1	0.1	0.1	85.1	14.7	-0.1
AM08-38	Huallaga	Mouth	0.05 ± 0.03	0.0	0.6	0.1	97.3	2.0	-0.7
AM08-40	Tigre	Nueva York							
AM08-05	Amazonas	Tamshiyacu	0.16 ± 0.06	0.0	0.2	0.5	98.0	1.3	-0.7
AM08-24	Maranon	San Regis	0.12 ± 0.07	0.0	0.4	0.6	97.1	1.9	-0.6
AM08-13	Ucayali	Jenaro Herrera	0.33 ± 0.11	0.0	0.1	0.5	98.2	1.2	-0.8
AM05-4	Solimoes	Manacapuru	0.14 ± 0.04	0.1	0.1	0.3	92.8	6.7	-0.5
AM06-15	Solimoes	Manacapuru	0.21 ± 0.07	0.1	0.1	0.3	94.9	4.6	-0.6
Solimoes (Huh et al.)	Solimoes	Iquitos	0.13 ± 0.04	0.0	0.1	0.5	95.8	3.6	-0.6
<i>Shield rivers</i>									
AM6/1-20	Tapajós	Mouth	0.20 ± 0.05	1.4	0.0	0.9	30.0	67.7	1.3
Tapajos 19	Tapajós	Mouth	0.22 ± 0.05	1.5	0.0	0.8	30.0	67.7	1.3
AM6/1-13	Trombetas	Mouth	0.33 ± 0.09	2.0	0.0	0.4	30.0	67.6	1.2
Trombetas 15	Trombetas	Mouth	0.42 ± 0.05	2.7	0.0	0.4	30.0	66.9	1.1
Urucara 10	Urucara	Mouth	0.36 ± 0.11	2.0	0.0	0.9	30.0	67.0	1.3
AM6/1-2	Rio Negro	Paricatuba	0.79 ± 0.17	1.1	0.0	0.1	30.0	68.8	1.1
Negro (Huh et al.)	Rio Negro	Paricatuba	0.47 ± 0.03	1.1	0.0	0.2	30.0	68.7	1.1
AM06-20	Rio Negro	Paricatuba	0.65 ± 0.11	1.7	0.0	0.0	30.0	68.4	1.1
AM01-22	Rio Negro	Paricatuba	0.81 ± 0.19	0.9	0.0	0.0	30.0	69.1	1.1
AM01-20	Jaciparana	Mouth	0.17 ± 0.08	0.1	0.0	0.3	30.0	69.0	1.2