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**Processes controlling  $\delta^7\text{Li}$  in rivers illuminated by study of streams and groundwaters draining basalts**

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25 **Abstract**

26 We evaluate the factors influencing the abundance, [Li], and isotopic composition of  
27 riverine Li delivered to the oceans through analyses and modeling of [Li] and  $\delta^7\text{Li}$  in streams and  
28 groundwaters draining a single continental lithology, the Columbia River Basalts (CRBs). The  
29 streams were sampled in different climate zones that lie east (dry), and west (wet) of the  
30 Cascades Mountains, and during two different seasons (summer and late winter) in order to  
31 evaluate climatic and seasonal influences on Li isotopes in rivers. Dissolved Li ( $\delta^7\text{Li}_{\text{dis}} = +9.3$  to  
32  $+30.4$ ) is systematically heavier than that of fresh or weathered CRBs ( $-4.7$  to  $+6.0$ , Liu et al.,  
33 2013, *GCA* 115, 73-91), suspended loads ( $-5.9$  to  $-0.3$ ), and shallow groundwaters ( $+6.7$  to  $+9.4$ ),  
34 consistent with previous studies showing that Li isotope fractionation is affected by equilibration  
35 between stream water and secondary minerals. However, the lack of correlation between  $\delta^7\text{Li}_{\text{dis}}$   
36 and climate zone, the uniform secondary minerals and bedrock, coupled with the highly variable  
37 ( $>20\%$ )  $\delta^7\text{Li}_{\text{dis}}$  indicate that other factors exert a strong control on  $\delta^7\text{Li}_{\text{dis}}$ . In particular, the  
38 heavier Li in streams compared to the shallow groundwaters that feed them indicates that  
39 continued isotopic fractionation between stream water and suspended and/or bed loads has a  
40 major influence on riverine  $\delta^7\text{Li}$ . Seasonal  $\delta^7\text{Li}$  variation is observed only for streams west of the  
41 Cascades, where the difference in precipitation rate between the dry and wet seasons is greatest.  
42 Reactive transport model simulations reveal that riverine  $\delta^7\text{Li}$  is strongly controlled by  
43 subsurface residence times and the Li isotope fractionation occurring within rivers. The latter  
44 explains why there is no positive correlation between  $\delta^7\text{Li}$  and traditional weathering proxies  
45 such as Si or normalized Si in rivers, as riverine Li isotope fractionation drives  $\delta^7\text{Li}$  to higher  
46 values during transport, whereas the concentrations of major cations and anions are diluted. The  
47 varying residence time for groundwaters feeding the western streams in summer (long residence  
48 times, higher  $\delta^7\text{Li}$ , greater weathering) and winter (short residence times, lower  $\delta^7\text{Li}$ , less  
49 weathering) explains the observed seasonal variations. A global, negative correlation between  
50  $\delta^7\text{Li}$  and Li/Na for streams and rivers draining basaltic catchments reflects the overall transport  
51 time, hence the amount of silicate weathering. Based on our results, the increase of  $\delta^7\text{Li}$  in  
52 seawater during the Cenozoic is unlikely related to changing climate, but may reflect mountain  
53 building giving rise to increased silicate weathering.

54

55 **Keywords:** lithium isotopes; chemical weathering; rivers and groundwaters, reactive transport  
56 modeling

57

## 58 **1. Introduction**

59 Chemical weathering of silicate rocks on Earth's surface plays a critical role in regulating  
60 the global carbon cycle over geological time-scales (e.g., Berner et al., 1983). Basalt weathering,  
61 in particular, may significantly contribute to the global silicate weathering flux. For example,  
62 Gaillardet et al. (1999), suggested a minimum of 25% of the silicate weathering flux to the  
63 oceans derives from weathering of basalt. Attempts to illuminate chemical weathering processes  
64 using natural samples generally take two approaches: studies of river waters (e.g., Dessert et al.,  
65 2001; Gaillardet et al., 1999), and studies of weathering profiles or weathered regoliths (e.g.,  
66 Brimhall et al., 1991; Nesbitt and Wilson, 1992). River chemistry is able to provide rate-related  
67 constraints, such as chemical weathering fluxes and CO<sub>2</sub> consumption rates (Gaillardet et al.,  
68 1999), although only for the present.

69 Li isotopes can potentially provide insights into the weathering flux from the continents  
70 over time (Liu and Rudnick, 2011), and changing climate, if the changes in  $\delta^7\text{Li}$  in the seawater  
71 record (Misra and Froelich, 2012) can be deciphered. The Li isotopic composition in seawater is  
72 a function of the input of rivers and hydrothermal fluid, and the output into secondary minerals  
73 formed via low temperature basalt alteration and sediment clay authigenesis (referred to as  
74 "reverse weathering") (Chan et al., 1992). The dramatic (8‰) increase in  $\delta^7\text{Li}$  in seawater  
75 through the Cenozoic has been interpreted to reflect the changing composition of riverine inputs  
76 that, in turn, reflect climatic and tectonic influences on continental weathering (Misra and  
77 Froelich, 2012). Assuming a constant hydrothermal input, the significant increase in  $\delta^7\text{Li}$   
78 through the Cenozoic may indicate increases in the riverine input (a greater flux and/or higher  
79  $\delta^7\text{Li}$ ), an increased output flux of low  $\delta^7\text{Li}$ , or both. Therefore, understanding the controls on  
80 riverine Li isotopes is a first-order requirement for understanding the secular evolution of  
81 seawater.

82 Li is contained mainly in silicates and is released, with attendant isotopic fractionation,  
83 during weathering (e.g., Huh et al., 2001; 1998; Kısakürek et al., 2005; 2004; Rudnick et al.,

84 2004). Lithium's two stable isotopes,  $^7\text{Li}$  and  $^6\text{Li}$ , have great fractionation potential due to their  
85 17% mass difference. Differences in Li isotopic composition are expressed as  $\delta^7\text{Li}$  (‰) =  
86  $([^7\text{Li}/^6\text{Li}]_{\text{sample}} / [^7\text{Li}/^6\text{Li}]_{\text{standard}} - 1) \times 1000$ , where the standard used is a lithium carbonate, L-SVEC  
87 (Flesch et al., 1973). Lithium is a water-soluble trace element, but neither primary basalt  
88 dissolution nor metamorphic dehydration appear to cause significant Li isotopic fractionation  
89 (Marschall et al., 2007; Pistiner and Henderson, 2003; Qiu et al., 2011a; 2011b; 2009; Teng et  
90 al., 2007; Wimpenny et al., 2010a). By contrast, Li isotopes fractionate significantly during  
91 incongruent continental weathering, due to the formation of secondary minerals, such as clays  
92 (e.g., Huh et al., 1998; Kiskurek et al., 2004; Pistiner and Henderson, 2003; Pogge von  
93 Strandmann et al., 2006; Rudnick et al., 2004; Teng et al., 2004). Lithium has a few more  
94 advantages as a potential geochemical tracer of weathering. Li has only one redox state (+1  
95 charge), and is thus insensitive to changes in oxygen fugacity compared to Fe, Cr, Cu, Mo, etc.  
96 In addition, Li is not a nutrient, so its elemental and isotopic behavior is not directly influenced  
97 by biological processes (e.g., Lemarchand et al., 2010). Finally, Li is enriched in silicates and  
98 depleted in carbonates, so its abundance and isotopic composition in rivers mainly reflect  
99 continental silicate weathering (one caveat is that riverine Li can be significantly influenced by  
100 the presence of evaporites, e.g., Huh et al., 1998).

101 Studies investigating the use of  $\delta^7\text{Li}$  as a weathering proxy (Huh et al., 2001; 1998; Millot et al.,  
102 2010; Pogge von Strandmann et al., 2006; Vigier et al., 2009) have not fully discerned why the  
103 Li isotope composition of rivers does not show consistent correlation with certain silicate  
104 weathering proxies. For instance, Huh et al. (1998) did not observe a clear correlation between  
105  $\delta^7\text{Li}_{\text{dis}}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^7\text{Li}_{\text{dis}}$  and  $[\text{Li}]$  (using square brackets around elements to indicate  
106 concentration) as well as between  $\delta^7\text{Li}_{\text{dis}}$  and  $\text{Si}/\text{TZ}^+$  (Total cation charge,  $\text{TZ}^+ =$   
107  $\text{Na}^+ + 2\text{Mg}^{2+} + \text{K}^+ + 2\text{Ca}^{2+}$  in  $10^{-3}$  equivalents per liter, mEq/L) when compiling global river data. By  
108 contrast, for the Orinoco drainage basin a strong inverse correlation was observed between  
109  $\delta^7\text{Li}_{\text{dis}}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  as well as between  $\delta^7\text{Li}_{\text{dis}}$  and  $\text{Si}/\text{TZ}^+$  (Huh et al., 2001). In addition, in some  
110 studies a correlation between  $\delta^7\text{Li}$  and chemical weathering rates (in mass/area/time) was  
111 observed (Vigier et al., 2009), whereas in others no clear relationship could be identified (Millot  
112 et al., 2010). The lack of consistent correlation may reflect variations in climate (e.g., tropical vs.  
113 temperate climates), lithologies, hydrology, and sampling seasons encompassed in previous river

114 studies. Here we seek to illuminate the causes of Li isotopic fractionation produced during  
115 weathering by studying surface waters draining a single lithology (basalt) as a function of  
116 climate, season, and groundwater residence time. The Columbia River Basalts (CRBs) afford this  
117 opportunity due to their large areal extent, which encompasses different climate zones and allows  
118 sampling within a single lithology having limited isotopic variability. Understanding the  
119 processes that control  $\delta^7\text{Li}_{\text{dis}}$  will, in turn, afford greater insight into the changing  $\delta^7\text{Li}$  observed  
120 in seawater with time.

121

## 122 ***2. Geological setting, climate and samples***

123 The geological setting of the sampling area is described in Liu et al. (2013) and a brief  
124 account is provided here. The CRBs are continental flood basalts that erupted during the  
125 Miocene (between 17 Ma to 6 Ma) in the US Pacific Northwest, covering large parts of southern  
126 Washington, northeastern Oregon and parts of western Idaho (Fig. 1).

127 The CRBs crop out both east and west of the Cascade Mountain Range. The Cascades  
128 developed progressively from subduction zone magmatism since the Late Eocene, with  
129 topography increasing more or less steadily since the Late Oligocene (Kohn et al., 2002 and  
130 references therein). The mountains created two different climate zones that affected the CRBs  
131 via the rain shadow effect; regions west of the Cascades have high mean annual precipitation  
132 (MAP) (1500-2000 mm), whereas annual precipitation east of the Cascades is less than 300 mm  
133 (Kohn et al., 2002; Takeuchi et al., 2010). In addition, the monthly precipitation rates vary more  
134 in the west, where the mean monthly precipitation rate during the wet season (October-May) is  
135 up to 10 times greater than that during the dry season (June to September) (Fig. A1). By contrast,  
136 differences in monthly precipitation rates east of the Cascades are usually less than a factor of 2.

137 The advantages of studying streams and groundwaters in this area include: 1) The streams  
138 only drain a single lithology, the CRBs. 2) Sampling streams from different climate zones allows  
139 investigation of how annual precipitation rates, and thus climate, may have influenced riverine Li  
140 isotopic composition. 3) Due to the variable seasonal precipitation (Fig. A1), sampling in two  
141 seasons allow us to assess the effect of seasonally variable precipitation rates and corresponding  
142 variable surface runoff (Fig. A2) on Li isotopic compositions. 4) Sampling of groundwaters that

143 are the potential sources of the streams allows distinction between Li isotope fractionation  
144 occurring in aquifers compared to fractionation occurring in rivers.

145

### 146 *3. Samples and analytical methods*

#### 147 *3.1 Sampling*

148 Dissolved and suspended load samples from 10 CRB streams were collected in July  
149 2010, and again in March 2012 to study possible seasonal variations; samples from the mouths of  
150 the much larger Deschutes and John Day rivers, which have lithologically diverse catchments,  
151 were also taken for comparison. In addition, five groundwater samples were collected in March  
152 2012, as well as an additional stream (Mosquito Creek, R11) (Fig. 1).

153 At each site, pH, temperature, electrical conductivity, and total dissolved solids (TDS)  
154 were measured using a multi-meter (Hanna® Instruments) with analytical accuracy of  $\pm 0.05$ ,  $\pm$   
155  $0.5^{\circ}\text{C}$ ,  $\pm 2\%$   $\mu\text{S}/\text{cm}$ , and  $\pm 2\%$  ppm, respectively. All stream water samples were obtained using  
156 a peristaltic pump and filtered using a 142 mm filter holder system with  $0.2\ \mu\text{m}$  cellulose acetate  
157 filters. Filtered waters were collected in pre-cleaned Nalgene® bottles. Filters were placed in air-  
158 tight Ziploc plastic bags for transport back to the lab. The suspended loads of the stream waters  
159 were recovered from the filters in the clean lab. The sample tubing was pumped dry after each  
160 sample collection and one liter of deionized water was pumped through the system to clean it  
161 between each sampling event. At the start of sampling at a new site, a liter of sample water was  
162 first collected into the pre-cleaned bottles and then discarded. Finally, about two liters of water  
163 were collected, acidified using five drops ( $\sim 0.25$  ml) of concentrated HCl and stored in  
164 Nalgene® bottles for transport to the lab. Following this procedure, two 125 ml pre-cleaned  
165 Nalgene® bottles were filled with water for anion (without acidification) and major and trace  
166 cation analyses (acidified using two drops of  $\sim 0.1$  ml concentrated HCl).

167 Groundwaters were sampled either from existing pumping systems that tap into deep-  
168 seated aquifers or faucets fed by shallow wells. The sampling method outlined above for streams  
169 was also used for the groundwaters (Table 2). One groundwater sample (G4, Lind) was taken  
170 from a new municipal well in the town of Lind, WA, which taps into an aquifer buried 220 m

171 below ground and is estimated to be >50 ka old based on radiocarbon age dating (T. Tolan,  
172 personal communication). A second groundwater sample (G1, Spring Creek) was collected at the  
173 Spring Creek National Fish Hatchery from an aquifer ~ 200 m deep, containing little or no  
174 modern water and having an overall age of thousands of years (Hinkle, 1996). Thus, these two  
175 groundwaters are unlikely to be the sources of waters in the streams.

### 176 ***3.2 Major and trace elements in dissolved loads***

177 Major and trace cations in dissolved loads were analyzed using an Element 2 single  
178 collector Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) at the University of  
179 Maryland. Calibration curves were created using pure element solutions (Alfa Aesar<sup>®</sup>) and  
180 standard and water samples were doped with the same amount of indium to correct for  
181 instrumental drift ([In] = 2 ppb). The accuracy and precision of the analyses were determined by  
182 repeat analyses of the international river standard SLRS-5, with accuracy of cations assessed at  
183 better than 4% (n = 11 for SLRS-5), except for K (<10%), based on its certified value (Table  
184 A.1).

185 Major anion concentrations were measured by ion chromatography in the  
186 Biogeochemical Lab at the University of Maryland. Anion concentrations were measured using a  
187 Dionex ICS-1500 ion chromatograph, equipped with an AS14 4-mm analytical column and a  
188 guard column. An eluent of 3.5 mM of Na<sub>2</sub>CO<sub>3</sub> with 1.0 mM NaHCO<sub>3</sub> was used at a flow rate of  
189 0.3 mL/min. The detection limits of the ion chromatograph are 0.01 mg/L, 0.01 mg NO<sub>3</sub>/L and  
190 0.02 mg SO<sub>4</sub>/L for Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, respectively. The accuracy of the analyses are better than  
191 ~5% based on repeat analyses of standards (see Table A.2). HCO<sub>3</sub><sup>-</sup> concentrations were  
192 estimated based on charge balance.

### 193 ***3.3 Lithium isotope analyses***

194 All sample preparation and analyses were performed in the Geochemical Laboratory at  
195 the University of Maryland. A description of sample dissolution, column chemistry, analytical  
196 blanks and instrumental analysis is provided in the electronic appendix (Text A1). Long-term  
197 precision is better than ± 1‰ (2 σ); several USGS rock standards were run repeatedly during the  
198 course of this study (Table A.3). BHVO-1 yielded δ<sup>7</sup>Li of +4.6 ± 1.0 (n= 5) cf. 4.0 to 5.6 in the  
199 literature (GeoReM database: <http://georem.mpch-mainz.gwdg.de/>); BCR-2 yielded δ<sup>7</sup>Li of +2.9

200  $\pm 1.5$  (n = 3) cf. 2.6 to 4.6 in the literature (GeoReM database); and AGV-1 yielded  $\delta^7\text{Li}$  of +5.2  
201  $\pm 0.6$  (n = 3) cf. 4.6 and 6.7 for AGV-1 in Liu et al. (2010) and Magna et al. (2004), respectively.

### 202 **3.3.1 Handling of dissolved loads**

203 Approximately 30 ml to 2 L of filtered stream and groundwaters (depending on the  
204 volume collected) were first weighed and then evaporated in large Savillex® Teflon beakers  
205 (160 ml) or Teflon evaporation dishes (400 ml) on a hot plate ( $T < 100^\circ\text{C}$ ). A 3:1 mixture of HF-  
206  $\text{HNO}_3$  was added to the samples, which were then transferred into screw-top Savillex® Teflon  
207 beakers (15ml) placed onto a hot plate ( $T < 120^\circ\text{C}$ ) for an overnight dissolution followed by an  
208 evaporation step. The sample was then treated with concentrated  $\text{HNO}_3$  and  $\text{HCl}$  until all solids  
209 were dissolved and the final solutions were clear. The final dried sample was picked up in 4 N  
210  $\text{HCl}$  for column separation.

### 211 **3.3.2 Dissolution of suspended loads**

212 Suspended load samples were washed off the filters into large Savillex® Teflon beakers  
213 (160 ml) using Milli-Q water and then transferred into screw-top Teflon beakers and dried on a  
214 hot plate ( $T < 70^\circ\text{C}$ ). The dried samples were then scraped off the beaker and weighed into clean  
215 Teflon beakers; sample sizes ranged from several milligrams to tens of milligrams. The samples  
216 were then dissolved using a 3:1 mixture of HF and  $\text{HNO}_3$  in a screw-top Teflon beaker on a hot  
217 plate ( $T \approx 90^\circ\text{C}$ ), dried, then pickup up by  $\text{HNO}_3$  and  $\text{HCl}$  addition until all solids were dissolved  
218 and the final solutions were clear. The final dried sample was dissolved in 4 N  $\text{HCl}$  for column  
219 separation.

### 220 **3.4 Reactive transport modeling**

221 In order to investigate the influence of silicate weathering on  $\delta^7\text{Li}_{\text{dis}}$ , a series of  
222 thermodynamically- and kinetically-controlled reactive transport model simulations were carried  
223 out using the code TOUGHREACT V2 (Xu et al., 2011). TOUGHREACT has been used to  
224 evaluate isotopic fractionation coupled to water-rock interaction and hydrological processes in a  
225 variety of subsurface environments and laboratory experiments (eg., Singleton et al., 2005;  
226 Sonnenthal et al., 1998; Wanner and Sonnenthal, 2013). Each modeled scenario is composed of  
227 two individual simulations to model silicate weathering and associated Li isotope fractionation (i)



228 during subsurface flow and (ii) within rivers (Fig. 2). The model setup is closely related to the  
229 simulations performed by Wanner et al. (2014) modeling Li isotope fractionation associated with  
230 granite weathering. Accordingly, only a short model description is provided below. Input  
231 parameters and specific code capabilities used to simulate Li isotope fractionations are described  
232 in detail in the electronic appendix (Text A2).

### 233 *3.4.1 Subsurface simulations*

234 Reactive transport along a basaltic subsurface was simulated for a fully saturated, 100 m  
235 long porous media having a porosity of 10%, the porosity previously used to simulate Columbia  
236 River Basalt weathering (Taylor and Lasaga, 1999). Fracture flow, the presence of highly porous  
237 flow tops, as well as the unsaturated zone, were not incorporated into the model because our  
238 focus is on assessing the sensitivity (i.e., trends) of dissolved  $\delta^7\text{Li}$  values as a function of  
239 residence time (i.e., amount of weathering), rather than on simulating detailed flow features of  
240 actual unsaturated zones feeding aquifers and streams. Subsurface simulations were run for an  
241 average linear groundwater flow velocity of 1 m/d to simulate a system dominated by advection.

242 Pure water in equilibrium with atmospheric  $\text{CO}_2$  was specified as the initial and boundary  
243 fluid compositions. A starting mineralogical composition similar to the normative mineralogy  
244 reported for different Columbia River Basalt members (BVSP, 1981) (e.g., plagioclase, pyroxene,  
245 olivine, glass) was assigned to the solid part of the porous medium (see Tables A.4 and A.5 for  
246 mineral stoichiometries, corresponding thermodynamic and kinetic parameters and specified  
247 initial and boundary conditions). Simulations were run for two different initial bulk Li  
248 concentrations of 4 and 20 ppm, encompassing most of the range of [Li] observed in fresh CRB  
249 (Liu et al., 2013), and to assess whether the initial Li concentration influences riverine  $\delta^7\text{Li}$   
250 values.

251 Because Li is moderately incompatible during igneous differentiation (Brenan et al.,  
252 1998), Li is assumed to be mostly contained within a glassy basalt matrix and is introduced into  
253 the model from a Li-bearing volcanic glass phase tabulated in the THERMODEM database  
254 (Blanc et al., 2012). Li-bearing hematite and kaolinite were allowed to precipitate. It should be

255 noted that kaolinite and hematite are likely not the only secondary minerals forming, but they  
256 serve as representatives for any other potentially precipitating Fe- and Al-bearing minerals.

257 To simulate the fate of individual Li isotopes,  $^6\text{Li}$  and  $^7\text{Li}$  were incorporated into the  
258 mineral stoichiometries of primary Li-bearing volcanic glass, and secondary kaolinite and  
259 hematite. An initial  $\delta^7\text{Li}$  value of +1 was assumed for Li-bearing glass, which corresponds to the  
260 average  $\delta^7\text{Li}$  value measured for two different CRBs members (Liu et al., 2013). Similar to the  
261 model of Bouchez et al. (2013), we do not distinguish between Li exchange-, Li surface  
262 complexation-, or Li substitution reactions and Li uptake by secondary minerals and associated  
263 Li isotopic fractionation is solely simulated during Li incorporation into precipitating kaolinite  
264 and hematite. Li bearing secondary mineral precipitation is simulated by means of a solid  
265 solution approach, such as described in detail by Wanner et al. (2014), as well as in the Text A2.  
266 A fractionation factor ( $\Delta^7\text{Li}_{\text{2ndMin-solution}} = \delta^7\text{Li}_{\text{2ndMin}} - \delta^7\text{Li}_{\text{solution}}$ ) of -10‰ was assigned for hematite  
267 and kaolinite precipitation, which is within the range of Li isotope fractionation factors reported  
268 or inferred for secondary mineral precipitation (Huh et al., 2001; Kısakürek et al., 2005; Pistiner  
269 and Henderson, 2003; Pogge von Strandmann, 2006; 2010; Vigier et al., 2008; Zhang et al.,  
270 1998). An extended discussion of fractionation factors can be found in the Text A2.

### 271 **3.4.2 River simulations**

272 River simulations were conducted essentially as batch simulations, where the flow  
273 velocity was set to zero. In doing so, it was assumed that the reactive suspended load (i.e., solid  
274 phase) is transported at the same velocity as the river water, which is in agreement with current  
275 knowledge about the transport of suspended river loads (Fryirs and Brierley, 2013).

276 Two grid blocks were defined to simulate groundwater exfiltrating into river systems,  
277 which is diluted by river water that previously experienced less water-rock interaction processes.  
278 By setting the interfacial area ( $A_{\text{inter}}$ , Fig. 2) between the two grid blocks to  $7000 \text{ m}^2$ , the Li  
279 concentration of the exfiltrating groundwater was diluted by a factor of  $\sim 10$  during a simulated  
280 river residence time of 20 days, roughly corresponding to the Li concentration difference  
281 observed between streams and groundwaters (Tables 1, 2). Reactions between the suspended

282 river load and river waters were only considered for the grid block initially containing  
283 exfiltrating groundwater.

284 The suspended river load was assigned the same initial mineralogical composition as the  
285 subsurface (Table A.5), assuming that this load contains a significant amount of primary silicate  
286 minerals in addition to the dominant clays and oxides (Gaillardet et al., 1999). This model  
287 assumption is consistent with Bouchez et al. (2011) who observed that the mineralogical  
288 composition of the suspended load is dependent on the particle size and that primary silicate  
289 minerals (e.g., feldspar) are enriched in the coarser fraction. Consequently, Li isotope  
290 fractionation in the simulated river is assumed to occur in the same fashion as in the subsurface  
291 simulations.

## 292 **4. Results**

293 Data for field measurements (pH, temperature, electrical conductivity, and TDS), major  
294 and trace elements, in addition to Li isotopic data are given in Tables 1 and 2, for streams and  
295 groundwaters, respectively. A comparison between summer and late winter data is shown in  
296 Figs. A3 and A4 for field parameters and selected dissolved species, respectively.

### 297 **4.1 Field measurements**

298 Streams sampled in July 2010 display a temperature range from 13 to 22°C with pH  
299 ranging from 7.2 to 8.7, while the streams sampled in March 2012 are cooler (1 to 9°C), but have  
300 a similar range in pH (6.7 to 8.3). Groundwaters are warmer (10 to 29°C), and have higher pH  
301 (7.7 to 9.6), compared to the streams sampled at the same time of the year (March). TDS in  
302 streams east of the Cascades do not show significant seasonal variations (32 to 154 mg/L in July,  
303 and 25 to 158 mg/L in March, Table 1) with the exception of Silva creek, where TDS varies by a  
304 factor of two between seasons (64 in summer vs. 33 ppm in winter). By contrast, TDS in the  
305 three streams west of the Cascades differ by up to a factor two between seasons (7-18 mg/L in  
306 July, 10-32 mg/L in March). Groundwaters range to higher TDS values (90 to 253 mg/L, Table  
307 2). The maximum TDS value was measured in a meromictic lake (i.e., a stratified lake that does  
308 not mix between layers), the TDS of which exceeded the range of the multi-meter.

## 309 *4.2 Major elements*

310 Major cations and anions in stream water and groundwater samples are plotted using a  
311 classic Piper Diagram (Piper, 1953), a trilinear diagram consisting of two equilateral triangles for  
312 cations and anions, respectively, which are projected onto a central diamond (Fig. 3). In the  
313 lower triangles, the points are expressed as a percentage of the total amount of cations or anions  
314 in milliequivalents per liter. River and groundwaters are plotted in Fig. 3a and 3b for summer  
315 and winter, respectively. River waters have clustered cation patterns in both summer and winter  
316 illustrating that the water chemistry is inherited from a single lithology. Three shallow  
317 groundwaters plot within the same domain as the streams, while two deep groundwaters (G1:  
318 Spring Creek, and G4: Lind) show very different cation and anion patterns. Major elements such  
319 as Na, Si and Ca, correlate with Mg, and hence with each other (Fig. A5). Similarly, the total  
320 cation charge,  $TZ^+$  ( $TZ^+ = Na^+ + 2Mg^{2+} + K^+ + 2Ca^{2+}$  in  $10^{-3}$  equivalents per liter, mEq/L), also  
321 correlates ( $R^2 = 0.98$ ) with [Mg] in stream waters. Groundwaters, except for the two deep  
322 groundwaters (G1: Spring Creek, and G4: Lind), follow the same major element correlation, but  
323 with higher concentrations. The sample from Silva Creek taken in July, 2010, has much higher  
324  $[Cl^-]$  (54 mg/L) and  $[SO_4^{2-}]$  (39 mg/L), compared to the other streams studied here and natural  
325 streams elsewhere (where  $[Cl^-]$  and  $[SO_4^{2-}]$  are typically less than 10 mg/L), indicating that this  
326 creek may have been subjected to anthropogenic contamination in the summer months (e.g.,  
327 fertilizers).

328 Major cations in streams show very little variation between summer and winter; however,  
329 anions show large variations (Fig. 3). Although little variation is observed for cation ratios,  
330 actual concentrations (e.g., Si, Mg, and Na) tend to be slightly higher during the summer  
331 sampling campaign (Table 1, Fig. A4). This observation corresponds well with pH values and  
332 TDS concentrations, which were also slightly larger during the summer sampling campaign  
333 (Table 1, Fig. A3). In the case of [Si] and TDS, the seasonal concentration increase is most  
334 prominent in the western streams, with an increase of up to a factor two. By contrast, in the  
335 eastern streams both concentration variations ([Si] and TDS) were significantly smaller, by a  
336 factor less than  $\sim 1.3$  (Table 1). In addition, although there is some seasonal variation of anion  
337 concentrations among streams, the overall pattern likely reflects a mixture of water sources,

338 since all streams and shallow groundwaters plot along a straight line; the two deep groundwaters  
339 fall off the trend in the upper diamond plot (Fig. 3).

#### 340 **4.3 Li elemental and isotopic data**

341 The Li concentrations of dissolved loads vary from 0.2 to 4.7  $\mu\text{g/L}$  for both sampling  
342 seasons. For individual streams, there is little difference in [Li] between the two sampling  
343 campaigns (Table 1, Fig. 4), where [Li] shows a weak positive correlation with [Mg] ( $R^2 = 0.7$ )  
344 and [Si] ( $R^2 = 0.4$ ).  $\delta^7\text{Li}_{\text{dis}}$  ranges from +10 to +30 in the streams sampled during the summer,  
345 and shows a similar range in the streams sampled in the late winter (+9 to +22). In streams east  
346 of the Cascades,  $\delta^7\text{Li}_{\text{dis}}$  does not change with season, except for Silva Creek (+30 vs. +14‰),  
347 which may reflect anthropogenic contamination, based on the high contents of  $[\text{Cl}^-]$  and  $[\text{SO}_4^{2-}]$ .  
348 A previous study has shown that anthropogenically contaminated groundwaters may show very  
349 heavy  $\delta^7\text{Li}$  values (up to  $\sim +1000\text{‰}$ ), due to the use of heavy Li-enriched fertilizer (Négre et al.,  
350 2010). By contrast, the streams to the west of the Cascades show consistently higher  $\delta^7\text{Li}$  values  
351 in the summer compared to the winter (Fig. 5).

352 Varying from 2 to 21  $\mu\text{g/L}$  (Table 1), groundwater [Li] is significantly higher than in the  
353 streams. Moreover, with the exception of the two groundwaters from deep wells (shown as open  
354 triangles in the figures), [Li] in groundwaters show similar correlations with [Si], but not with  
355 [Mg], as seen in stream waters (Fig. 4). Except for the deep-seated Lind well water (G4,  
356 +21.4‰), groundwater  $\delta^7\text{Li}$  ( $\delta^7\text{Li}_{\text{GW}}$ ) are between +6.7 and +9.4‰, which is on the very low end  
357 of observed  $\delta^7\text{Li}_{\text{dis}}$  (Tables 1, 2).

358 [Li] in the suspended loads varies from 7 to 24  $\mu\text{g/g}$  in the streams sampled during the  
359 summer, and shows a greater range in the streams sampled during the late winter (from 13 to 66  
360  $\mu\text{g/g}$ ). The  $\delta^7\text{Li}$  of the suspended load ( $\delta^7\text{Li}_{\text{sus}}$ ) is generally the same from season to season,  
361 except for the Dechutes River, which shows a large change in  $\delta^7\text{Li}_{\text{sus}}$  according to season (+4.2  
362 in summer to -0.3 in late winter). With the exception of the summer Deschutes River sample,  
363  $\delta^7\text{Li}_{\text{sus}}$  are lower compared to the average  $\delta^7\text{Li}$  measured in fresh CRBs ( $\delta^7\text{Li} = 1.1$ , Liu et al.,  
364 2013). The low  $\delta^7\text{Li}_{\text{sus}}$  are comparable to the lower than average  $\delta^7\text{Li}$  observed in weathered  
365 CRB ( $\delta^7\text{Li} = -5$  to 0) and the upper continental crust ( $\delta^7\text{Li} = 0$  on average, Teng et al., (2004)).

## 366 **4.4 Simulation results**

### 367 **4.4.1 [Li] and $\delta^7\text{Li}$**

368 Simulated steady-state [Li] and [Si] profiles along our model domain (subsurface + river),  
369 as well as corresponding  $\delta^7\text{Li}$  profiles (i.e.,  $\delta^7\text{Li}_{\text{dis}}$ ,  $\delta^7\text{Li}_{2\text{ndMin}}$  and  $\delta^7\text{Li}_{\text{bulk-rock}}$ ) are shown in Figs.  
370 6a and 6b for two different parental basalt Li concentrations of 4 and 20 ppm. Increasing [Li] in  
371 basalt yields larger dissolved Li concentrations for a specific subsurface residence time (Fig. 6a),  
372 but does not change  $\delta^7\text{Li}$  values, as illustrated by superimposing  $\delta^7\text{Li}_{\text{dis}}$  vs. residence time  
373 behavior (Fig. 6b). These results thus imply that subsurface and riverine  $\delta^7\text{Li}$  values are not  
374 sensitive to the Li concentrations of the parent rock, nor to the subsequent variable riverine [Li].  
375 This simulation result is supported by a lack of correlation observed between  $\delta^7\text{Li}_{\text{dis}}$  and [Li]  
376 (Table 1).

377 The  $\delta^7\text{Li}_{\text{dis}}$  and  $\delta^7\text{Li}_{2\text{ndMin}}$  values steadily increase with increasing subsurface and/or  
378 riverine residence time in the model (Fig. 6b). The slope of the  $\delta^7\text{Li}$  increase with time is  
379 dependent on the specified fractionation factor. For a lower fractionation factor (i.e., less  
380 fractionation), longer residence time is needed to reach the same  $\delta^7\text{Li}$  as for  $\Delta^7\text{Li} = -10\%$ , or vice  
381 versa. However, the pattern of increasing  $\delta^7\text{Li}$  with increasing residence time is not sensitive to  
382 the specified fractionation factor. The  $\delta^7\text{Li}_{\text{dis}}$  increases seen along the model domain are  
383 produced by our solid solution approach (Wanner et al., 2014), ensuring that [Li] in precipitating  
384 hematite and kaolinite increases with increasing [Li]. This assumption is consistent with an  
385 experimental study showing that [Li] in synthesized smectite increases linearly with aqueous [Li]  
386 (Decarreau et al., 2012). Because the dissolution rate of the parent rock remains constant (Table  
387 A.4), the ratio between Li that is incorporated into hematite and kaolinite, and the Li being  
388 released from the parent rock increases with increasing residence time, thus, continuously  
389 driving  $\delta^7\text{Li}_{\text{dis}}$  and  $\delta^7\text{Li}_{2\text{ndMin}}$  to higher values. The Li isotopic composition of the bulk rock is not  
390 changed (Fig. 6b) because the amount of secondary minerals formed during the 100 years for  
391 which the simulation were run were too low to drive the bulk rock  $\delta^7\text{Li}$  to lower values. In  
392 contrast to  $\delta^7\text{Li}_{\text{dis}}$  and  $\delta^7\text{Li}_{2\text{ndMin}}$ , aqueous [Li] and [Si] decrease (Fig. 6a) due to dilution when  
393 water flowing along the subsurface exfiltrates into the river.

### 394 **4.4.2 Weathering proxies**

395 Simulated profiles for silicate weathering proxies such as [Si], normalized Si ( $\text{Si}/\text{TZ}^+$ ),  
396 [Li], normalized Li ( $\text{Li}/\text{TZ}^+$ ), and Li/Na that have been previously used to constrain silicate  
397 weathering intensity (e.g., Huh et al., 2001; 1998; Millot et al., 2010; Pogge von Strandmann et  
398 al., 2010; 2006) are shown in Fig. 6c. These profiles reflect a proxy's ideal behavior, because  
399 processes potentially affecting the use of a specific weathering proxy (e.g., biological activity,  
400 anthropogenic contamination, salt leaching) were not considered in our simulations.

401 A negative correlation between  $\delta^7\text{Li}_{\text{dis}}$  and Li/Na (Fig. 6c) reflects Li incorporation into  
402 hematite and kaolinite, whereas Na remains in solution. Accordingly, although [Li] also  
403 increases with residence time in the subsurface, the Li/Na ratio's decrease with increasing  
404 residence time is due to Li incorporation into these secondary minerals. Other weathering proxies  
405 show a distinct correlation with  $\delta^7\text{Li}_{\text{dis}}$  only within a specific model domain (subsurface vs. river).  
406 In particular, concentration proxies such as [Si] and [Li] are positively correlated with  $\delta^7\text{Li}_{\text{dis}}$   
407 along the subsurface domain, but once exfiltrated, the correlations change sign because Li  
408 isotope fractionation is ongoing, whereas aqueous species concentrations decrease due to mixing  
409 with more superficial (i.e., meteoric) water.

## 410 **5. Discussion**

411 The observation that riverine  $\delta^7\text{Li}_{\text{dis}}$  (+9 to +30) is systematically higher than  $\delta^7\text{Li}$  values  
412 of the corresponding suspended loads ( $\delta^7\text{Li}_{\text{sus}} = -6$  to 0), as well as fresh and weathered CRBs  
413 ( $\delta^7\text{Li} = -5$  to +5, Liu et al., 2013), confirms that high  $\delta^7\text{Li}_{\text{dis}}$  is mainly generated by Li isotope  
414 fractionation occurring during basalt weathering (e.g., Huh et al., 2001; 1998; Pogge von  
415 Strandmann et al., 2010; 2006).

416 The most striking observation from our measurements, however, is the large variation in  
417  $\delta^7\text{Li}_{\text{dis}}$  (about 20‰ in summer, and > 10‰ in late winter) covering almost the entire range of  
418  $\delta^7\text{Li}$  (+6 to +32) reported in major world rivers (Huh et al., 1998). This observation is especially  
419 remarkable because we sampled only small streams and groundwaters within the CRBs, for  
420 which catchment lithological differences are small. Some previous studies attribute large  $\delta^7\text{Li}_{\text{dis}}$   
421 variations to formation of different secondary minerals that have different fractionation factors  
422 with water (Millot et al., 2010; Wimpenny et al., 2010b). However, we see no evidence that the  
423 large  $\delta^7\text{Li}_{\text{dis}}$  variations in our study are due to the presence of different Li-bearing secondary

424 minerals, as saturation index (SI) calculations (Fig. A7) and studies of weathering profiles (Liu et  
425 al. 2013) suggest that all of the streams and groundwaters are saturated with the same secondary  
426 mineral assemblage (hematite, kaolinite and gibbsite). We therefore postulate that factors other  
427 than mineralogical differences (i.e., primary and secondary Li bearing phases) have a major  
428 control on the Li isotopic composition of the streams.

### 429 *5.1 Residence time*

430 The rise of  $\delta^7\text{Li}$  with increasing residence time seen in the simulation (Fig. 6b) implies  
431 that subsurface residence time in particular, and the hydrological cycle in general have major  
432 controls on  $\delta^7\text{Li}_{\text{dis}}$ . In fact, in a plot of  $\delta^7\text{Li}_{\text{dis}}$  vs. Li/Na, our sample observations fall between the  
433 two curves defined by the minimum and maximum simulated bulk rock [Li] (Fig. 6d). We infer  
434 that the Li/Na ratio is an excellent proxy for residence time, because [Na] is at least three orders  
435 of magnitude higher than [Li] (Tables 1 and 2) and thus is not as strongly affected by small  
436 amounts of secondary mineral precipitation. However, Li/Na is also affected by the bulk rock  
437 concentration and the slope of the  $\delta^7\text{Li}_{\text{dis}}$  vs. Li/Na correlation seems to be a function of the bulk  
438 rock [Li], whereas the location along a particular correlation (i.e., the measured  $\delta^7\text{Li}_{\text{dis}}$  value)  
439 defines the residence time (Fig. 6d).

440 Significant seasonal precipitation variations are only observed for areas west of the  
441 Cascades (Fig. A.1). Since precipitation rates have a primary control on the hydrological cycle,  
442 this observation suggests that western streams are characterized by a more seasonally variable  
443 subsurface residence time distribution, whereas eastern streams show a less variable residence  
444 time distribution. Accordingly, the strong control of  $\delta^7\text{Li}_{\text{dis}}$  by residence time accounts for the  
445 seasonal  $\delta^7\text{Li}_{\text{dis}}$  variations observed in streams west of the Cascades and the lack of variations  
446 seen in eastern streams (Tables 1, 2).

447 The increase in  $\delta^7\text{Li}_{\text{dis}}$  seen with an increasing river to subsurface residence time ratio  
448 (Fig. 6b) also explains why riverine  $\delta^7\text{Li}_{\text{dis}}$  is generally greater than groundwater  $\delta^7\text{Li}_{\text{dis}}$  (Fig. 7  
449 and Tables 1 and 2). Accordingly, our observations and simulation results support the hypothesis  
450 that suspended river loads are reactive due to the presence of fine-grained primary silicate  
451 mineral particles, and therefore continued Li isotope fractionation is occurring within streams.



452 This is also supported by a recent study of Lemarchand et al. (2010), who found  $\delta^7\text{Li}_{\text{dis}}$  in  
453 streams draining a granitic catchment to be significantly greater than that of springs feeding these  
454 streams.

## 455 *5.2 Climate control*

456 There is no clear distinction in  $\delta^7\text{Li}_{\text{dis}}$  values between western and eastern streams,  
457 suggesting that the amount of annual precipitation, and thus climatic conditions, do not have a  
458 direct influence on  $\delta^7\text{Li}$ . This lack of climatic influence is consistent with the results of Millot et  
459 al. (2010), who suggested that neither mean annual precipitation nor distance to the coast have an  
460 influence on  $\delta^7\text{Li}_{\text{dis}}$  in waters from the Mackenzie River basin. In addition, despite the large  
461 temperature difference between summer and late winter ( $\sim 10^\circ\text{C}$ ), there is no change in riverine  
462  $\delta^7\text{Li}_{\text{dis}}$  in eastern streams.

463 Interestingly, as discussed in the previous section, a clear seasonal control on  $\delta^7\text{Li}_{\text{dis}}$  was  
464 observed for streams west of the Cascades (Fig. 5), which is probably related to the large  
465 seasonal difference in monthly precipitation observed there (Fig. A1). The proposal that average  
466 subsurface residence time is longer during drier periods is in good agreement with significantly  
467 larger TDS and [Si] observed for western streams during the summer compared to the winter  
468 (Table 1). A correlation between subsurface residence times and aqueous concentrations, and  
469 thus TDS, is expected because longer residence times allow for increased mineral dissolution and  
470 exchange (Fig. 6). Overall, climate indirectly affects  $\delta^7\text{Li}$  as precipitation rates control the  
471 hydrological cycle and thus residence time distributions. However,  $\delta^7\text{Li}$  is a poor proxy for  
472 climate because many other parameters affect the hydrological cycle as well (e.g., mountain  
473 building,  $\text{pCO}_2$ , temperature, vegetation).

## 474 *5.3 $\delta^7\text{Li}$ as a tracer of chemical weathering*

475 This study has illuminated the factors that control Li isotopic fractionation in the  
476 dissolved loads of rivers ( $\delta^7\text{Li}_{\text{dis}}$ ). Li isotopic fractionation in rivers is caused by fractionation  
477 between solution and secondary minerals (e.g., Huh et al., 2001; 1998; Pogge von Strandmann et  
478 al., 2010; 2006), and it has been suggested that the large variability in  $\delta^7\text{Li}_{\text{dis}}$  may be partially  
479 caused by different fractionation factors associated with Fe-Mn oxyhydroxides in places without  
480 soils or clays (Millot et al., 2010; Wimpenny et al., 2010b). Our study shows that  $\delta^7\text{Li}_{\text{dis}}$  is not

481 simply controlled by mineral-specific fractionation, as there is no correlation between  $\delta^7\text{Li}_{\text{dis}}$  and  
482 SI of the oversaturated secondary minerals, such as hematite and kaolinite (Fig. A7). We have  
483 shown that parameters such as reservoir residence time and reaction between suspended and  
484 dissolved loads in rivers can significantly influence  $\delta^7\text{Li}_{\text{dis}}$ , given a constant fractionation factor  
485 between solution and secondary minerals (Fig. 6), and there is no need (or evidence) to call upon  
486 variable fractionation factors related to the dominance of different secondary to explain variable  
487  $\delta^7\text{Li}_{\text{dis}}$  in rivers.

488 Our simulations (Fig. 6) agree very well with observations (Fig. 7), as we see a clear  
489 negative correlation between  $\delta^7\text{Li}_{\text{dis}}$  and the Li/Na ratio, whereas,  $\delta^7\text{Li}_{\text{dis}}$  does not correlate with  
490 [Si] or Si/TZ<sup>+</sup>, and shows only a weak negative correlation with Li/TZ<sup>+</sup> (Fig. 6c). Based on our  
491 simulations and data, we infer that, with the exception of Li/Na,  $\delta^7\text{Li}_{\text{dis}}$  and various silicate  
492 weathering proxies based on elemental concentrations (e.g., [Li], [Si], TZ<sup>+</sup>) are only correlated  
493 when a natural system is dominated by either Li isotope fractionation occurring in the subsurface  
494 (in which case there is a positive correlation between  $\delta^7\text{Li}_{\text{dis}}$  and the weathering proxies), or  
495 occurring in rivers (in which case there is a negative correlation between  $\delta^7\text{Li}_{\text{dis}}$  and the proxies).  
496 If Li isotope fractionation occurs in both settings, there will be no correlation, as seen in our  
497 results. This finding may explain why correlations between  $\delta^7\text{Li}_{\text{dis}}$  and concentration proxies are  
498 observed in some studies (e.g., Huh et al., 2001; Pogge von Strandmann et al., 2010), but not in  
499 others (this study; Millot et al., 2010).

500 Overall, this study also has implications for using Li isotopes as tracers of chemical  
501 weathering in rivers, and consequently, in seawater through time. In previous studies, multiple  
502 weathering proxies, such as [Si] and Si/TZ<sup>+</sup>, [Li], combined with Li isotopes (e.g., Huh et al.,  
503 2001; 1998; Pogge von Strandmann et al., 2006), have been used to try to constrain silicate  
504 weathering intensity. However, correlations between  $\delta^7\text{Li}_{\text{dis}}$  and these proxies may be produced  
505 or destroyed due to the effects we simulated, such as the residence time in the subsurface (as  
506 suggested in Millot et al., 2010), Li isotope fractionation and mineral dissolution in rivers. Our  
507 study suggests that  $\delta^7\text{Li}_{\text{dis}}$  is more robust than other tracers of silicate weathering, because it is  
508 linked to the degree of water-rock interactions along a specific flow path (e.g., in the subsurface  
509 and in rivers). In general, the larger the  $\delta^7\text{Li}_{\text{dis}}$  in a specific river, the more water-rock  
510 interactions (primary mineral dissolution + secondary mineral precipitations) have occurred such

511 as shown by Wanner et al. (2014). We demonstrate that, in rivers draining single lithology  
512 catchments,  $\delta^7\text{Li}_{\text{dis}}$  is negatively correlated with Li/Na, suggesting that the combined  $\delta^7\text{Li}_{\text{dis}}$  vs.  
513 Li/Na plot (Fig. 7d) may be a sensitive indicator of the extent of chemical weathering occurring  
514 in streams and groundwater reservoirs. Moreover, this finding is observed globally by clear  
515 negative correlations between  $\delta^7\text{Li}_{\text{dis}}$  vs. Li/Na for river waters worldwide that drain only or  
516 mainly basalts (Fig. 8). The global correlations observed in Fig. 8 is well related to our  
517 simulations (Fig. 6d), where we show that a perfect correlation is only observed for constant  
518 basalt [Li], which is clearly not the case when comparing basalts from the world over (e.g., [Li]  
519 = 3 to 23 ppm in fresh CRBs).

520 Finally,  $\delta^7\text{Li}_{\text{dis}}$  is influenced by many hydrological parameters, so it is not straightforward  
521 to use  $\delta^7\text{Li}_{\text{dis}}$  as a silicate weathering tracer in terms of interpreting secular evolution of riverine  
522 inputs to seawater. For example, for very fast flow at a high discharge, the overall silicate  
523 weathering rate (in moles/year) is very high. However, the  $\delta^7\text{Li}$  value should remain low because  
524 of the short residence time. Assuming the rise in  $\delta^7\text{Li}$  in seawater in the past 60 Ma (Misra and  
525 Froelich, 2012) is due primarily to changing riverine input with minor effects of discharge  
526 variations (Wanner et al., 2014), our work suggests that this signature reflects increased silicate  
527 weathering rates on the continents, which may or may not be directly related to changing climate  
528 (as we see no direct correlation between  $\delta^7\text{Li}_{\text{dis}}$  and climate), but could well be due to tectonic  
529 uplift that causes an increase in water-rock reaction.

530

## 531 **6. Conclusions**

532 The main conclusions from this study are:

- 533 1. Large  $\delta^7\text{Li}_{\text{dis}}$  variations (up to 20‰) are observed in streams that only drain basalts,  
534 suggesting that Li isotopic compositions in streams are controlled by factors other  
535 than the lithology of their catchments.
- 536 2.  $\delta^7\text{Li}_{\text{dis}}$  is significantly higher than  $\delta^7\text{Li}$  of groundwaters, suggesting that Li isotope  
537 fractionation occurring in rivers themselves play a major role on riverine  $\delta^7\text{Li}_{\text{dis}}$ .

- 538 3. A lack of direct correlation between climatic conditions (i.e., mean annual  
539 precipitation, temperature) and riverine  $\delta^7\text{Li}_{\text{dis}}$ , and correlations between seasonal  
540 precipitation variations and  $\delta^7\text{Li}_{\text{dis}}$  suggest that subsurface residence times strongly  
541 influence riverine  $\delta^7\text{Li}_{\text{dis}}$ .
- 542 4. Model simulations of reactive transport with variable residence times show that Li  
543 isotope fractionation occurs in both the subsurface and in rivers, causing many  
544 traditional silicate weathering proxies (e.g., [Si], Si/TZ+) to show no, or only a weak  
545 correlation with  $\delta^7\text{Li}_{\text{dis}}$ .
- 546 5.  $\delta^7\text{Li}_{\text{dis}}$  and Li/Na in dissolved loads of rivers are only sensitive to the amount of  
547 water-rock interaction over time and are, thus, useful tracers of the degree of silicate  
548 chemical weathering occurring in single lithology catchments.
- 549 6. If the increase in  $\delta^7\text{Li}$  in seawater through the Cenozoic is due primarily to changing  
550 riverine input, our results suggest that the increase may be uniquely related to tectonic  
551 uplift, which causes increased weathering due to the increase in denudation and the  
552 decreasing weathering intensity. Climatic controls on chemical weathering are  
553 apparently not as important.

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Table 1. Sample locations, field measurements, major and trace element concentrations and Li isotopic compositions in dissolved and suspended loads of rivers.

2010 summer	units	Cameron	Milton	N. Scapoose	Silva	Deschutes	John Day	Hay	Wenas	Cowiche	Ahtanum	Mill	Asotin
Sample #		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R12	R13
Longitude	°	-123.16707	-122.84415	-122.91550	-121.26745	-120.90903	-120.65085	-120.31797	-120.79715	-120.82127	-120.90663	-118.11638	-117.29242
Latitude	°	46.20735	45.86973	45.79293	45.71217	45.63033	45.72850	45.47992	46.89620	46.66437	46.51642	46.00358	46.27363
Location*		west	west	west	east	east	east	east	east	east	east	east	east
T	°C	15.6	18.6	15.2	18.1	19.2	21.9	19.6	12.6	18.8	14.6	14.1	18.1
pH		7.2	7.7	7.9	8.0	8.7	8.5	7.8	7.9	8.0	7.8	7.8	8.1
Conductivity	µS/cm	21	64	65	130	120	160	310	95	88	65	74	82
TDS	mg/l	10	32	32	64	58	82	150	47	44	32	35	41
Na	mg/l	2.7	4.9	5.3	6.5	9.6	7.0	17	3.9	4.0	3.2	3.8	3.5
Mg	mg/l	0.8	2.1	1.9	5.4	4.7	5.9	11	4.5	3.8	2.7	2.5	3.1
Al	µg/l	30	12	22	6.5	6.1	4.7	1.8	9.1	15	10	6.5	20
Si	mg/l	6.5	17	22	31	20	14	41	29	32	27	29	30
K	mg/l	0.4	1.1	1.3	1.5	1.7	1.4	3.7	1.6	2.1	1.8	2.3	2.3
Ca	mg/l	1.7	4.9	5.2	11	6.8	16	28	8.9	7.9	6.3	6.6	8.0
Fe	µg/l	130	320	170	28	21	32	54	130	180	79	50	35
F <sup>-</sup>	mg/l	0.06	0.08	0.04	0.56	-	0.13	0.13	0.04	0.06	0.03	0.07	0.08
Cl <sup>-</sup>	mg/l	2.6	4.0	18	54	13	8.5	8.6	16	13	16	3.2	2.8
NO <sub>3</sub> <sup>-</sup>	mg/l	-	-	-	-	-	-	0.01	-	-	0.01	-	-
SO <sub>4</sub> <sup>2-</sup>	mg/l	2.1	4.7	5.5	39	1.3	4.3	18	2.7	1.4	5.1	3.4	1.9
HCO <sub>3</sub> <sup>-</sup>	mg/l	0.9	0.9	1.3	1.0	1.5	2.7	-0.4	0.6	1.1	0.9	0.9	1.5
Li <sub>dis</sub>	µg/l	0.1	0.7	1.6	0.4	4.7	1.6	3.2	0.7	1.1	0.7	0.9	1.0
δ <sup>7</sup> Li <sub>dis</sub>		21.1	22.1	14.9	30.4	12.2	16.6	20.0	20.2	17.0	13.0	10.6	9.3
Li <sub>sus</sub>	µg/g	-	-	14	-	7.5	15	-	24	-	-	-	7.2
δ <sup>7</sup> Li <sub>sus</sub>		-	-	-5.6	-	4.2	-1.6	-	-3.1	-	-	-	-4.2

Note: “\*” location relative to the Cascades (west or east). “-” under detection limit.

Table 1. Sample locations, field measurements, major and trace element concentrations and Li isotopic compositions in dissolved and suspended loads of rivers continued.

2012 winter	units	Cameron	Milton	N. Scapoose	Silva	Deschutes	John Day	Hay	Wenas	Cowiche	Ahtanum	Mill	Asotin	Mosquito
Sample #		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R12	R13	R11
Longitude	°	-123.16707	-122.84415	-122.91550	-121.26745	-120.90903	-120.65085	-120.31797	-120.79715	-120.82127	-120.90663	-118.11638	-117.29242	-123.06510
Latitude	°	46.20735	45.86973	45.79293	45.71217	45.63033	45.72850	45.47992	46.89620	46.66437	46.51642	46.00358	46.27363	46.20202
Location*		west	west	west	east	east	east	east	east	east	east	east	east	west
T	°C	5.8	6.0	5.2	5.6	8.0	6.9	9.0	1.4	2.2	2.9	4.3	5.2	5.6
pH		6.7	6.9	8.3	7.6	8.0	7.7	7.8	7.6	7.6	7.6	7.4	7.6	6.7
Conductivity	µS/cm	14	31	37	65	110	130	320	97	100	91	51	74	20
TDS	mg/l	7	16	18	33	52	62	160	48	51	44	25	37	10
Na	mg/l	2.2	3.1	3.2	4.2	8.2	5.6	16	4.0	4.6	3.9	3.1	2.9	2.4
Mg	mg/l	0.6	1.0	1.0	2.7	4.0	4.4	10	4.3	4.4	3.6	1.7	2.7	0.8
Al	µg/l	16	4.9	8.9	86	43	40	2.1	57	23	22	180	240	12
Si	mg/l	4.1	9.2	12	21	22	19	34	27	30	30	24	27	4.8
K	mg/l	0.3	0.6	0.8	0.9	1.5	1.3	3.8	1.5	1.9	2.0	1.5	1.7	0.3
Ca	mg/l	1.6	2.8	3.1	6.3	6.4	12	27	8.6	8.8	7.9	4.8	6.9	1.9
Fe	µg/l	20	14	16	55	34	51	57	93	76	55	220	250	37
F <sup>-</sup>	mg/l	0.01	0.02	0.03	0.04	0.10	0.08	0.42	0.09	0.10	0.07	0.15	0.08	0.01
Cl <sup>-</sup>	mg/l	3.3	2.6	2.9	1.6	1.8	1.2	11	0.4	0.9	0.4	0.5	0.7	2.7
NO <sub>3</sub> <sup>-</sup>	mg/l	2.0	3.3	2.8	0.0	0.4	0.3	1.5	0.0	0.0	0.0	0.2	0.3	4.8
SO <sub>4</sub> <sup>2-</sup>	mg/l	0.5	1.2	1.6	0.7	1.8	3.9	15	2.0	3.2	1.6	0.6	1.3	0.5
HCO <sub>3</sub> <sup>-</sup>	mg/l	0.6	0.4	0.7	2.5	2.6	2.6	3.9	1.7	1.8	3.1	7.2	9.6	0.6
Li <sub>dis</sub>	µg/l	0.1	0.4	0.9	0.3	3.5	1.1	2.9	0.5	1.1	0.8	0.7	0.7	0.2
δ <sup>7</sup> Li <sub>dis</sub>		17.4	13.0	8.8	14.0	12.5	13.5	18.8	21.6	16.1	13.1	10.9	8.9	15.9
Li <sub>sus</sub>	µg/g	16	20	66	18	13	20	21	24	16	16	19	36	17
δ <sup>7</sup> Li <sub>sus</sub>		-1.4	-2.5	-4.5	-0.9	-0.3	-1.5	-0.2	-3.1	-5.7	-5.9	-2.8	-5.2	-1.0

Note: “\*” location relative to the Cascades (west or east). “-” under detection limit.

Table 2. Sample locations, field measurements, major and trace element concentrations and Li isotopic compositions of groundwaters and one alkaline lake.

Groundwater	units	Spring Creek	Selah	Ryegrass	Lind	Hatton	Soap Lake
Sample #		G1	G2	G3	G4	G5	L1
Longitude	°	-121.54613	-120.44327	-120.20900	-118.62250	-118.74282	-119.49877
Latitude	°	45.72737	46.69758	46.94738	46.96828	46.79410	47.42263
Sampling*		well	faucet	faucet	well	faucet	
T	°C	17.6	18.1	14.7	28.6	10.9	10.2
pH		8.8	8.0	7.7	9.1	7.9	9.6
Conductivity	µS/cm	180	320	340	350	510	> 3999
TDS	mg/l	90	160	170	180	250	>2000
Na	mg/l	33	21	13	78	19	280
Mg	mg/l	0.4	12	15	0.3	19	4.4
Al	µg/l	6.9	27	0.5	4.9	0.1	-
Si	mg/l	45	33	40	64	35	4.9
K	mg/l	4.5	3.9	2.9	3.9	4.0	590
Ca	mg/l	1.9	17	19	3.1	40	6.9
Fe	µg/l	47	6.9	5.7	17	54	1.3
F <sup>-</sup>	mg/l	0.76	0.48	0.39	3.3	0.28	0.31
Cl <sup>-</sup>	mg/l	3.6	8.6	7.0	7.9	46	130
NO <sub>3</sub> <sup>-</sup>	mg/l	0.01	-	11	0.1	18	-
SO <sub>4</sub> <sup>2-</sup>	mg/l	1.5	3.7	12	4.7	50	210
HCO <sub>3</sub> <sup>-</sup>	mg/l	3.5	1.8	2.4	2.4	3.4	-0.87
Li <sub>dis</sub>	µg/l	21	9.8	6.5	8.9	3.3	1.5
δ <sup>7</sup> Li <sub>dis</sub>		6.8	8.1	9.4	21.4	6.7	20.5

Note: “\*” sampling methods (well or faucet). “-” below detection limit.

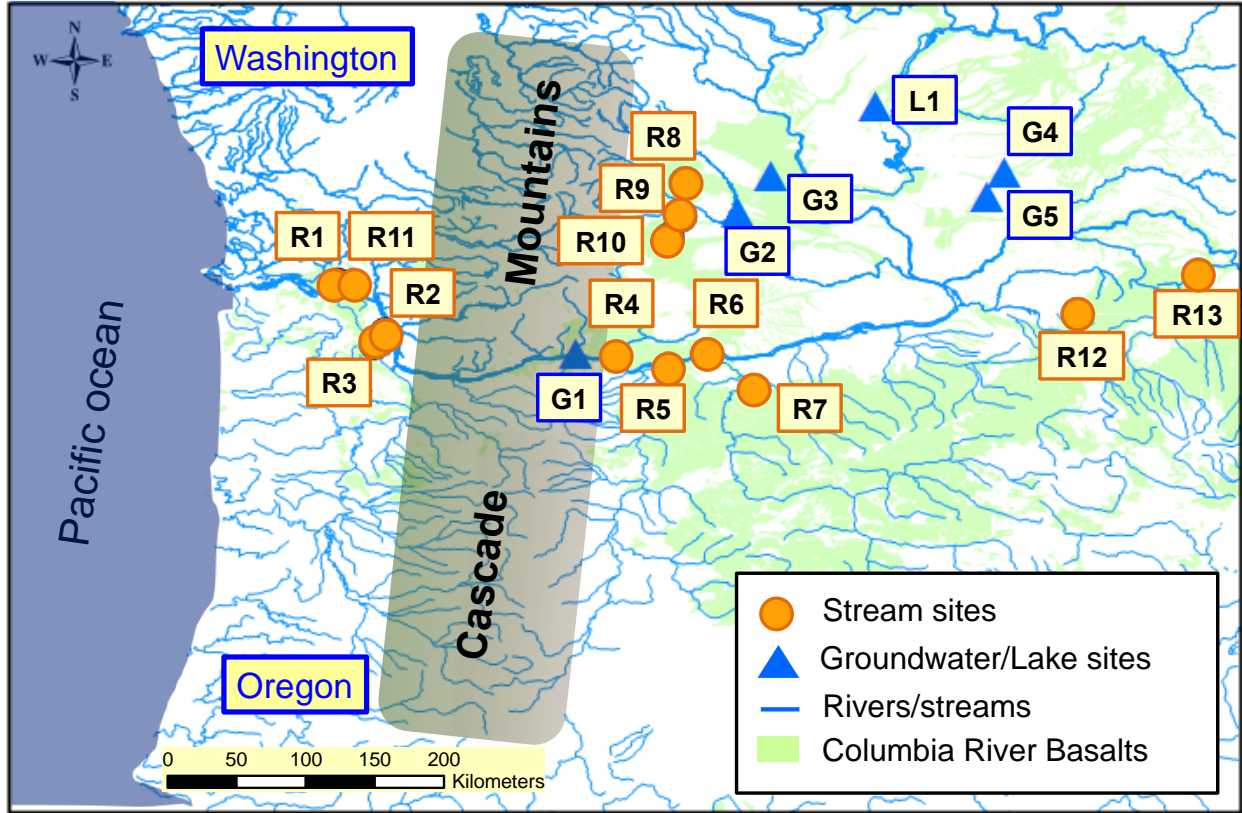


Figure 1. Map of sample locations. Geological data are from USGS. Streams are shown in orange circles and numbered with Rx. R11 was only sampled during late winter of 2012 and the rest rivers were sampled both in summer of 2010 and late winter of 2012. Groundwater and one lake are shown in blue triangles, all of which were sampled during late winter.

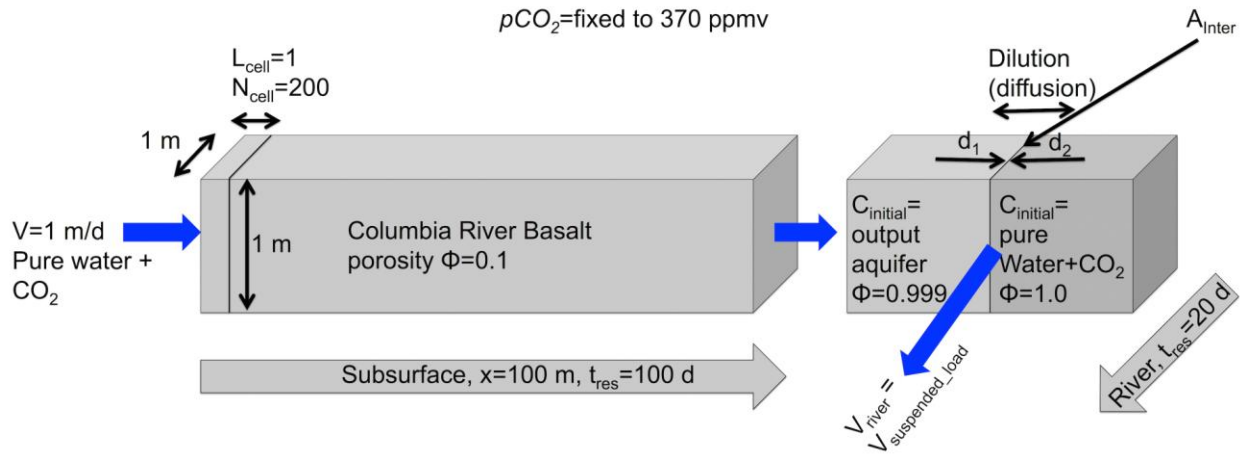
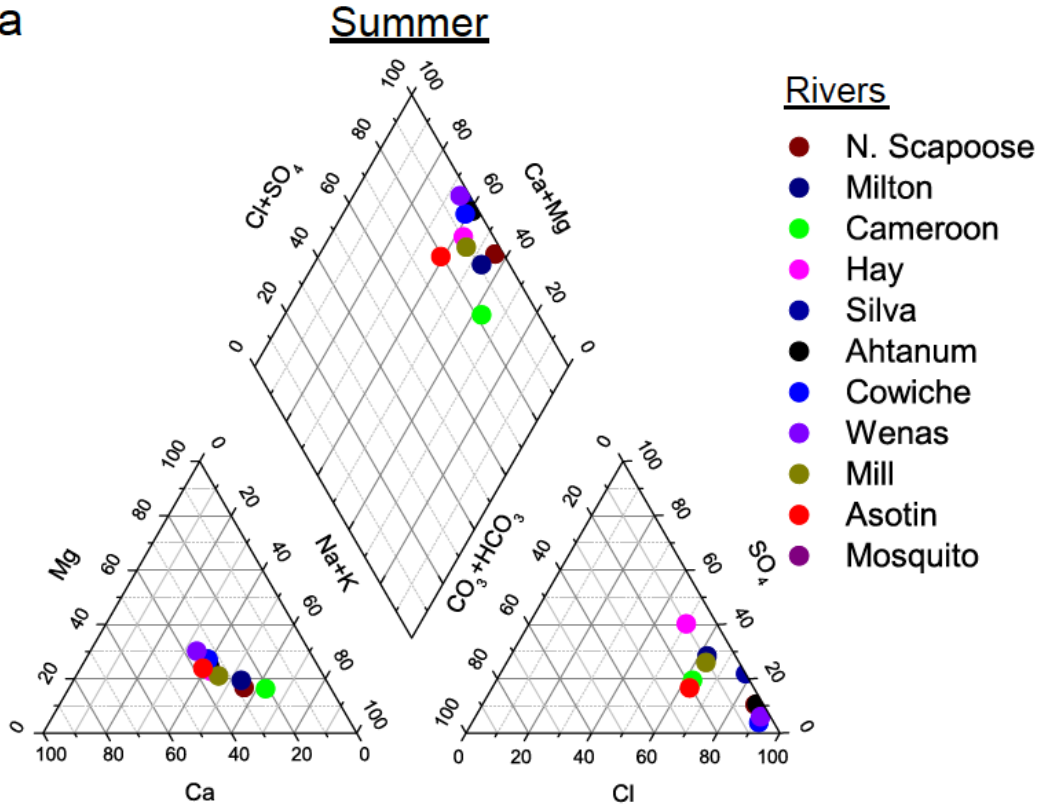


Figure 2: Model setup illustrating that simulations were run for a 100 m long aquifer exfiltrating into a river system, eventually. River simulations were run as batch simulations (no flow) assuming that the suspended load is transported at the same velocity as river water. Moreover, river simulations consider a diffusive dilution of the exfiltrated groundwater with water that experienced no previous water-rock interaction (i.e., pure water+CO<sub>2</sub>). For both systems (aquifer and river), Li isotope fractionation is simulated to occur during hematite and kaolinite precipitation.

a



b

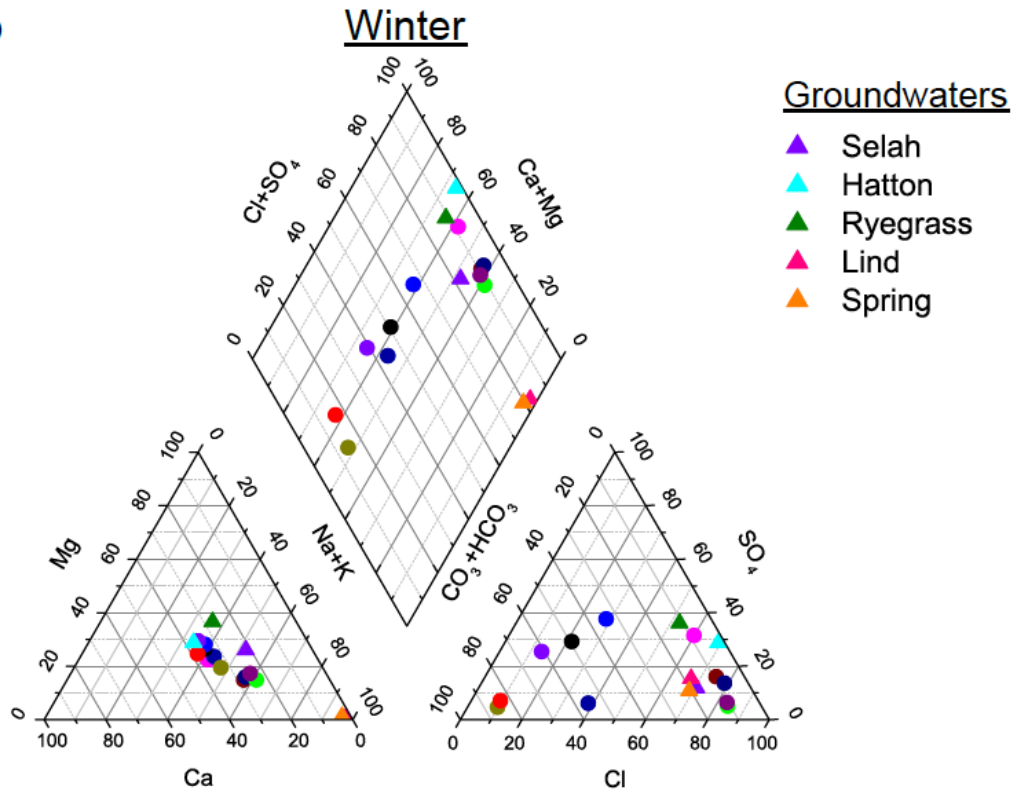


Figure 3. Piper diagram (Piper, 1953) of streams and groundwaters in summer (a) and late winter (b). Stream waters and groundwaters are shown in circles and triangles, respectively.

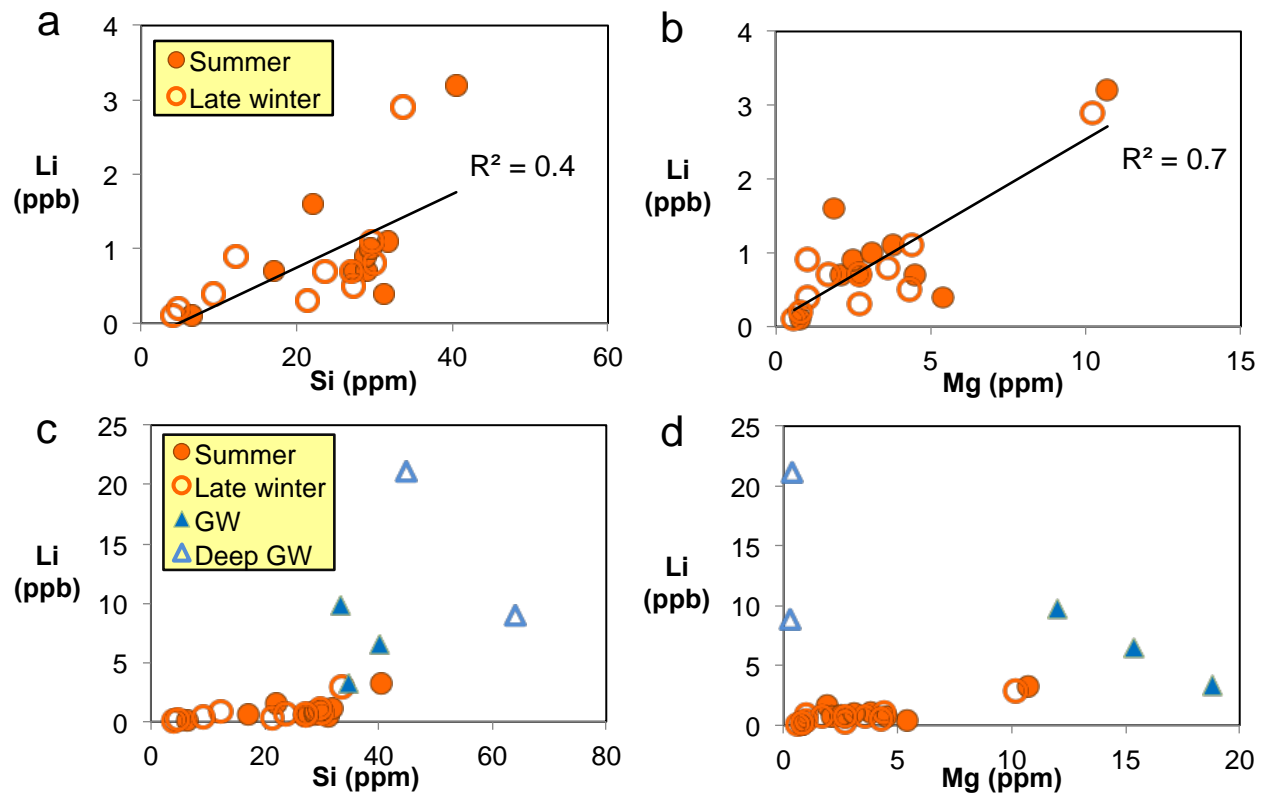


Figure 4. Plots of [Li] versus [Si] and [Mg] in streams and groundwaters. Summer and late winter stream waters are shown in open and closed orange circles, respectively. Groundwaters feeding the streams are in solid blue triangles, deep seated and ancient groundwaters are shown in open blue symbols.



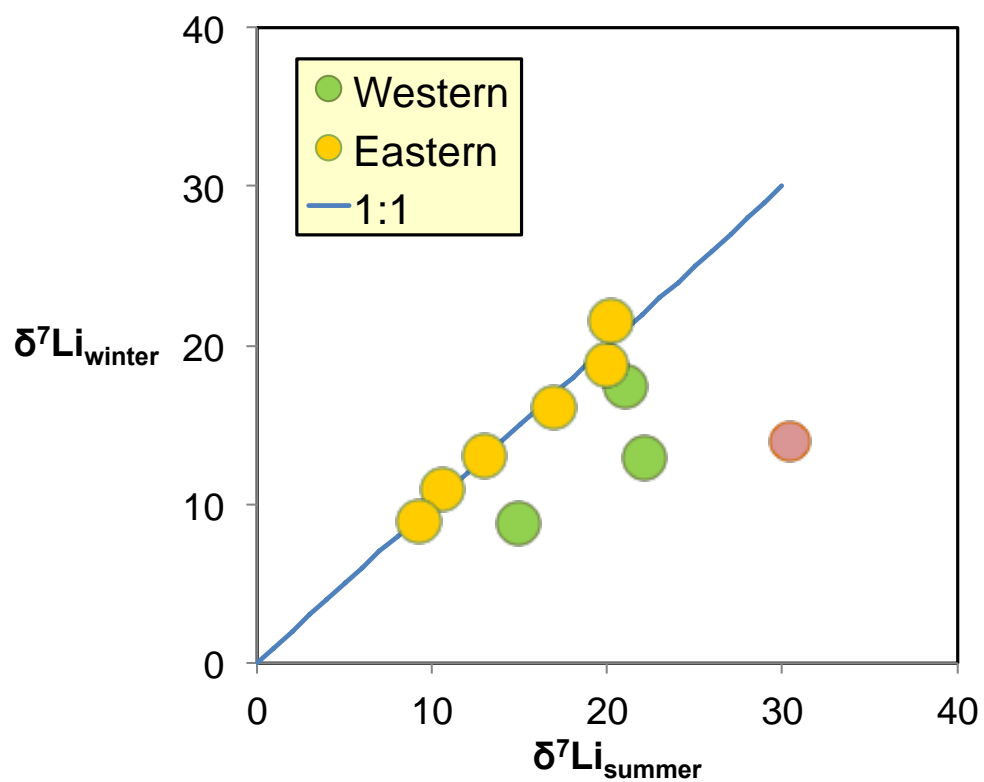


Figure 5.  $\delta^7\text{Li}_{\text{dis}}$  in summer vs. winter for western and eastern streams. The sample showing suspected anthropogenic contamination (Silva, eastern) is plotted as a red circle (see main text for details).

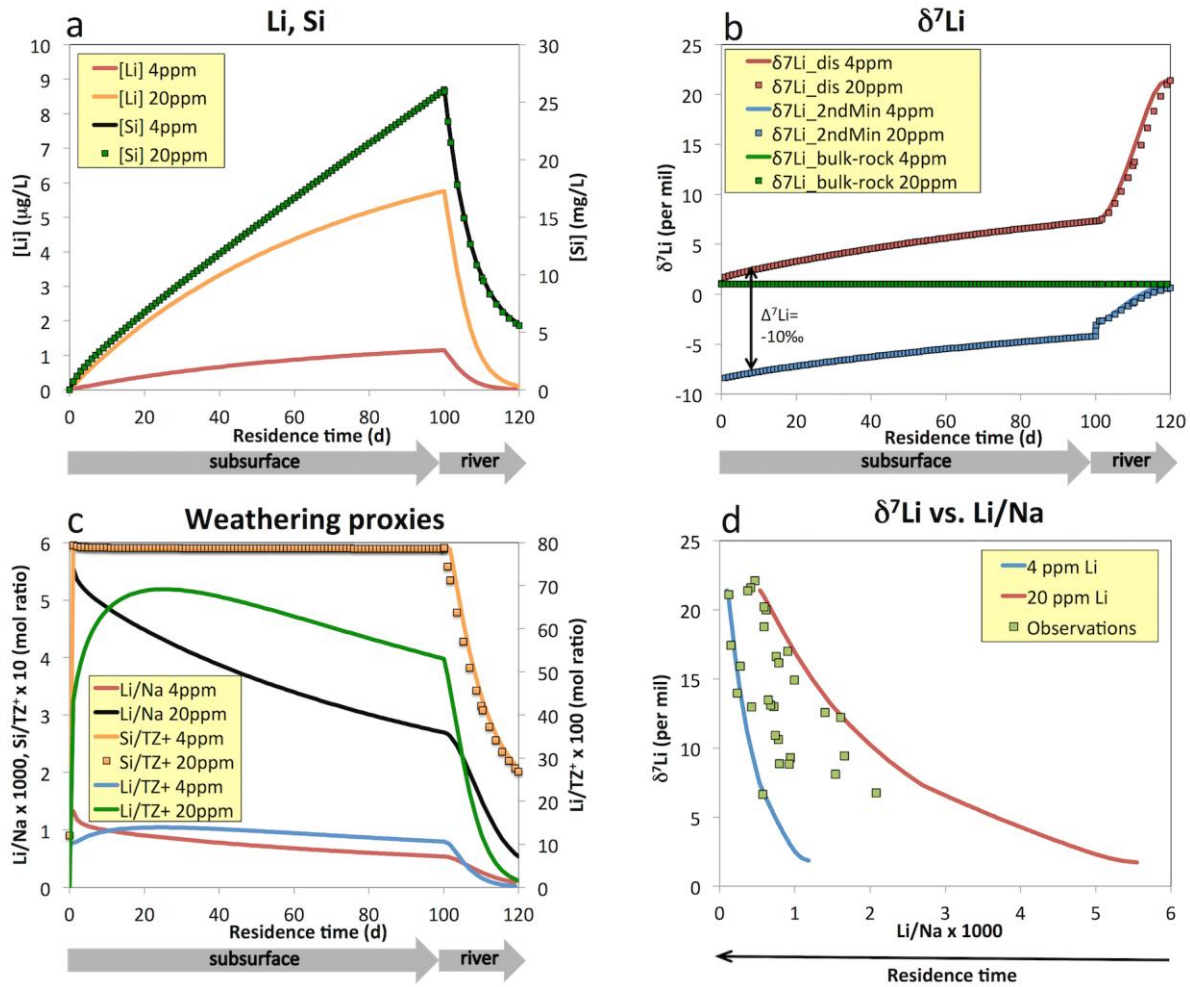


Figure 6: Model results for initial CRB Li concentrations of 4 ppm and 20 ppm. a illustrates steady state Li and Si concentration profiles along the full model domain (subsurface + river). b presents corresponding steady-state  $\delta^7\text{Li}$  profiles for aqueous Li ( $\delta^7\text{Li}_{\text{dis}}$ ), Li in precipitating secondary clays ( $\delta^7\text{Li}_{\text{kaolinite}} = \delta^7\text{Li}_{\text{hematite}}$  summarized as  $\delta^7\text{Li}_{\text{2ndMin}}$ ) and Li of the bulk solid. c illustrates steady state profiles of typical silicate weathering tracers such as  $\text{Si/TZ}^+$ ,  $\text{Li/TZ}^+$  and  $\text{Li/Na}$ . d Comparison between the simulated  $\delta^7\text{Li}$  vs.  $\text{Li/Na}$  relation (curves) and the one observed in groundwaters and streams draining the Columbia River Basalt (Tables 1 and 2). Decreasing  $\text{Li/Na}$  ratio reflects increasing subsurface and/or river residence time. All profiles are plotted against fluid residence time to simultaneously illustrate subsurface and river simulations. In the subsurface domain, fluid residence time (x-axis) also corresponds to the distance along the subsurface domain because the flow velocity was 1 m/d.

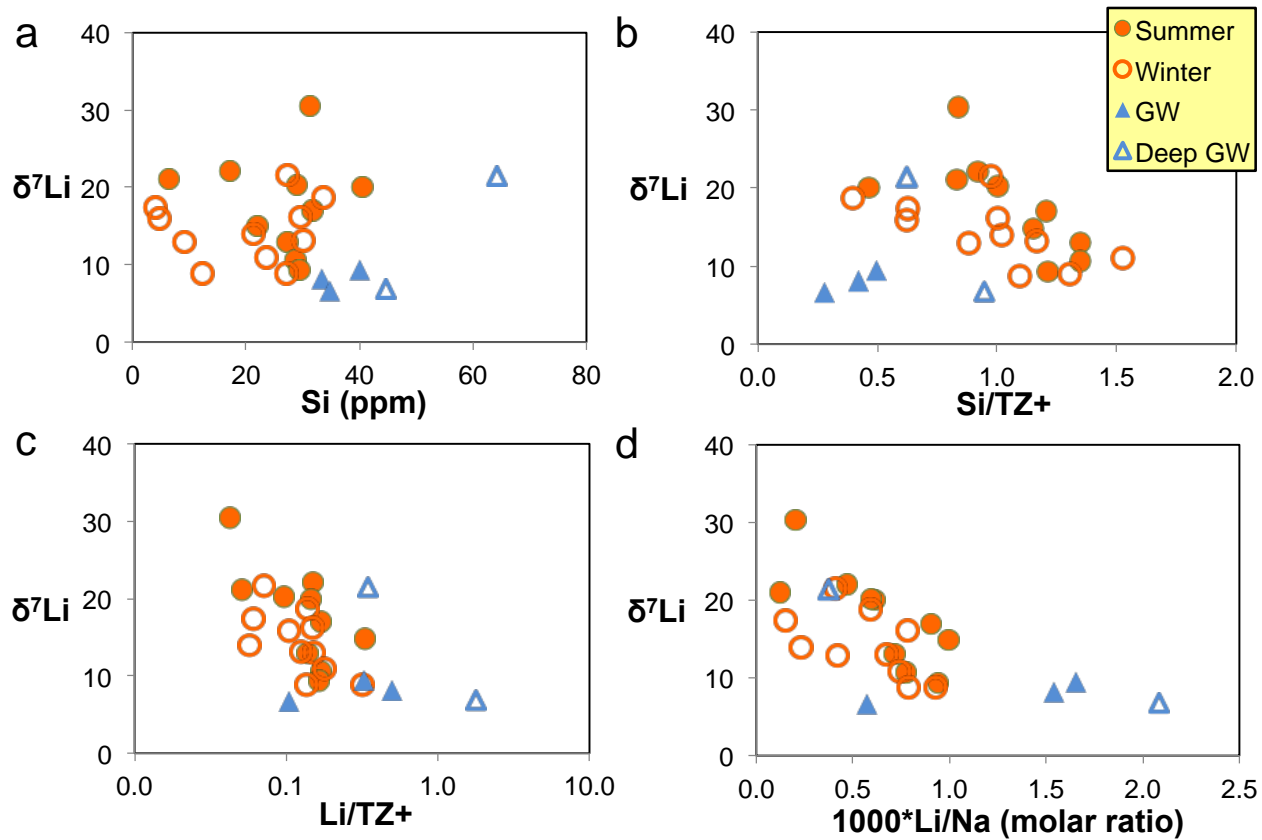


Figure 7.  $\delta^7\text{Li}_{\text{dis}}$  versus  $[\text{Si}]$ ,  $\text{Si}/\text{TZ}^+$ ,  $\text{Li}/\text{TZ}^+$ , and  $1000 \times \text{Li}/\text{Na}$  (molar ratio) in stream waters and groundwaters. Summer and late winter stream waters are shown in open and closed orange circles, respectively. Groundwaters feeding streams are in solid blue triangles, deep-seated groundwaters are in open blue triangles. The total cation charge ( $\text{TZ}^+$ ) is defined as  $\text{TZ}^+ = \text{Na}^+ + 2\text{Mg}^{2+} + \text{K}^+ + 2\text{Ca}^{2+}$  in  $10^{-3}$  equivalents per liter, mEq/L.

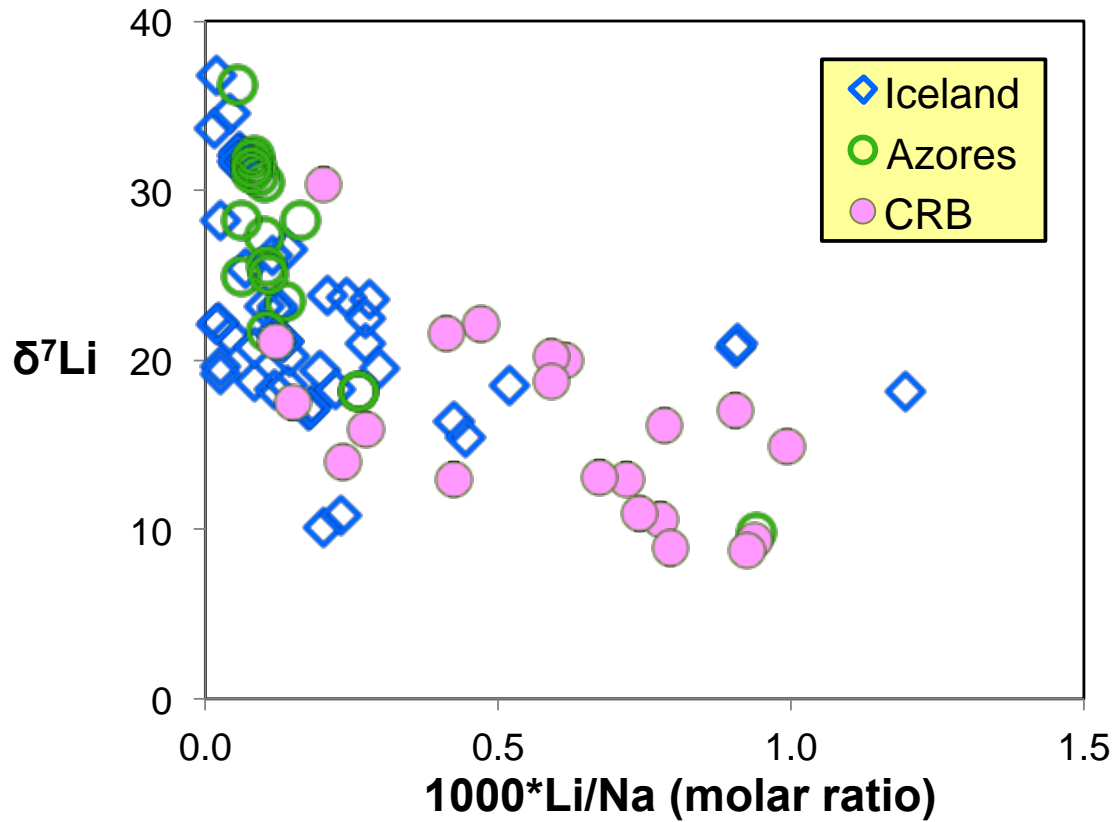


Figure 8.  $\delta^7\text{Li}$  versus  $1000 \times \text{Li}/\text{Na}$  (molar ratio) in dissolved loads of streams and rivers draining basalts. Data are from this study, Pogge von Strandmann et al. (2006; 2010), and Vigier et al. (2006; 2009).