

1 Seawater  $\delta^7\text{Li}$ : a direct proxy for global  $\text{CO}_2$  consumption by  
2 continental silicate weathering?

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8

9 **ABSTRACT**

10 The fractionation of stable Li isotopes ( $^6\text{Li}$ ,  $^7\text{Li}$ ) has become a promising proxy for  
11 assessing changes related to continental silicate weathering patterns. Recently, the first complete  
12 record of Cenozoic seawater Li isotopic composition ( $\delta^7\text{Li}$ ) was reported (Misra and Froelich,  
13 2012, *Science* 335, 818-821) showing a stepwise increase of +9‰ over the last 56 Ma. This  
14 increase was attributed to a general change in continental silicate weathering behavior caused by  
15 tectonic uplift. In particular, the low global average riverine  $\delta^7\text{Li}$  inferred for the Paleocene-  
16 Eocene boundary was explained by congruent silicate weathering of primary silicate minerals,  
17 which is inconsistent with the stoichiometry of secondary minerals and the resultant water  
18 chemistry.

19 In this study, we present a novel reactive transport modeling approach that explicitly  
20 includes Li isotopic fractionation to assess alternative geochemically-constrained interpretations  
21 that do not rely on congruent weathering. Simulations show that riverine  $\delta^7\text{Li}$  is mainly  
22 controlled by the subsurface residence time, the corresponding weathering intensity, and the

23 concentration of a river's suspended load. Based on these factors, we suspect that the low  $\delta^7\text{Li}$   
24 observed at the Paleocene-Eocene boundary was inherited from a high weathering intensity with  
25 predominant weathering of previously formed secondary mineral phases (e.g., clays, oxides)  
26 having low  $\delta^7\text{Li}$  values. Moreover, we conclude that the Cenozoic  $\delta^7\text{Li}$  increase was caused by  
27 an increasing amount of primary silicate mineral dissolution inherited from an increasing  
28 suspended river load concentration and a decreasing weathering intensity both likely induced by  
29 tectonic uplift. In contrast, Cenozoic cooling and corresponding  $p\text{CO}_2$  and precipitation  
30 variations do not seem to have a distinct control on the Cenozoic  $\delta^7\text{Li}$  record.

31 Finally, our simulations revealed a close relation between  $\delta^7\text{Li}$  and  $\text{CO}_2$  consumption by  
32 silicate weathering implying that the Cenozoic seawater  $\delta^7\text{Li}$  record could be potentially used to  
33 quantify such  $\text{CO}_2$  consumption through time. However, more experimental and modeling work  
34 is required to quantify the correlation between seawater  $\delta^7\text{Li}$  and global  $\text{CO}_2$  consumption by  
35 silicate weathering. Key parameters are the temperature-dependent thermodynamic properties of  
36 specific Li-bearing primary and secondary minerals (e.g., crystallographic Li substitution  
37 reaction, maximum Li substitution, Li solubility, Li isotopic fractionation factor) as well as the  
38 determination of global average subsurface and river discharges through time.

39

## 40 **1. INTRODUCTION**

41 Continental chemical weathering forms a major  $\text{CO}_2$  sink and is therefore an important  
42 input parameter for climate models (e.g., Berner and Kothavala, 2001; Berner et al., 1983;  
43 Francois and Godderis, 1998; Godderis et al., 2009; Li and Elderfield, 2013). However, the  
44 present and past global  $\text{CO}_2$  consumption by continental silicate weathering has not been  
45 precisely quantified (Li and Elderfield, 2013). Climate models simulating the carbon cycle over

46 Earth's history typically calibrate CO<sub>2</sub> consumption by chemical weathering against the observed  
47 seawater <sup>87</sup>Sr/<sup>86</sup>Sr ratio. Using <sup>87</sup>Sr/<sup>86</sup>Sr is challenging because it reflects chemical weathering of  
48 carbonates, as well as weathering of silicate minerals (Godderis et al., 2009; Oliver et al., 2003).  
49 Tracking the individual contribution of continental silicate weathering is, however, crucial  
50 because it may demonstrate whether an observed global CO<sub>2</sub> drawdown is caused by increased  
51 tectonic activity, such as the onset of the Himalayan orogeny ca. 30 Ma years ago (Raymo and  
52 Ruddiman, 1992), or by a decrease in total Earth CO<sub>2</sub> degassing (Berner et al., 1983). In contrast  
53 to Sr, lithium is a trace element that is almost exclusively found in silicate minerals, which  
54 makes it a useful tracer for silicate weathering (e.g., Huh et al., 2001; 1998; Kisakürek et al.,  
55 2005; 2004; Liu et al., 2013; Millot et al., 2010; Pogge von Strandmann et al., 2010; 2006;  
56 Rudnick et al., 2004; Vigier et al., 2009). In particular, tracking Li isotopic fractionation is  
57 promising because the two stable Li isotopes (<sup>6</sup>Li, <sup>7</sup>Li) fractionate when Li-bearing primary  
58 silicate minerals (e.g., micas) are weathered and secondary mineral phases (e.g., clays) are  
59 formed (Pistiner and Henderson, 2003; Vigier et al., 2008; Wimpenny et al., 2010; Zhang et al.,  
60 1998).

61 Hathorne and James (2006) presented the first record of seawater Li isotopic composition  
62 ( $\delta^7\text{Li}$ ) over the past 18 Ma years using foraminifera as a proxy. Misra and Froelich (2012)  
63 extended the record to 68 Ma showing a +9‰ increase over the last ca. 56 Ma. Unlike the steady  
64 <sup>87</sup>Sr/<sup>86</sup>Sr increase,  $\delta^7\text{Li}$  increased stepwise, which was attributed to specific tectonic events (e.g.,  
65 Himalayan orogeny) (Misra and Froelich, 2012). Specifically, the latter authors argued that  
66 tectonic uplift shifted the global silicate weathering pattern from a congruent, transport-limited  
67 regime to an incongruent, weathering-limited regime. However, the latter interpretation cannot  
68 be fully justified from a geochemical perspective, because secondary minerals typically observed

69 under a transport-limited weathering regime (e.g., Fe- and Al-oxides) are inconsistent with  
70 congruent silicate weathering.

71         Among the earth sciences, reactive transport modeling has become a powerful tool for a  
72 predictive understanding of many subsurface systems (Steeffel et al., 2005). To the best of our  
73 knowledge, it has not yet been used for a quantitative understanding of Li isotope fractionation  
74 processes. Instead, field-derived Li isotopic data were usually explained by using closed system  
75 Rayleigh distillation models (Kisakürek et al., 2004; Rudnick et al., 2004; Tipper et al., 2012;  
76 Yoon, 2010). Such models greatly simplify Li isotope fractionation processes because they only  
77 consider fractionation effects associated with the precipitation of Li-bearing minerals from an  
78 aqueous solution having a specific initial Li concentration. In contrast, they neglect that aqueous  
79 Li concentrations, and thus corresponding Li isotope fractionation effects, are also controlled by  
80 the simultaneous dissolution of Li-bearing primary minerals. Recently, Bouchez et al. (2013)  
81 presented a box-type mass balance and flux model that considers both dissolution of Li-bearing  
82 primary minerals and the precipitation of Li-bearing secondary minerals. Similar to Rayleigh-  
83 type models, the Bouchez et al. (2013) model does not take into account mineralogical, kinetic  
84 and thermodynamic properties of mineral phases involved in Li isotope fractionation processes  
85 (e.g., mineral stoichiometry, dissolution and precipitation rates, mineral solubilities).

86         In this paper we present a reactive transport modeling approach explicitly including the  
87 fractionation of Li isotopes to quantitatively test alternative interpretations for the Cenozoic  
88 seawater  $\delta^7\text{Li}$  record that do not rely on congruent silicate weathering. By doing so, we show that  
89 global average riverine and seawater  $\delta^7\text{Li}$  values are mainly controlled by the cumulative extent  
90 of water-rock interaction taking place along a flow path and are thus closely related to the  
91 corresponding  $\text{CO}_2$  consumption.

92

## 93 **2. Global Li isotopic fractionation model**

94

### 95 **2.1. The Misra and Froelich (2012) model**

96       Using a mass balance approach Misra and Froelich (2012) argued that the change in  
97 seawater  $\delta^7\text{Li}$  was solely attributed to a change in riverine  $\delta^7\text{Li}$ . The conclusion that changing  
98 seawater  $\delta^7\text{Li}$  values are mainly caused by a changing fate of continental Li seems reasonable as  
99 there is evidence that the seawater hydrothermal fluid input and oceanic Li isotopic fractionation  
100 processes remained roughly constant during the Cenozoic (Müller et al., 2008; Rowley, 2002).  
101 However, the rate of past oceanic crust production is still under debate. For example, various  
102 GEOCARB models (e.g., Berner, 1994; Berner and Kothavala, 2001) consider a variable  
103 hydrothermal fluid input. Moreover, the low seawater  $\delta^7\text{Li}$  values observed at the Paleocene-  
104 Eocene boundary (Misra and Froelich, 2012) could be inherited from a lower global average  
105 riverine  $\delta^7\text{Li}$  value (at constant riverine Li flux), from a lower dissolved riverine Li flux (at a  
106 constant  $\delta^7\text{Li}$  value), or from a combination of both. In fact, it is rather unlikely that processes  
107 causing a shift of the global average riverine Li isotopic composition do not vary the global  
108 average riverine Li flux and [Li].

109       It is well accepted that Li isotopic fractionation is mainly associated with secondary  
110 mineral precipitation (Kisakürek et al., 2005; Millot et al., 2010; Pogge von Strandmann et al.,  
111 2010; 2006; Vigier et al., 2009). By contrast, Li isotopes stoichiometrically dissolve from  
112 primary silicate minerals (Huh et al., 2004; Pistiner and Henderson, 2003). Riverine  $\delta^7\text{Li}$  is thus  
113 controlled by the ratio of Li released by primary silicate mineral dissolution to Li removed by  
114 secondary mineral precipitation and by Li isotopic fractionation associated with precipitation.

115 Consequently, host rock mineralogy does not show a distinct control on riverine  $\delta^7\text{Li}$  (Kisakürek  
116 et al., 2005; Millot et al., 2010). Changing global average riverine  $\delta^7\text{Li}$  values thus reflect a  
117 changing silicate weathering pattern only.

118 For the Paleocene-Eocene boundary (~56 Ma ago) a global average riverine  $\delta^7\text{Li}$  value of  
119 +3‰ was inferred (Misra and Froelich, 2012), being ca. 20‰ lower than the average  $\delta^7\text{Li}$  value  
120 of modern rivers. Misra and Froelich (2012) concluded that this light value was inherited from  
121 congruent weathering of primary silicate minerals having a  $\delta^7\text{Li}$  value in the same order of  
122 magnitude, whereas the current value is inherited from incongruent silicate weathering including  
123 secondary mineral precipitation (e.g., clays, oxides, and hydroxides) and accompanying Li  
124 isotopic fractionation. Whereas average continental bulk rock  $\delta^7\text{Li}$  values close to +3‰ are  
125 justified by the studies of Teng et al. (2004; 2008; 2009) reporting  $\delta^7\text{Li}$  values for the average  
126 ( $\delta^7\text{Li}=+2.0\pm 2.3\%$ ), upper ( $\delta^7\text{Li}=0\pm 2\%$ ) and lower continental crust ( $\delta^7\text{Li}=+1.6\pm 8.9\%$ ),  
127 congruent silicate weathering seems rather questionable. Specifically, Misra and Froelich (2012)  
128 argued that the global weathering regime at the Paleocene-Eocene boundary was similar to the  
129 current low-relief, peneplained type and transport-limited weathering pattern inferred for the  
130 Guayana Shield (Edmond et al., 1995). The Guayana Shield is located at the border of  
131 Venezuela, Colombia and Brazil and one of the so far lowest riverine  $\delta^7\text{Li}$  values was measured  
132 for a sample collected from this area (+6.6‰, Huh et al., 1998). Edmond et al. (1995) indeed  
133 characterized the weathering regime of the Guayana Shield as being weathering-intense and  
134 transport-limited but they explicitly stated that primary silicate minerals are incongruently  
135 dissolved. In fact, only incongruent silicate mineral dissolution can explain the formation of  
136 thick saprolites with an accumulation of quartz, clays, Fe- and Al-oxides typically observed at  
137 locations experiencing a high weathering intensity (Kisakürek et al., 2004; Liu et al., 2013;

138 Rudnick et al., 2004; White et al., 2001). Incongruent silicate weathering is also consistent with  
139 the low Al solubility at near neutral pH values, typical of these systems.

140 Furthermore, it is questionable if the average riverine  $\delta^7\text{Li}$  value at the Paleocene-Eocene  
141 boundary was as low as +3‰. If this is true, similar riverine  $\delta^7\text{Li}$  values should be found  
142 somewhere on Earth today reflecting weathering conditions for an isolated location that are  
143 similar to the global weathering pattern observed in the past (Hathorne and James, 2006). In fact,  
144 the compilation of available current riverine  $\delta^7\text{Li}$  values showed that the minimum values were  
145 larger, on the order of 6‰ (Misra and Froelich, 2012). Values close to +6‰, however, have so  
146 far only been published for two specific samples and only one of them originated from a  
147 weathering intense location (Guyana Shield, Huh et al., 1998). The other sample was collected  
148 from a Siberian river (Yana) where the weathering intensity is lower (Huh et al., 1998).  
149 Nevertheless, it is notable that +6‰ is in the same order of magnitude as the asymptotic riverine  
150  $\delta^7\text{Li}$  value Misra and Froelich (2012) obtained for the Paleocene-Eocene ocean by performing a  
151 sensitivity analysis on their mass balance calculations. Based on this analysis, the lack of present  
152 river  $\delta^7\text{Li}$  values less than +6‰, and a recent refinement of the Li cycle at the Paleocene-Eocene  
153 boundary ( $\delta^7\text{Li}_{\text{riverine}}=+12\text{‰}$ , Li and West, 2014), we propose that the Paleocene-Eocene riverine  
154  $\delta^7\text{Li}$  was likely around +6‰ or larger. Inferring a global average riverine  $\delta^7\text{Li}$  that is higher than  
155 the value of the upper continental crust ( $\delta^7\text{Li}=0.0\pm 2\text{‰}$ , Teng et al., 2004) implies that Li isotopic  
156 fractionation between bulk crustal rocks and global rivers was taking place. Moreover, it rules  
157 out congruent weathering as being responsible for the minimum seawater  $\delta^7\text{Li}$  observed at the  
158 Paleocene-Eocene boundary.

159

## 160 **2.2. Alternative hypotheses explaining the Cenozoic seawater $\delta^7\text{Li}$ value record**

161           Following the arguments of Misra and Froelich (2012), we assume that increasing  
162 Cenozoic seawater  $\delta^7\text{Li}$  values are mainly attributed to a change in riverine  $\delta^7\text{Li}$ . We do,  
163 however, not *a priori* assume that the riverine Li flux and the hydrothermal seawater Li input  
164 remained constant. Nevertheless, we focus on changing riverine  $\delta^7\text{Li}$  values rather than possible  
165 effects of changing Li isotopic fractionation processes in the ocean (i.e., reverse weathering) and  
166 a variable seawater hydrothermal Li input. Also, we assume that the composition of the  
167 continental crust exposed to chemical weathering remained roughly constant since the  
168 Paleocene-Eocene boundary, thus neglecting potential effects of time-varying lithology on global  
169 average riverine and seawater  $\delta^7\text{Li}$  values. Similar to Misra and Froelich (2012), we speculate  
170 that the Cenozoic seawater  $\delta^7\text{Li}$  value increase is most likely inherited from a changing  
171 continental silicate weathering pattern induced by an increasing global relief owing to major  
172 global orogenies (e.g., Himalayan, Andean orogeny) and by the cooling trend observed since the  
173 humid Paleocene-Eocene thermal maximum (PETM) (Clementz and Sewall, 2011; Miller et al.,  
174 1987). An increasing relief (Fig. 1) and cooler temperatures have the following first order effects  
175 on chemical silicate weathering, which have potentially caused the observed  $\delta^7\text{Li}$  shift:

- 176           1)       An increasing relief shifts the hydraulic gradient to higher values, increasing flow  
177                        velocities and shortening residence times along a specific subsurface flow path  
178                        (Fig. 1). Cooler temperatures decrease the dissolution rates of primary silicate  
179                        minerals (Lasaga, 1984). Hence, increasing relief and cooler temperatures limit  
180                        water-rock interaction along specific flow paths.
- 181           2)       For a low relief, such as inferred for the Paleocene-Eocene boundary (Misra and  
182                        Froelich, 2012), the hydraulic gradient is low and the average subsurface  
183                        residence time is high. Long residence times under hot and humid climatic

184 conditions (Clementz and Sewall, 2011; Miller et al., 1987) cause a high  
185 degree of water rock-interaction with plenty of newly formed secondary  
186 mineral phases, which is usually described as a weathering-intensive or  
187 transport-limited weathering pattern (Misra and Froelich, 2012). We thus  
188 assume that at the Paleocene-Eocene boundary, the global average saprolite  
189 thickness (composed of mostly quartz, clays, Fe- and Al-oxides) was higher  
190 than it is today (Fig. 1). Following this argument, and taking into account an  
191 increasing global relief as well as decreasing temperatures, the degree of  
192 exposure of the silicate bedrock to chemical weathering must have increased  
193 over the last 56 Ma, which is equivalent to proposing a decreasing weathering  
194 intensity. It should be noted that our use of “weathering intensity” throughout  
195 this paper strictly refers to the chemical index of alteration (CIA), which is the  
196 commonly used proxy for expressing the chemical weathering intensity of a  
197 particular rock or soil sample (Nesbitt and Young, 1982). This definition is  
198 particularly useful because it takes into account the ratio between immobile  
199 (e.g., Al) and mobile (e.g., Na, Ca, K) elements, on which the amount of newly  
200 formed clays, oxides and hydroxides has a first order control. Alternatively,  
201 riverine aqueous species concentrations (e.g., [Si], normalized [Si]) have been  
202 proposed to operate as weathering intensity proxies (Kisakürek et al., 2005;  
203 Pogge von Strandmann et al., 2006). The drawback of using riverine aqueous  
204 species concentrations is that, once chemical equilibrium is reached, their  
205 concentrations become discharge independent (Maher, 2011), whereas  
206 chemical silicate weathering fluxes and corresponding weathering rates are

207 linearly increasing with increasing discharge (Gaillardet et al., 1999; Maher,  
208 2011). The strong dependence on discharge implies that also chemical silicate  
209 weathering rates do not necessarily correspond to weathering intensity. For  
210 instance, a relatively low chemical weathering rate was calculated for the  
211 weathering intense Guyana Shield (Gaillardet et al., 1999).

212 3) Owing to the higher hydraulic gradient, an increasing global relief shifts the  
213 physical erosion rate (i.e., denudation rate) to higher values (Bouchez et al.,  
214 2013). A higher denudation rate leads to an increase of the suspended river  
215 load concentration, as long as the suspended load is not deposited in lowland  
216 areas (Gaillardet et al., 1999; Milliman and Meade, 1983). Consequently, we  
217 speculate that the global average suspended river load concentration increased  
218 over the last 56 Ma such as already argued by Misra and Froelich (2012).

219

### 220 **3. Methods**

221 A series of thermodynamically- and kinetically-controlled reactive transport model simulations  
222 using TOUGHREACT V2 (Xu et al., 2011) were performed to assess the effect of the identified  
223 changing weathering parameters on Cenozoic global average riverine and seawater  $\delta^7\text{Li}$  (i.e.,  
224 decreasing subsurface residence time, cooling trend, decreasing weathering intensity, increasing  
225 suspended river load concentration). TOUGHREACT has been used to evaluate isotopic  
226 fractionation coupled to water-rock interaction and hydrological processes in a variety of  
227 subsurface environments and laboratory experiments (e.g., Singleton et al., 2005; Sonnenthal et  
228 al., 1998; Wanner and Sonnenthal, 2013).

229

230 **3.1. Model Setup**

231 Two different types of simulations were carried out to model silicate weathering and associated  
232 Li isotopic fractionation (i) in the subsurface and (ii) within rivers (Fig. 2).

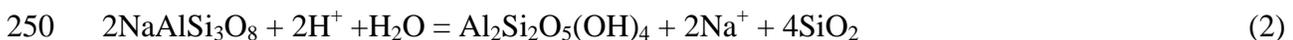
233

234 *3.1.1. Subsurface simulations*

235 Reactive transport of infiltrating meteoric water along a typical subsurface flow path (e.g.,  
236 arrows on Fig. 1) was simulated for a fully water-saturated, 200 m long porous media with an  
237 assumed porosity of 10%. The unsaturated zone was neglected because our focus was on  
238 assessing the sensitivity (i.e., trends) of dissolved  $\delta^7\text{Li}$  values as a function of residence time,  
239 climate, and weathering intensity rather than on simulating detailed flow features of infiltration  
240 through the unsaturated zone and recharge to aquifers and rivers. Subsurface simulations were  
241 run for an average linear flow velocity of 1 m/d to simulate a system dominated by advection.  
242 The 200 m long model domain (Fig. 2) was divided into 200 cubic grid blocks of 1x1x1 m each  
243 to numerically solve the governing differential equations using TOUGHREACT's integral finite  
244 differences approach (Xu et al., 2011).

245 Pure water in equilibrium with atmospheric  $\text{CO}_2$  was specified as initial and boundary fluid  
246 compositions. In doing so, atmospheric  $\text{CO}_2$  is partially dissolved and provides  $\text{H}^+$  necessary for  
247 silicate weathering reactions such as illustrated for the weathering of albite to kaolinite:

248



251

252 The CO<sub>2</sub> partial pressure  $pCO_2$  was fixed during the course of the simulations to approximate the  
253 buffering caused by an almost unlimited CO<sub>2</sub> source from the atmosphere. This specification  
254 allows tracking the amount of CO<sub>2</sub> consumed by silicate weathering reactions assuming that the  
255 reaction product HCO<sub>3</sub><sup>-</sup> exiting the model domain is further transported to the sea, where it  
256 precipitates as carbonates (Godderis et al., 2009) (Fig. 1).

257 A granitic mineral assemblage (quartz, potassium-feldspar, plagioclase, biotite) was assigned to  
258 the solid part of the porous media to simulate typical continental silicate weathering processes.  
259 Subsequently, the model was divided into a “fresh granite” domain and a domain that  
260 experienced previous weathering (e.g., “altered granite”) (Fig. 2), thus corresponding to the  
261 saprolite zone of our conceptual model (Fig. 1). By varying the volume ratio between the “fresh  
262 granite” and “altered granite” domain the effect of the proposed increasing exposure of the  
263 silicate bedrock to chemical weathering on  $\delta^7Li$  was assessed. By running the model for a  
264 variable “fresh granite” contribution (i.e., varying volume ratio) we simulated the effect of a  
265 varying chemical weathering intensity (i.e., varying saprolite thickness) on  $\delta^7Li$  because a large  
266 “fresh granite” or large “altered granite” contribution corresponds to a low or high weathering  
267 intensity, respectively. Accordingly, we also assess earlier findings reporting that the chemical  
268 silicate weathering intensity forms a first order control on aqueous  $\delta^7Li$  (Huh et al., 2001;  
269 Kisakürek et al., 2005; Pogge von Strandmann et al., 2006).

270 A mineralogical composition typical for the Sierra Nevada Batholith (Economos et al., 2010)  
271 was defined for the “fresh granite” domain (Table 1). The initial mineralogical definition  
272 included a bulk Li concentration of 24 ppm (Economos et al., 2010), which is similar to the  
273 average upper-crustal Li concentration of  $35\pm 11$  ppm (Teng et al., 2004). Owing to their similar  
274 ionic radii, Li<sup>+</sup> substitutes easily for Mg<sup>2+</sup> into the structural octahedral sites of silicate minerals

275 (Vigier et al., 2008). Furthermore, Li tends to accumulate in biotite (Kretz et al., 1989).  
 276 Accordingly, Li was introduced into the model by specifying Li-bearing biotite using a  $Mg^{2+}$ -  
 277  $Li^+K^+$  exchange (Table 2). Because in granitic environments, silicate mineral phases are  
 278 predominantly weathered to kaolinite (Maher et al., 2009; Rudnick et al., 2004; White, 2002),  
 279 and because goethite is the most widespread form of secondary iron oxides (Tardy and Nahon,  
 280 1985) Li-bearing kaolinite, and Li-bearing goethite were allowed to precipitate. By neglecting  
 281 secondary Ca- and Mg-bearing minerals we do not fully investigate the fate of these two  
 282 elements during silicate weathering. Our conceptual model (Fig. 1), however, assumes that  
 283 riverine [Ca] and [Mg] are affected by carbonate weathering to ensure that carbonate  
 284 precipitation and subsequent CO<sub>2</sub> consumption is occurring in the ocean, eventually.

285 TOUGHREACT V2 (Xu et al., 2011) computes mineral dissolution and precipitation reactions  
 286 as kinetic reactions based on transition state theory (TST) (Lasaga, 1984)

287

$$288 \quad r = A \cdot k \cdot \left( 1 - \left( \frac{Q}{K} \right)^m \right)^n \quad (3)$$

289

290 where A refers to the mineral reactive surface area ( $m^2_{\text{mineral}}/kg_{H_2O}$ ), k is the reaction rate  
 291 constant ( $mol/m^2/s$ ), Q refers to the ion activity product of a mineral dissolution/precipitation  
 292 reaction (Table 2) and K is the corresponding equilibrium constant. Exponents m and n are fitting  
 293 parameters that must be experimentally determined. For this study they were taken as equal to  
 294 one, which is usually, but not always the case. In order to calculate effective precipitation and  
 295 dissolution rates (eq. 3) reaction rate constants were defined according to Palandri and Kharaka  
 296 (2004) whereas equilibrium constants were taken from the Soltherm.H06 database (Reed and

297 Palandri, 2006), which was derived using SUPCRT92 (Johnson et al., 1992). Mineral  
298 stoichiometries, thermodynamic and kinetic parameters, and initial mineral and fluid  
299 compositions are summarized in Tables 1 and 2.

300

### 301 *3.1.2. River simulations*

302 River simulations were conducted essentially as batch simulations, where the flow velocity was  
303 set to zero (Fig. 2). In doing so, it was assumed that the reactive suspended load (i.e., solid  
304 phase) is transported at the same velocity as river water, which is in agreement with current  
305 knowledge about transport of suspended river loads (Fryirs and Brierley, 2013). Simulating  
306 reactive transport in rivers by means of a batch simulation is justified because only the relative  
307 transport velocity between aqueous and solid phase (i.e., suspended load) matters, whereas the  
308 actual velocity of the two phases has no effect as long as aqueous and solid phases are  
309 transported at the same velocity.

310 Two grid blocks of 1x1x1 m each were defined to simulate that subsurface waters exfiltrating  
311 into river systems are diluted by river water, which previously experienced no or only minor  
312 water-rock interaction. Consequently, steady-state concentrations obtained at the downstream  
313 model boundary of the subsurface simulations were taken as input concentrations for one of the  
314 two grid blocks, while pure water in equilibrium with CO<sub>2</sub> was defined as the initial  
315 concentration for the second grid block (Fig. 2). It should be noted, that this particular grid block  
316 has no geochemical meaning other than ensuring that exfiltrated subsurface water is diluted  
317 during its transport in the river. Due to the initial concentration gradient, a diffusive flux  $J_{Di}$   
318 occurred between the two grid blocks, expressed as

319

320 
$$J_{D_i} = \frac{\phi \cdot \tau \cdot D_{aq} \cdot A_{interface}}{d_1 + d_2} \cdot \frac{dC_i}{dx} \quad (4)$$

321  
322 where  $D_{aq}$  refers to the molecular diffusion coefficient of aqueous species ( $\sim 10^{-9}$  m<sup>2</sup>/s),  $A_{interface}$   
323 (m<sup>2</sup>) is the interfacial area between the two grid blocks,  $dC_i/dx$  (mol/kg<sub>H2O</sub>/m) is the  
324 concentration gradient of species  $i$ ,  $d_1$  and  $d_2$  (m) refer to the distances from the center of the two  
325 grid blocks to their mutual interface, and  $\Phi$  and  $\tau$  are the porosity and tortuosity, respectively.  
326 Reactions between the suspended river load and river waters were only considered for the grid  
327 block initially containing exfiltrating subsurface water. By setting the corresponding porosity to  
328 a very large value of 99.9% (Fig. 2), it was ensured that the suspended load only forms a minor  
329 fraction of the total river volume. The tortuosity was set to 1.0 for both grid blocks.

330 The same initial granitic mineralogical composition as for the subsurface “fresh granite” domain  
331 was assigned to the suspended river load (Table 2). In doing this, we assume that the suspended  
332 load contains a significant amount of primary silicate minerals in addition to the dominant clays  
333 and oxides (Gaillardet et al., 1999). This model assumption is consistent with Bouchez et al.  
334 (2011) who observed that the mineralogical composition of the suspended load is dependent on  
335 the particle size and that primary silicate minerals (e.g., quartz, albite) are enriched in the coarser  
336 fraction. Consequently, new goethite and kaolinite are allowed to precipitate and Li isotope  
337 fractionation in the simulated river thus occurs in the same fashion as in the subsurface  
338 simulations. As long as primary silicate minerals are exposed to chemical weathering, our river  
339 simulations are not sensitive to the ratio between primary and secondary minerals. Accordingly,  
340 we did not change the initial mineral volume fraction when compared to the subsurface  
341 simulations (Table 1).

342

### 343 **3.2. Simulation of Li isotopic fractionation**

344 To simulate Li isotopic fractionation,  $^6\text{Li}$  and  $^7\text{Li}$  were incorporated into the mineral  
345 stoichiometries of biotite, kaolinite and goethite (Table 2). An initial  $\delta^7\text{Li}$  value of 0.0‰ was  
346 assumed for Li-bearing biotite corresponding to the average  $\delta^7\text{Li}$  value of the upper continental  
347 crust (Teng et al., 2004). Assuming stoichiometric biotite dissolution, our simulations agree with  
348 previous studies showing that no or only minor Li isotopic fractionation occurs during mineral  
349 dissolution (Huh et al., 2004; Pistiner and Henderson, 2003). In contrast, our model considers Li  
350 isotopic fractionation during Li incorporation into precipitating kaolinite and goethite, using a  
351 solid solution approach similar to the one described for simulating Sr and Cr isotopic  
352 fractionation (Sonnenenthal et al., 1998; Wanner and Sonnenenthal, 2013). It should be noted,  
353 however, that Li must be treated slightly differently because it is incorporated into secondary  
354 minerals as a trace element, whereas Cr and Sr can be major constituents of minerals controlling  
355 the fate of Cr and Sr isotopes (e.g.,  $\text{Cr}(\text{OH})_3$  and  $\text{SrCO}_3$ ). Particularly challenging is the fact that,  
356 although some suggestions are found in the literature (Pistiner and Henderson, 2003; Vigier et  
357 al., 2008), it has not yet been shown how Li structurally substitutes into kaolinite and goethite.  
358 Because of this lack of detailed mineralogical knowledge, our model assumes a solid solution  
359 with three different endmembers (Fig. 3) to simulate Li uptake and associated Li isotopic  
360 fractionation during kaolinite and goethite precipitation: (i) a pure, non-Li bearing kaolinite and  
361 goethite endmember, (ii) a pure  $^6\text{Li}$  bearing mineral endmember and (iii) a pure  $^7\text{Li}$  bearing  
362 endmember. The pure  $^6\text{Li}$  and  $^7\text{Li}$  endmembers are hypothetical, but their specification allows  
363 fitting experimentally observed aqueous Li concentrations as well as measured amounts of Li  
364 that are incorporated in secondary minerals by calibrating the corresponding  $\log(K)$  values.

365 The precipitation rate  $r_{prec}$  of the Li bearing kaolinite and goethite solid solution is defined as the  
 366 sum of the individual endmember (Fig. 3) precipitation rates  $r_{pure2nd}$ ,  $r_{6Li}$  and  $r_{7Li}$ :

367

$$368 \quad r_{prec} = r_{pure2nd} + r_{6Li} + r_{7Li} \quad (5)$$

369

370 The rate of a specific endmember,  $r_{endm}$ , is calculated according to a TST-like expression

371

$$372 \quad r_{endm} = A \cdot k \cdot \left( 1 - \frac{Q_{endm}}{K_{endm}} \right) + k \cdot A \cdot (x_{endm} - 1) \quad (6)$$

373

374 where  $x_{endm}$  refers to the mole fraction of a specific secondary mineral endmember. For the  
 375 hypothetical, pure  ${}^6Li$  and  ${}^7Li$  endmembers  $x_{6Li}$  and  $x_{7Li}$  are calculated according to:

376

$$377 \quad x_{6Li} = \frac{Q_{6Li} / K_{6Li}}{Q_{6Li} / K_{6Li} + Q_{7Li} / K_{7Li}} \quad (7)$$

$$378 \quad x_{7Li} = \frac{Q_{7Li} / K_{7Li}}{Q_{6Li} / K_{6Li} + Q_{7Li} / K_{7Li}} \quad (8)$$

379

380 Equations (7) and (8) ensure that the amount of Li that is incorporated into goethite and kaolinite  
 381 reflects the Li concentration of the aqueous solution. Accordingly, the amount of Li removed by  
 382 precipitation increases with increasing aqueous Li concentration. By doing so, our model is in  
 383 good agreement with an experimental study showing that [Li] of synthesized smectites are  
 384 linearly correlated with the corresponding aqueous [Li] (Decarreau et al., 2012).

385 Using the solid solution approach described above allows conveniently specifying a particular Li  
386 isotopic fractionation factor  $\alpha$  and corresponding enrichment factor  $\varepsilon$  for our simulations:

387

$$388 \quad \alpha = \frac{K_{6Li}}{K_{7Li}} \quad (9)$$

389

$$390 \quad \varepsilon = (\alpha - 1) \cdot 1000 \approx \Delta^7Li = \delta^7Li_{2ndMin} - \delta^7Li_{solution} \quad (10)$$

391

392 Experimentally-determined Li isotopic enrichment factors for Li incorporation into precipitating  
393 minerals ( $\Delta^7Li_{2ndMin-solution} = \delta^7Li_{2ndMin} - \delta^7Li_{solution}$ ) have so far only been reported for smectite,  
394 yielding values between -1.6 (at T=250°C) and -16.5‰ (at T=25°C), depending on the  
395 experimental temperature (Vigier et al., 2008; personal communication). Other studies  
396 determined  $\Delta^7Li$  values between dissolved and suspended Li loads in rivers yielding  $\Delta^7Li_{suspended-}$   
397  $_{dissolved}$  from -6 to -36‰ (Huh et al., 2001; Kısakürek et al., 2005; Pogge von Strandmann et al.,  
398 2010; 2006). Because of this relatively sparse dataset, we assigned a Li isotopic enrichment  
399 factor of -20‰ for kaolinite as well as for goethite precipitation, which is within the range of Li  
400 isotopic enrichment factors reported or inferred for secondary mineral precipitation.

401 Li adsorption on solid surfaces has been proposed as an additional process causing Li isotopic  
402 fractionation (Pistiner and Henderson, 2003; Zhang et al., 1998). Significant fractionation ( $\varepsilon = -$   
403 13‰) was reported for an experiment involving Li adsorption via surface complexation reactions  
404 at gibbsite surfaces (Pistiner and Henderson, 2003). Moreover, enrichment factors of -21‰ and -  
405 29‰ were experimentally determined for Li adsorption on kaolinite and vermiculite,  
406 respectively (Zhang et al., 1998). These enrichment factors, however, were determined by solely

407 studying the dissolved Li and no information regarding the surface complexation or substitution  
408 reaction is available. In contrast, very little Li isotopic fractionation was observed during Li  
409 exchange (i.e., ion exchange reaction) with smectite interlayers (Pistiner and Henderson, 2003,  
410 Vigier et al., 2008). Overall, experimental data suggest that Li isotopic fractionation is caused by  
411 surface complexation reactions associated with a changing Li coordination chemistry or by Li  
412 substitution into crystal lattices. In contrast, physical Li adsorption by ion exchange reactions  
413 does not seem to cause significant fractionation. Similar to Bouchez et al. (2013) our model does  
414 not distinguish between Li exchange-, Li surface complexation-, or Li substitution reactions and  
415 Li uptake by secondary minerals and associated Li isotopic fractionation is solely simulated as a  
416 crystallographic substitution reaction during the formation of kaolinite and goethite such as  
417 discussed earlier.

418 Li isotope fractionation inherited from differences in the aqueous  $^6\text{Li}$  and  $^7\text{Li}$  diffusive flux was  
419 neglected because kaolinite and goethite precipitation was not assumed to be transport-limited by  
420 Li diffusion.

421

## 422 **4. Model results and discussion**

423

### 424 **4.1. Simulation of the current weathering pattern (Fig. 1b)**

425 To simulate the inferred current weathering pattern with predominant weathering of primary  
426 silicate minerals (Fig. 1) a “fresh granite” mineralogical composition was assigned to the entire  
427 subsurface model domain (i.e., 100% “fresh granite”) and the  $p\text{CO}_2$  was fixed to the approximate  
428 current atmospheric  $p\text{CO}_2$  of ca. 370 ppm volume (ppmV) (Keeling, 1960). The solubility of the  
429 pure, but hypothetical Li-bearing kaolinite and goethite endmember ( $\log(K)$ ) was calibrated to -

430 2.6 (Table 2) to get a maximum kaolinite and goethite Li concentration within the subsurface  
431 domain of 200 ppm. A maximum value of 200 ppm is in agreement with Li concentration  
432 measurements in continental clays (Tardy et al., 1972). For the subsurface simulations, reactive  
433 surface areas for primary mineral phases were set to 1-2 cm<sup>2</sup>/g (Table 2) to obtain a Li  
434 concentration at the end of the subsurface domain (4.08 μg/L, Fig. 4a,d) that is larger than the  
435 global average riverine value of 1.83 μg/L (Misra and Froelich, 2012). A reactive surface area of  
436 1-2 cm<sup>2</sup>/g also ensured that chemical equilibrium was not fully established within the subsurface  
437 domain and that primary mineral dissolution was occurring along the full domain (Fig. 4b,e).  
438 Reactive surface areas of precipitating kaolinite and goethite were set to the high value of 6824  
439 cm<sup>2</sup>/g based on Dobson et al. (2003).

440 With the specified parameters, our model yielded a continuous δ<sup>7</sup>Li increase along the  
441 subsurface model domain reaching a dissolved δ<sup>7</sup>Li value of roughly +10‰ at the downstream  
442 model boundary (Fig. 4a,d). It should be noted that the slope of the δ<sup>7</sup>Li increase with residence  
443 time is dependent on the specified enrichment factor. For lower factors (i.e., less fractionation),  
444 longer residence time is needed to reach the same δ<sup>7</sup>Li as for ε= -20‰, or vice versa. However,  
445 the correlation between δ<sup>7</sup>Li and residence time is not sensitive to the specified enrichment  
446 factor. A δ<sup>7</sup>Li value of +10‰ is significantly lower than the current global average riverine δ<sup>7</sup>Li  
447 value of +23‰, (Misra and Froelich, 2012) implying that Li isotopic fractionation occurring in  
448 rivers form a major contribution on riverine δ<sup>7</sup>Li. This simulation finding is supported by δ<sup>7</sup>Li  
449 values derived from groundwaters and rivers draining the Columbia River basalt as well as small  
450 granitic catchments yielding significantly larger δ<sup>7</sup>Li values for river samples (Lemarchand et al.,  
451 2010; Liu et al., 2014). Consequently, the reactive surface area of the suspended river load  
452  $A_{\text{suspended\_load}}$  was calibrated to 6000 cm<sup>2</sup>/g (Table 2) for the corresponding river simulation to

453 match the global average riverine  $\delta^7\text{Li}$  value (+23‰) after a simulated river residence time of 20  
454 days, for which all river simulations were run (Fig. 4a). Similarly, the interfacial area between  
455 the two grid blocks of the river simulation  $A_{\text{interface}}$  (eq. 4, Fig. 2) was set to 2560 m<sup>2</sup> to result in  
456 dilution of the exfiltrated groundwater by a factor of roughly 2. In doing so, the obtained Li  
457 concentration at the end of the river simulation (0.79,  $\mu\text{g/L}$ , Fig. 4a) was somewhat lower but  
458 still in the same order of magnitude as the global average riverine Li concentration of 1.83  $\mu\text{g/L}$   
459 (Misra and Froelich, 2012).

460 To explore the sensitivity of riverine  $\delta^7\text{Li}$  on the reactivity of the suspended river load and thus  
461 on the actual suspended load concentration, the river simulation was performed for an  
462  $A_{\text{suspended\_load}}$  of 375 cm<sup>2</sup>/g (Table 2). This value is 16 times lower than the initial surface area  
463 (6000 cm<sup>2</sup>/g), and thus corresponds to the Misra and Froelich (2012) interpretation proposing  
464 that “the riverine Li flux has changed the ratio of dissolved to suspended partitioning from 4:1 in  
465 Paleocene to 1:4 today”. Simulation results show that only minor Li isotopic fractionation takes  
466 place if the reactivity of the suspended load is this low (Fig. 4d). The high sensitivity of riverine  
467  $\delta^7\text{Li}$  on  $A_{\text{suspended\_load}}$  implies that an increasing suspended river load concentration may have  
468 formed an important contribution on the seawater and global average riverine  $\delta^7\text{Li}$  increase  
469 observed during the Cenozoic (Misra and Froelich, 2012).

470 Our simulation results also imply that riverine  $\delta^7\text{Li}$  values increase with increasing subsurface  
471 residence time (Fig. 4a,d). This particular finding is in good agreement with seasonal riverine  
472  $\delta^7\text{Li}$  variations observed in streams draining the Columbia river basalt west of the Cascade  
473 Range, where seasonal precipitation and thus subsurface residence time variations are large (Liu  
474 et al., 2014). It is, however, unlikely that a Cenozoic global average subsurface residence time

475 increase caused the Cenozoic seawater  $\delta^7\text{Li}$  increase because for an increasing relief (e.g., over  
476 the Cenozoic), residence times tend to decrease and not to increase.

477

#### 478 **4.2. Simulation of the Paleocene-Eocene boundary weathering pattern (Fig. 1a)**

479 A series of simulations with a varying “fresh granite” volume fraction corresponding to a varying  
480 contribution of “fresh granite” weathering (i.e., varying weathering intensity) were run to match  
481 riverine  $\delta^7\text{Li}$  values inferred for the Paleocene-Eocene boundary. These simulations were run for  
482 a fixed  $p\text{CO}_2$  of 1200 ppmV to account for the atmospheric  $p\text{CO}_2$  inferred for the Paleocene-  
483 Eocene boundary (Li and Elderfield, 2013). For the “altered granite” domain the reactive surface  
484 area of primary silicates was set to zero, thus simulating an extreme weathering intensity where  
485 primary minerals are either fully replaced or fully coated by secondary minerals. Moreover, the  
486 initial presence of Li-bearing kaolinite and goethite was specified for this model domain,  
487 whereas their Li isotopic composition and initial volume fractions (e.g.,  $\delta^7\text{Li} = -10\text{‰}$ , Table 1)  
488 were input from the results of a pure “fresh granite” run (i.e., 100% “fresh granite”) after a  
489 simulated time period of 100 years. In contrast to the runs simulating the current weathering  
490 pattern, the varying weathering intensity runs were only performed for the subsurface domain  
491 (Fig. 2) because our simulation results imply that only minor Li isotopic fractionation occurs  
492 within rivers where the suspended river load concentration is low (Fig. 4d), which has been  
493 inferred for the Paleocene-Eocene boundary (Misra and Froelich, 2012).

494 Model results show that downstream  $\delta^7\text{Li}$  values become more positive with an increasing  
495 contribution of “fresh granite” weathering (i.e., decreasing weathering intensity) (Fig. 5a). A  
496 strong correlation between  $\delta^7\text{Li}$  and fresh granite is, however, only observed for fresh granite  
497 contributions  $<10\%$ , which is inherited from the strong Li solubility contrast between the “fresh

498 granite” (i.e., Li-bearing biotite) and the “altered granite” domain (i.e., Li bearing kaolinite and  
499 goethite) (Fig. 6). Nevertheless, our simulations imply that a decreasing weathering intensity  
500 over the Cenozoic may have formed an important contribution to the Cenozoic seawater and  
501 global average riverine  $\delta^7\text{Li}$  increase (Misra and Froelich, 2012) in addition to the increasing  
502 suspended river load concentration (Fig. 4a,d). Moreover, our simulations show that low global  
503 average riverine  $\delta^7\text{Li}$  values inferred for the Paleocene-Eocene boundary (Misra and Froelich,  
504 2012) may have been inherited from predominant dissolution of previously formed secondary  
505 mineral phases having a low  $\delta^7\text{Li}$  value (e.g., -10‰, Fig. 6a) and a minor contribution of primary  
506 silicate rock dissolution and corresponding precipitation of newly formed secondary mineral  
507 phases associated with Li isotopic fractionation. For our simplified system (Fig. 2), a fresh  
508 granite contribution of about 5% is required to obtain a  $\delta^7\text{Li}$  value similar to the minimum value  
509 inferred for the Paleocene-Eocene boundary at the downstream subsurface model boundary (e.g.,  
510 +6‰, Fig. 5a). It should be noted that this particular interpretation is entirely different from the  
511 one of Misra and Froelich (2012) because it does not rely on congruent weathering of primary  
512 silicate minerals.

513

#### 514 *4.2.1. Model uncertainty and mass balance considerations*

515 If a significant proportion of Li was adsorbed to goethite and kaolinite surfaces rather than fully  
516 substituted into the crystal structure, Li solubility of weathering-intense, secondary mineral  
517 dominated systems could be much higher than shown in Figure 6a. Especially for estuaries  
518 where the ionic strength is higher than it is in aquifers or rivers, Li complexed to kaolinite and  
519 goethite surfaces could be readily desorbed by surface complexation reactions involving other,

520 highly concentrated cations (e.g., Na, K, Ca, Mg). Such estuarine desorption has been shown for  
521 various other trace metals (Du Laing et al., 2009).

522 Distinguishing between Li surface complexation and Li substitution reactions in our model  
523 would simply change the slope and curvature of the  $\delta^7\text{Li}$  vs. weathering intensity relation (Fig.  
524 5a). Consequently, it would also change the amount of fresh granite weathering that is required  
525 to obtain an inferred  $\delta^7\text{Li}$  value of +6‰. The same applies if we were using a Li isotopic  
526 enrichment factor other than -20‰, or if exchanged/complexed Li did not show the same  $\delta^7\text{Li}$   
527 value than structural Li, which was observed for Mg (Wimpenny et al., 2014). However, our  
528 main model observations, the overall inverse correlation between weathering intensity and  
529 riverine  $\delta^7\text{Li}$  would remain unchanged (Fig. 5a).

530 The above discussion illustrates that riverine [Li] derived from our model should be considered  
531 as an end-member, minimum [Li] scenario for the Paleocene-Eocene boundary ([Li]=0.25  $\mu\text{g/L}$ ,  
532 Fig. 5a). Updating the Misra and Froelich (2012) mass balance calculation with this [Li] as well  
533 as the inferred minimum riverine  $\delta^7\text{Li}$  (+6‰) yields seawater  $\delta^7\text{Li}$  and [Li] of +24‰ and 112  
534  $\mu\text{g/L}$ , respectively. Whereas the calculated seawater  $\delta^7\text{Li}$  is close to the observed value (+22‰,  
535 Misra and Froelich, 2012), 112  $\mu\text{g/L}$  is significantly lower than the inferred Paleocene-Eocene  
536 seawater [Li] (179  $\mu\text{g/L}$ ), which is based on the assumption that seawater [Li] remained constant  
537 throughout the Cenozoic (Misra and Froelich, 2012). If seawater [Li] was indeed constant, the  
538 contradiction with the updated mass balance calculation could be resolved by increasing the  
539 hydrothermal Li flux by a factor of about 1.6 or by increasing continental discharge by a factor  
540 of ca. 7.3, both having only a minor effect on seawater  $\delta^7\text{Li}$  (<1‰). However, only the  
541 hydrothermal [Li] flux increase seems to be in a reasonable order of magnitude (Berner and  
542 Kothavala, 2001; Otto-Bliesner, 1995).

543 When discussing mass balance calculations for the global Li cycle it should be noted that the  
544 calculations performed by Misra and Froelich (2012) are highly sensitive to Li isotopic  
545 fractionation occurring in the ocean during Li uptake by pelagic sediments and alteration of the  
546 basaltic oceanic crust (i.e., reverse weathering). For oceanic Li isotopic fractionation to cause a  
547 seawater  $\delta^7\text{Li}$  shift less than +16‰, the Paleocene-Eocene boundary mass balance also works  
548 (i.e., seawater  $\delta^7\text{Li}$ =+22‰) for riverine  $\delta^7\text{Li}$  and/or [Li] (i.e., Li flux) larger than the ones  
549 derived from our end-member considerations ([Li]=0.25  $\mu\text{g/L}$ ,  $\delta^7\text{Li}$ =+6‰, Fig. 5a).

550 In summary, a reasonable mass balance can be formulated with riverine [Li] and  $\delta^7\text{Li}$  derived  
551 from our model ([Li]=0.25  $\mu\text{g/L}$ ,  $\delta^7\text{Li}$ =+6‰, Fig. 5a). This suggests that for the Paleocene-  
552 Eocene boundary, riverine [Li] could have been significantly lower than it is today (Fig. 5a).  
553 However, it has to be appreciated that any mass balance calculation for past global Li cycles is  
554 affected by a relatively large uncertainty and it is beyond the scope of this study to provide  
555 accurate numbers for the one at the Paleocene-Eocene boundary. Without knowing the true  
556 global average riverine  $\delta^7\text{Li}$  and [Li] for the Paleocene-Eocene boundary, our study can thus not  
557 rule out a (minor) contribution from a changing seawater hydrothermal Li flux and a changing  
558 magnitude of oceanic Li isotopic fractionation on the Cenozoic seawater  $\delta^7\text{Li}$  increase.

559

## 560 **5. Implications for using $\delta^7\text{Li}$ as a silicate weathering proxy**

561 Previous studies did not show a distinct correlation between riverine  $\delta^7\text{Li}$  and traditional silicate  
562 weathering proxies such as [Si], total cation charge  $\text{TZ}^+$  ( $\text{TZ}^+=\text{Na}^++\text{K}^++2\text{Mg}^{2+}+2\text{Ca}^{2+}$ ),  
563 normalized [Si] ( $\text{Si}/\text{TZ}^+$ ), [Li],  $^{87}\text{Sr}/^{86}\text{Sr}$ , and Li/Na. (Huh et al., 2001; 1998; Millot et al., 2010;  
564 Pogge von Strandmann et al., 2010; 2006). For instance, Huh et al. (1998) did not observe a clear  
565 correlation between riverine  $\delta^7\text{Li}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^7\text{Li}$  and [Li], as well as between  $\delta^7\text{Li}$  and  $\text{TZ}^+$ ,

566 whereas  $\delta^7\text{Li}$  tended to be slightly negatively correlated with  $\text{Si}/\text{TZ}^+$  when compiling available  
567 global river data. Completing the Huh et al (1998) compilation with the numerous studies that  
568 have emerged since the original publication displays an even more random distribution between  
569  $\delta^7\text{Li}$  and  $\text{TZ}^+$  (Fig. 7a), which was also observed for  $\delta^7\text{Li}$  vs.  $[\text{Li}]$  (Misra and Froelich, 2012). In  
570 contrast, the weak negative correlation between  $\delta^7\text{Li}$  and  $\text{Si}/\text{TZ}^+$  is still identified when updating  
571 the global river compilation (Fig. 7b). For specific river systems, additional correlations were  
572 observed. Examples include the strong inverse correlation between  $\delta^7\text{Li}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  as well as  
573 between  $\delta^7\text{Li}$  and  $\text{Si}/\text{TZ}^+$  observed for the Orinoco drainage basin (Huh et al., 2001) and the  
574 inverse correlation between  $\delta^7\text{Li}$  and  $[\text{Si}]$  as well as between  $\delta^7\text{Li}$  and  $[\text{Li}]$  observed in rivers  
575 draining mostly basalt (Pogge von Strandmann et al., 2010; 2006). More recently, Millot et al.  
576 (2010) and Liu et al. (2014) have shown that  $\delta^7\text{Li}$  can display a negative correlation with  $\text{Li}/\text{Na}$   
577 that also might have global significance. In fact, a negative correlation between  $\delta^7\text{Li}$  and  $\text{Li}/\text{Na}$  is  
578 also identified in our updated global river compilation (Fig. 7c).

579 Plotting  $[\text{Li}]$ ,  $[\text{Si}]$  and  $\text{TZ}^+$  along our model domain as well as against  $\delta^7\text{Li}$  reveals that  $\delta^7\text{Li}$  only  
580 forms a distinct correlation with such concentration proxies for a particular system (subsurface  
581 vs. river) (Figs. 4a,c and 5a-b). The transition from a positive correlation in the subsurface to a  
582 negative one within rivers occurs because once exfiltrated into a river, aqueous species  
583 concentrations decrease due to mixing with more diluted river water, while Li isotopic  
584 fractionation is ongoing. We thus propose that the identified great importance of Li isotopic  
585 fractionation occurring in rivers forms the main reason why concentration proxies do not show a  
586 distinct correlation with global riverine  $\delta^7\text{Li}$  values (e.g.,  $\delta^7\text{Li}$  vs.  $\text{TZ}^+$ , Fig. 7a;  $\delta^7\text{Li}$  vs.  $[\text{Li}]$ ,  
587 Misra and Froelich, 2012). If Li isotopic fractionation was only occurring in the subsurface we  
588 would expect a positive correlation between  $\delta^7\text{Li}$  and concentrations proxies such as  $\text{TZ}^+$  (i.e.,

589 subsurface trend, Figs. 7a) because  $\delta^7\text{Li}$  and  $\text{TZ}^+$  (and any other concentration proxies) mainly  
590 reflect the subsurface residence time (Figs. 4a-b) as well as the corresponding weathering  
591 intensity (Fig. 5a-b). Instead, our simulations suggest that riverine  $\delta^7\text{Li}$  values reflect a particular  
592 combination of Li isotopic fractionation occurring within the subsurface as well as in rivers such  
593 as illustrated with the corresponding trends (Fig. 7a).

594 Subsurface and riverine trends shown on Figure 7a are derived from simulating a mono  
595 lithological subsurface that does not fully reach chemical equilibrium. Accordingly, the  
596 simulation results should be considered as simplified trends only. The observation that in natural  
597 aquifers  $\delta^7\text{Li}$  and  $[\text{Li}]$  are not always positively correlated (Meredith et al., 2013; Négre et al.,  
598 2010; Tomascak et al., 2003) implies that additional parameters such as host rock mineralogy,  
599 hydrodynamic mixing of various groundwater types and aquifer residence time distribution in  
600 relation to chemical equilibrium (Maher, 2011) must be all taken into account to fully understand  
601 the relation between  $\delta^7\text{Li}$  and concentration proxies of a particular system (subsurface+river).

602 Moreover, we emphasize that the riverine trend on Figure 7a does not imply that  $\delta^7\text{Li}$  is  
603 increasing with distance along a river, which would be in contradiction to field observations  
604 (Kisakürek et al., 2005; Pogge von Strandmann et al., 2006). For our river simulations a  
605 correlation between  $\delta^7\text{Li}$  and residence time (i.e., distance) is observed (Fig. 4a) because the ratio  
606 between Li isotopic fractionation occurring in rivers vs. the one occurring in aquifers is  
607 increasing with increasing river residence time. In other words, for natural rivers we only expect  
608 increasing riverine  $\delta^7\text{Li}$  with distance if the ratio of riverine Li isotopic fractionation vs.  
609 subsurface fractionation is increasing with flow distance. This ratio, however, is only changing if  
610 the subsurface residence time distribution is changing along a river.

611 Our simulation results agree well with the globally observed negative correlations between  $\delta^7\text{Li}$   
612 and  $\text{Li}/\text{TZ}^+$  and between  $\delta^7\text{Li}$  and  $\text{Li}/\text{Na}$  (Fig. 7b-c) because the parameters that increase  $\delta^7\text{Li}$   
613 (residence time increase, suspended river load concentration increase, weathering intensity  
614 decrease) cause a decrease in the simulated  $\text{Si}/\text{TZ}^+$  and  $\text{Li}/\text{Na}$  ratio (Figs. 4c and 5b). For a  
615 silicate setting also affected by newly formed secondary Ca- and Mg-bearing phases, we would  
616 expect a similar behavior for  $\text{Ca}/\text{TZ}^+$  and  $\text{Mg}/\text{TZ}^+$  as well as for  $\text{Ca}/\text{Na}$  and  $\text{Mg}/\text{Na}$ . The  
617 simulated negative correlation between  $\delta^7\text{Li}$  and  $\text{Si}/\text{TZ}^+$  as well as between  $\delta^7\text{Li}$  and  $\text{Li}/\text{Na}$  (Figs.  
618 4a and 5b) is mainly observed because the  $\delta^7\text{Li}$  increase is inherited from an increasing amount  
619 of Li being incorporated in kaolinite and goethite with increasing aqueous  $[\text{Li}]$ , whereas Na  
620 remains in solution. Precipitation of Li-bearing kaolinite also removes Si from the aqueous  
621 solution, which explains why  $\text{Si}/\text{TZ}^+$  is decreasing with increasing Si concentration (Fig. 4a-b  
622 and 5b). The  $\text{Si}/\text{TZ}^+$  decrease is most prominent if  $[\text{Si}]$  approaches a solubility controlled  
623 maximum such as observed towards the end of our subsurface domain (i.e.,  $t > 100\text{d}$ , Fig. 4a-b).  
624 In fact, the low sensitivity of  $\delta^7\text{Li}$  on  $\text{Si}/\text{TZ}^+$  for short subsurface residence times (Fig. 4b) is  
625 likely the reason why the negative correlation between  $\delta^7\text{Li}$  and  $\text{Si}/\text{TZ}^+$  is less pronounced than  
626 the one between  $\delta^7\text{Li}$  and  $\text{Li}/\text{Na}$  in global rivers (Fig. 7b-c).

627

### 628 **5.1. Seawater $\delta^7\text{Li}$ : a proxy for Cenozoic continental silicate weathering rates?**

629 We propose that  $\text{Si}/\text{TZ}^+$  as well as  $\text{Li}/\text{Na}$  are only particular and thus somewhat arbitrary proxies  
630 that correlate with  $\delta^7\text{Li}$  (Figs. 7b-c). Most importantly, it has not been shown yet how these  
631 ratios could serve as quantitative proxies for silicate weathering rates. We therefore postulate that  
632 the extent of water-rock interaction occurring along a particular flow path (subsurface + river)  
633 forms a more fundamental parameter that defines a system's  $\delta^7\text{Li}$ . In fact, our simulation results

634 (Figs. 4c and 5b) clearly show that the amount of primary silicate mineral dissolution (quartz,  
635 feldspars, biotite) is positively correlated with  $\delta^7\text{Li}$ . The correlation occurs because the amount  
636 of mineral dissolution reflects an aquifer's residence time, the suspended river load  
637 concentration, and the weathering intensity, which have been identified to form the major  
638 controls on riverine  $\delta^7\text{Li}$  (Figs. 4c and 5b). Our simulations thus imply that aqueous  $\delta^7\text{Li}$  is  
639 highly correlated with the total amount of water-rock interaction occurring along a particular  
640 flow path (in moles) suggesting that  $\delta^7\text{Li}$  is almost a perfect silicate weathering tracer. The  
641 positive correlation between  $\delta^7\text{Li}$  and silicate mineral dissolution (Figs. 4c and 5b), however,  
642 does not necessarily imply a correlation between  $\delta^7\text{Li}$  and silicate weathering rates (in  
643 moles/year). To obtain such weathering rates for a particular flow path, amounts of primary  
644 silicate mineral dissolution have to be multiplied by subsurface and riverine discharges.  
645 Subsurface and riverine discharges are closely related to the corresponding residence times.  
646 Accordingly, the previously identified lack of sensitivity of Cenozoic residence time variations  
647 on the Cenozoic seawater  $\delta^7\text{Li}$  record implies that this particular  $\delta^7\text{Li}$  record is not sensitive to  
648 discharge variations either. This finding is supported by Otto-Bliesner (1995) reporting that  
649 continental runoff remained roughly constant over the Cenozoic ( $\pm 10\%$ ).

650 Assuming minor effects from discharge variations, the simulated positive correlation between  
651 primary silicate mineral dissolution and riverine  $\delta^7\text{Li}$  (Figs. 4c and 5b) suggests that the  
652 Cenozoic seawater  $\delta^7\text{Li}$  increase (Misra and Froelich, 2012) was most likely caused by globally  
653 increasing continental silicate weathering rates. This finding strongly supports the Misra and  
654 Froelich (2012) hypothesis arguing that the Cenozoic seawater  $\delta^7\text{Li}$  increase is inherited from  
655 increasing riverine  $\delta^7\text{Li}$  values as a result of major Cenozoic tectonic uplift (e.g., Himalayan  
656 orogeny). The main argument for this statement is that uplift has a first order control on both

657 parameters identified to increase silicate weathering rates as well as riverine  $\delta^7\text{Li}$  values  
658 (weathering intensity and suspended river load concentration, Figs. 4c and 5a). This agreement is  
659 notable because our understanding of Li isotope fractionation processes does not rely on  
660 congruent weathering and is thus entirely different from the one of Misra and Froelich (2012).  
661 In contrast to tectonic uplift, Cenozoic cooling occurring since the humid PETM (Clementz and  
662 Sewall, 2011; Miller et al., 1987) does not seem to have a distinct effect on  $\delta^7\text{Li}$ . Whereas  
663 Cenozoic cooling may have contributed to the Cenozoic weathering intensity decrease and  
664 corresponding  $\delta^7\text{Li}$  increase, cooling reduces the amount of primary silicate mineral dissolution  
665 along a specific flow path and drives  $\delta^7\text{Li}$  to lower values (Fig. 4c).  $\delta^7\text{Li}$  measurements from  
666 streams draining the Columbia River basalt under significantly different climatic conditions (dry  
667 vs. wet) confirm that climate does not necessarily have a first order control on riverine  $\delta^7\text{Li}$  (Liu  
668 et al., 2014).

669

## 670 **6. Implications for CO<sub>2</sub> consumption by silicate weathering**

671 The identified positive correlation between  $\delta^7\text{Li}$  and the amount of primary silicate mineral  
672 dissolution (Figs. 4c and 5b) suggests that, over the last 56 Ma, riverine  $\delta^7\text{Li}$  was closely  
673 correlated to the amount of CO<sub>2</sub> consumed by silicate weathering reactions (Table 2) assuming  
674 that carbonic acid (H<sub>2</sub>O+CO<sub>2</sub>, eq. 1) forms the major proton source for these reactions and that  
675 continental discharge remained roughly constant (Otto-Bliesner, 1995). Accordingly, the  
676 Cenozoic seawater  $\delta^7\text{Li}$  record and the derived global average riverine  $\delta^7\text{Li}$  record provide a  
677 potential opportunity to quantify the amount of CO<sub>2</sub> that was consumed by silicate weathering  
678 reactions throughout the Cenozoic.

679 In particular, reactive transport modeling such as performed here allows explicitly quantifying  
 680 the amount of CO<sub>2</sub> that was consumed along a specific flow path by integrating the amount of  
 681 each mineral N<sub>Mineral</sub> (mole) that was dissolved along the full model domain during a specific  
 682 simulation period:

683

$$684 \quad N_{CO_2} = 4 \cdot \sum N_{albite} + 4 \cdot \sum N_{anorthite} + 4 \cdot \sum N_{Kspar} + 10 \cdot \sum N_{biotite} + 0 \cdot \sum N_{quartz} - 6 \cdot \sum N_{kaolinite} - 2 \cdot \sum N_{goethite}$$

685 (11)

686

687 The dissolved mineral amounts (N<sub>Mineral</sub>) are scaled by the amount of H<sup>+</sup> that is required to  
 688 dissolve one mole of a specific mineral phases (e.g., 4 for albite, Table 2) because one mole of  
 689 H<sup>+</sup> is added to the solution (i.e., CO<sub>2</sub> is consumed by mineral dissolution) if one mole of  
 690 atmospheric CO<sub>2</sub> is dissolved (eq. 1). The amount of kaolinite precipitation times 6 and the  
 691 amount of goethite precipitation times 2, respectively (i.e., stoichiometric coefficient of H<sup>+</sup>,  
 692 Table 2) were subtracted because kaolinite and goethite precipitation adds H<sup>+</sup> to the system and  
 693 liberates the same mole amount of CO<sub>2</sub> to keep the pCO<sub>2</sub> at the specified fixed value (i.e., CO<sub>2</sub> is  
 694 liberated by kaolinite and goethite precipitation). Equation (11) assumes that dissolved HCO<sub>3</sub><sup>-</sup>  
 695 precipitates as carbonates in the ocean (Fig. 1) such as shown here for calcite (CaCO<sub>3</sub>)  
 696 precipitation:

697



699

700 Applying equation (11) to our simulation runs indeed yields a positive correlation between δ<sup>7</sup>Li  
 701 and CO<sub>2</sub> consumption (Figs. 4c and 5b) implying that CO<sub>2</sub> consumption by continental silicate

702 weathering increased over the Cenozoic. This finding agrees well with the carbon cycle model of  
703 Li and Elderfield (2013) also suggesting an increase in continental silicate weathering and  
704 corresponding CO<sub>2</sub> consumption rates over the Cenozoic. However, our modeling approach  
705 relies on thermodynamic parameters for Li-bearing minerals that are only roughly constrained so  
706 far (e.g., fractionation factor, crystallographic substitution reaction, Li concentration of  
707 secondary minerals, Li solubility). Accordingly, our modeling approach should only be applied  
708 to qualitatively identify geochemical trends related to Li isotopic fractionation such as performed  
709 here. Once these thermodynamic parameters have been determined, a reliable quantification of  
710 the amount of CO<sub>2</sub> consumed by silicate weathering over the Cenozoic would require  
711 incorporating basalt weathering in addition to granite weathering, because basalt weathering  
712 accounts for more than 30% of global CO<sub>2</sub> consumption by silicate weathering even though  
713 basalts only form about 8% of exposed silicate rocks today (Gaillardet et al., 1999).

714 Our CO<sub>2</sub> consumption calculations also show that the amount of CO<sub>2</sub> consumed by pure “fresh  
715 granite” weathering (e.g., 100% contribution) was the same for the current and the Paleocene-  
716 Eocene weathering pattern simulations (17 kmol, Figs. 4b and 5b). The same applies for the  
717 simulated  $\delta^7\text{Li}$  values at the downstream subsurface model boundary (+10‰). This observation  
718 emphasizes that CO<sub>2</sub> consumption by continental silicate weathering reactions is more sensitive  
719 to specific primary silicate mineral phases that are exposed to chemical weathering rather than to  
720 atmospheric  $p\text{CO}_2$ . Moreover, it suggests that  $p\text{CO}_2$  variations during the Cenozoic (Li and  
721 Elderfield, 2013) do not seem to have a distinct control on the Cenozoic seawater  $\delta^7\text{Li}$  record.

722 To extend the use of seawater  $\delta^7\text{Li}$  values to reconstruct CO<sub>2</sub> consumption by continental silicate  
723 weathering for geological times other than the past 56 Ma, potential significant changes in  
724 continental river discharge have to be taken into account as well. Whereas discharge variations

725 seem less important for the Cenozoic, a dramatic acceleration of the hydrological cycle caused  
726 by a short term atmospheric  $pCO_2$  increase shifted seawater  $\delta^7Li$  values by about -10‰ within a  
727 short period of time (100 ky) during Cretaceous Oceanic Anoxic Event 2 (OAE2) (Pogge von  
728 Strandmann et al., 2013). Because an accelerated hydrological cycle likely shifted discharge to  
729 higher values and residence times to lower values, the low OAE2  $\delta^7Li$  values correspond well  
730 with our simulated positive correlation between residence time and  $\delta^7Li$  (Fig. 4a). Interestingly,  
731 the negative  $\delta^7Li$  excursion observed for OAE2 was attributed to enhanced continental silicate  
732 weathering forming a negative feedback on the inferred  $pCO_2$  increase (Pogge von Strandmann  
733 et al., 2013). This finding is opposite to the one made for the Cenozoic because for the past 56  
734 Ma, inferred increasing silicate weathering rates are manifested by a  $\delta^7Li$  increase (Misra and  
735 Froelich, 2012; this study) while for OAE2 they are accompanied by a  $\delta^7Li$  decrease (Pogge von  
736 Strandmann et al., 2013). This apparent contradiction is, however, well explained by our  
737 modeling results revealing that seawater and inferred riverine  $\delta^7Li$  values are simply a function  
738 of the amount of silicate weathering and corresponding  $CO_2$  consumption along a specific flow  
739 path (in moles) (Figs. 4c and 5b). However, they are not necessarily correlated with silicate  
740 weathering and  $CO_2$  consumption rates (in moles/year) on which discharge has a first order  
741 control (Gaillardet et al., 1999). The opposing behavior of  $\delta^7Li$  with increasing silicate  
742 weathering rates thus highlights the importance of reconstructing past discharge rates, which,  
743 owing to the strong correlation between silicate weathering rates and discharge (Gaillardet et al.,  
744 1999), is indispensable for quantifying past  $CO_2$  consumption rates based on seawater  $\delta^7Li$   
745 measurements.

746

## 747 **7. Summary and conclusions**

748 A novel reactive transport modeling approach was developed to simulate Li isotopic  
749 fractionation during Li uptake by secondary mineral phases. Simulation results show that  
750 riverine  $\delta^7\text{Li}$  is controlled not only by the Li isotopic fractionation factor but also by the  
751 subsurface residence time of infiltrating meteoric water, the corresponding weathering intensity  
752 and the concentration of a river's suspended load.

753 Based on these identified factors, we presented a new interpretation of the previously reported  
754 Cenozoic seawater  $\delta^7\text{Li}$  record (Misra and Froelich, 2012) that does not rely on geochemically  
755 unlikely congruent weathering. In particular, modeling results imply that the low seawater  $\delta^7\text{Li}$   
756 observed at the Paleocene-Eocene boundary could be inherited from a high weathering intensity  
757 with predominant weathering of previously-formed secondary mineral phases (e.g., clays,  
758 oxides, hydroxides) having a low  $\delta^7\text{Li}$  and a low contribution of incongruent silicate mineral  
759 dissolution with associated secondary mineral formation and Li isotopic fractionation. Moreover,  
760 simulation results imply that the Cenozoic seawater  $\delta^7\text{Li}$  increase was likely caused by an  
761 increasing amount of primary silicate mineral dissolution (i.e., decreasing weathering intensity,  
762 increasing suspended river load concentration) inherited from tectonic uplift and a corresponding  
763 global relief increase. In contrast, Cenozoic cooling and corresponding  $p\text{CO}_2$  and precipitation  
764 variations do not seem to have a distinct control on the Cenozoic seawater  $\delta^7\text{Li}$  record. It is thus  
765 emphasized that our modeling results strongly favor the original Raymo and Ruddiman (1992)  
766 model stating that a tectonically-driven increase in silicate weathering rates may have caused the  
767 inferred Cenozoic atmospheric  $p\text{CO}_2$  decrease. However, another Li isotope study has shown that  
768 for dramatic, short term events increasing atmospheric  $p\text{CO}_2$  and triggering warmer temperatures  
769 (e.g., Cretaceous OAE2), silicate weathering and corresponding  $\text{CO}_2$  consumption rates can be  
770 dramatically increased without major tectonic uplift (Pogge von Strandmann et al., 2013).

771 The identified strong correlation between Cenozoic silicate weathering rates and  $\delta^7\text{Li}$  implies  
772 that seawater and global average riverine  $\delta^7\text{Li}$  values are closely related to global  $\text{CO}_2$   
773 consumption by continental silicate weathering. For an actual quantitative correlation, however,  
774 more experimental and modeling work is required. Key parameters are the temperature-  
775 dependent thermodynamic properties of specific Li bearing primary and secondary minerals  
776 (e.g., crystallographic Li substitution and surface complexation reactions, maximum Li  
777 substitution, Li solubility, Li isotope fractionation factor) as well as the determination of global  
778 average continental discharge through time.

779 Incorporating Li isotopic fractionation into reactive transport model simulations of subsurface  
780 and river systems also improved the understanding of the  $\delta^7\text{Li}$  distribution observed in global  
781 rivers today. Simulation results revealed that Li isotope fractionation occurs in the subsurface as  
782 well as in river systems. Fractionation occurring in both systems seems to be the main reason  
783 why no or only weak correlations between global riverine  $\delta^7\text{Li}$  values and traditional silicate  
784 weathering proxies such as  $[\text{Si}]$ ,  $[\text{Li}]$ ,  $\text{Si}/\text{TZ}^+$  are observed. The lack of correlation is observed  
785 because once exfiltrated into rivers, elemental concentrations are diluted by a larger flux of  
786 superficial river waters while Li isotopic fractionation is still ongoing.

787 Finally, this study illustrates that reactive transport modeling is a powerful tool for a (semi)-  
788 quantitative interpretation of stable isotope ratios. In comparison to closed system Rayleigh-type  
789 or steady state flux models, it bears the advantage of considering the full thermodynamic  
790 properties of involved mineral phases (e.g., mineral stoichiometry, mineral solubility, kinetic  
791 dissolution/precipitation) as well as assessing the effect of transport on isotopic fractionation.  
792 The presented solid solution approach can be easily applied to other isotopic systems (e.g., Si,

793 Mg, Ca, Mo), which have also been shown to serve as potentially powerful weathering proxies  
794 (Moore et al., 2013; Tipper et al., 2012; Voegelin et al., 2012; Ziegler et al., 2005).

795

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802 anonymous reviewer.

803

## 804 **Figure and table captions**

805

806 Fig. 1

807 Proposed weathering and Li isotopic fractionation model for the Paleocene-Eocene boundary (a)  
808 and for today (b) in terms of idealized crustal cross sections along a major river system. Black  
809 arrows show typical flow paths for meteoric water infiltrating into the subsurface and being  
810 transported in groundwater systems before exfiltrating into a major river system. Increasing  
811 Cenozoic seawater  $\delta^7\text{Li}$  values (Misra and Froelich, 2012) are explained by an increasing  
812 availability of bedrock (primary) silicates for chemical weathering (i.e., decreasing weathering  
813 intensity, increasing suspended river load) as the global relief increases and the average saprolite  
814 thickness becomes smaller. For the current weathering pattern, chemical weathering of primary  
815 silicates and subsequent precipitation of secondary minerals (clays, Fe- and Al-hydroxides)

816 fractionate Li isotopes by accumulating  $^7\text{Li}$  in the groundwater and  $^6\text{Li}$  in the precipitating  
817 mineral phases. If only secondary silicate minerals are exposed to chemical weathering such as  
818 inferred for the Paleocene-Eocene boundary (a) no significant Li isotopic fractionation occurs.  
819 An increasing relief yields decreasing subsurface residence times as well as increasing suspended  
820 river load concentrations, both potentially affecting riverine  $\delta^7\text{Li}$  in addition to the decreasing  
821 weathering intensity.

822

823 Fig. 2:

824 Model setup for simulating reactive transport in the subsurface and within rivers. Subsurface  
825 simulations were run for meteoric water infiltrated and transported along a 200 m long flow path  
826 eventually exfiltrating into a river system (e.g., arrows on Fig. 1). They were run for various  
827 fresh-to-altered granite volume fractions to simulate the effects of a varying silicate weathering  
828 intensity on  $\delta^7\text{Li}$ . Fluids flowing along the two model domains were fully mixed in the  
829 downstream model boundary (“mixing”) to track the integrated Li isotopic signal. River  
830 simulations were run as batch simulations (no flow) assuming that the suspended load is  
831 transported at the same velocity as river water. Moreover, river simulations consider a diffusive  
832 dilution of the exfiltrated groundwater with water that experienced no previous water-rock  
833 interaction (i.e., pure water+CO<sub>2</sub>). For both systems (subsurface and river), Li isotopic  
834 fractionation is simulated to occur during kaolinite and goethite precipitation.

835

836 Fig. 3:

837 Schematic illustration of the composition of modeled Li bearing secondary minerals, which were  
838 simulated as ideal solid solutions. The three endmembers were defined as pure goethite or

839 kaolinite with known thermodynamic properties, and hypothetical, but pure  $^6\text{Li}$  and pure  $^7\text{Li}$ , for  
840 which  $\log(K)$  values have to be calibrated by matching observed secondary mineral and aqueous  
841 Li concentrations.

842

843 Fig. 4:

844 Model results for the simulated current weathering pattern with 100% “fresh granite”  
845 contribution (Fig. 1b). (a) and (d) illustrate steady state  $[\text{Li}]$  and  $[\text{Si}]$  along the full model domain  
846 (subsurface + river), as well as corresponding  $\delta^7\text{Li}$  profiles ( $\delta^7\text{Li}_{\text{dissolved}}$  and  
847  $\delta^7\text{Li}_{\text{kaolinite}}=\delta^7\text{Li}_{\text{goethite}}=\delta^7\text{Li}_{\text{solids}}$ ) for a reactive suspended river load surface area of  $6000\text{ cm}^2/\text{g}$   
848 and  $375\text{ cm}^2/\text{g}$ , respectively, illustrating that the simulated  $\Delta^7\text{Li}_{\text{solids-dissolved}}$  was equal to the  
849 initially specified Li isotope enrichment factor of  $\epsilon=-20\%$ . (b) and (e) present corresponding  
850 steady state profiles of typical silicate weathering tracers such as  $\text{TZ}^+$  (in meqv/kg),  $\text{Si}/\text{TZ}^+$ ,  
851  $\text{Li}/\text{TZ}^+$  and  $\text{Li}/\text{Na}$  (molar ratio). Also shown are the cumulative primary mineral dissolution  
852 (quartz + feldspars + biotite) and corresponding  $\text{CO}_2$  consumption (eq. (11)) profiles (in kmol)  
853 during a simulated time period of 100 years. c) and (f) illustrates the relationship between the  
854 parameters shown in (b) and (e) as a function of  $\delta^7\text{Li}_{\text{dissolved}}$ . Note that profiles except the ones  
855 shown in (c) and (f) are plotted against fluid residence time to simultaneously illustrate  
856 subsurface and river simulations. Along the subsurface domain (gray shaded area) fluid  
857 residence time (x-axis) corresponds also to the distance along the subsurface domain because the  
858 flow velocity was 1 m/d.

859

860 Fig. 5:

861 Model results for the simulated Paleocene-Eocene boundary weathering pattern (Fig. 1a). (a)  
862 Steady state [Si], [Li] and  $\delta^7\text{Li}$  at the downstream subsurface model boundary (“mixing”, Fig. 2)  
863 plotted as a function of the simulated “fresh granite” contribution or inverse weathering intensity,  
864 respectively. The dashed line illustrates that 5% fresh granite contribution is required to get an  
865 assumed Paleocene-Eocene boundary riverine  $\delta^7\text{Li}$  value of +6‰, which in turn yields a  
866 corresponding [Li] of 0.25  $\mu\text{g/L}$ . (b) Cumulative amounts of primary mineral dissolution  
867 (feldspars, biotite, quartz) and  $\text{CO}_2$  consumption (in kmol) within the entire subsurface model  
868 domain during a simulated time period of 100 years as a function of steady state  $\delta^7\text{Li}$  values at  
869 the downstream subsurface model boundary. Also shown are steady state  $\text{TZ}^+$  (in meqv/kg),  
870  $\text{Si}/\text{TZ}^+$  and  $\text{Li}/\text{Na}$  (molar ratio) at the downstream subsurface model boundary as a function of  
871 corresponding  $\delta^7\text{Li}$  values.

872

873 Fig. 6:

874 Simulated steady-state [Li] and  $\delta^7\text{Li}$  profiles along the altered (a) and fresh granite domain (b) of  
875 the Paleocene-Eocene boundary weathering pattern (Fig. 1a).

876

877 Fig. 7:

878 Compilation of previously published riverine  $\delta^7\text{Li}$  (Huh et al., 2001; 1998; Millot et al., 2010;  
879 Pogge von Strandmann et al., 2010; 2006; Vigier et al., 2009; Wimpenny et al., 2010b) plotted  
880 against various weathering tracers. (a)  $\delta^7\text{Li}$  vs.  $\text{TZ}^+$  ( $\text{TZ}^+=[\text{Na}^+]+[\text{K}^+]+2[\text{Ca}^{2+}]+2[\text{Mg}^{2+}]$ ) and  
881 corresponding subsurface and riverine trend identified from simulation results (Fig. 4). (b)  $\delta^7\text{Li}$   
882 vs.  $\text{Si}/\text{TZ}^+$ . (c)  $\delta^7\text{Li}$  vs.  $\text{Li}/\text{Na}$ . Samples affected by hydrothermal springs are not shown.

883

884 Table 1

885 Initial and boundary conditions

886

887 Table 2:

888 Simulated silicate weathering reactions

889

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Figure 1  
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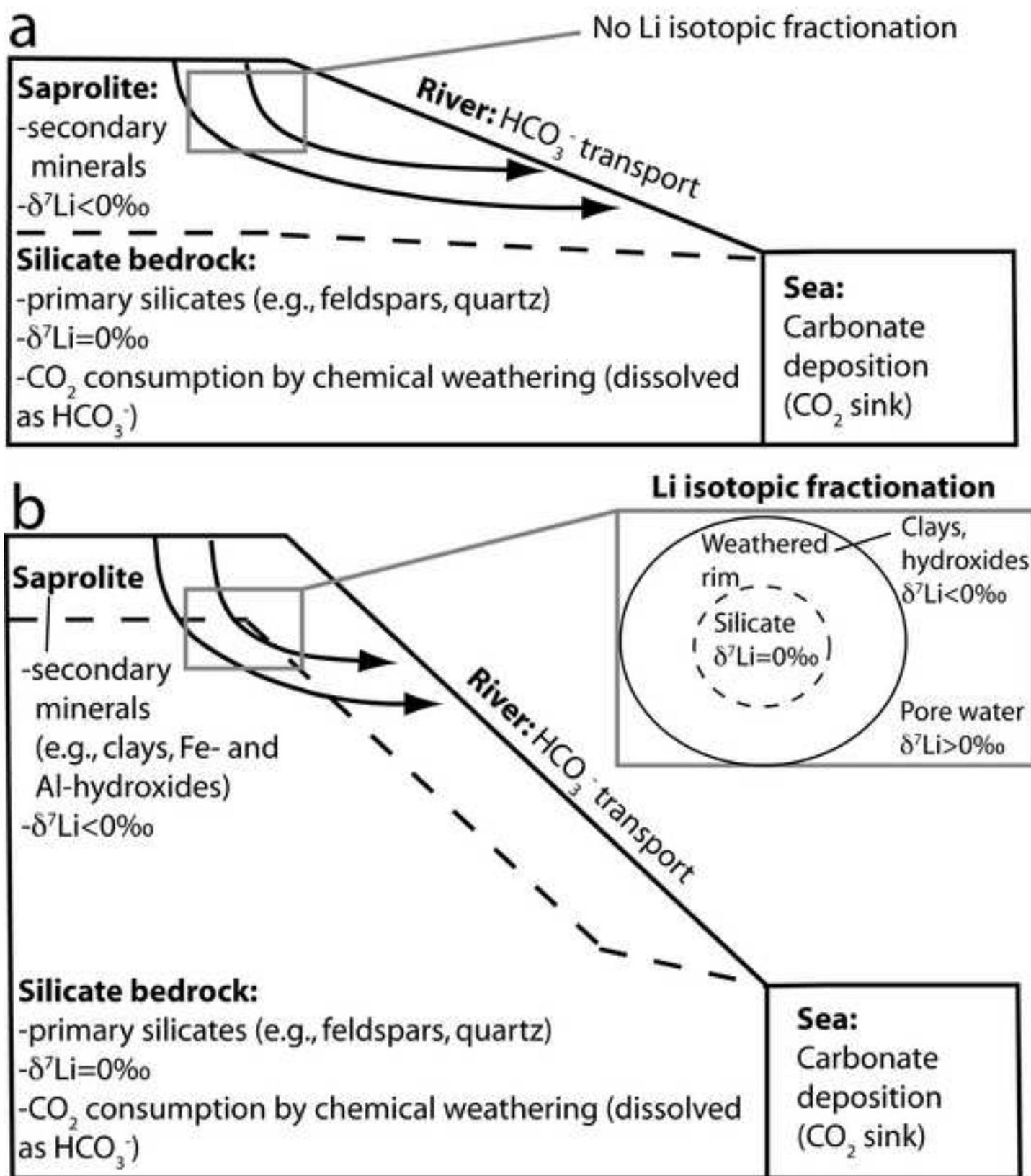


Figure 2  
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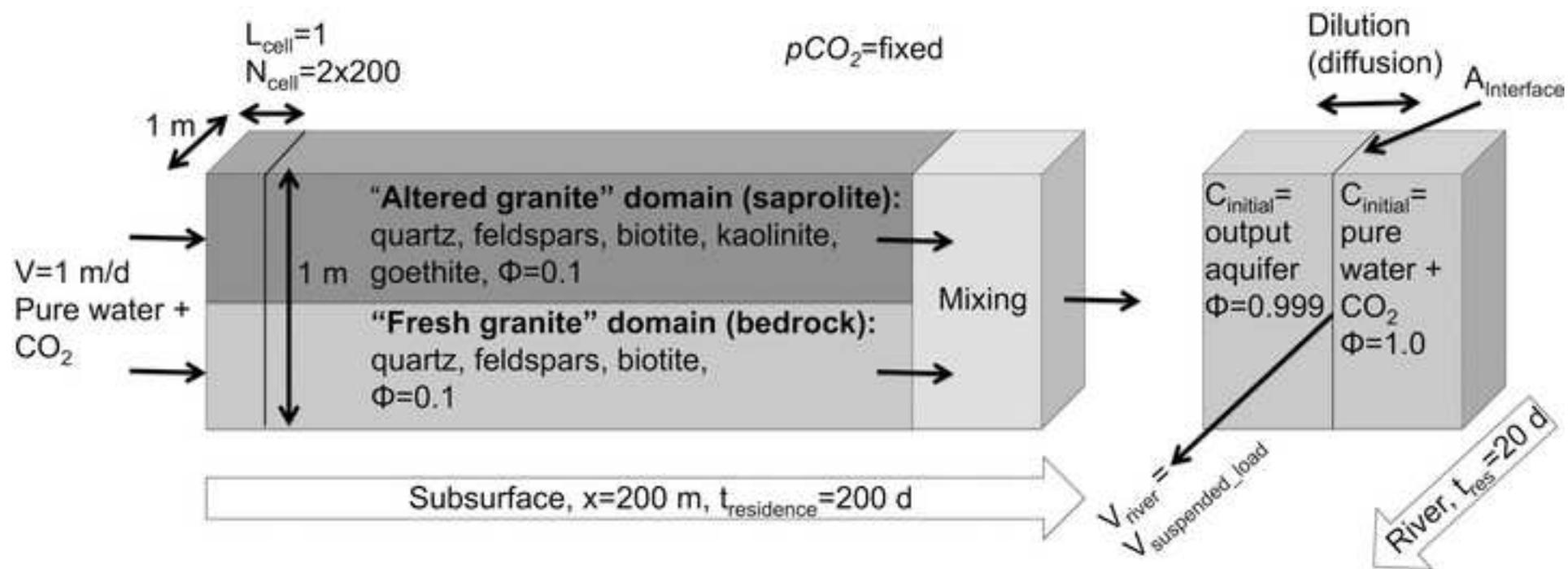
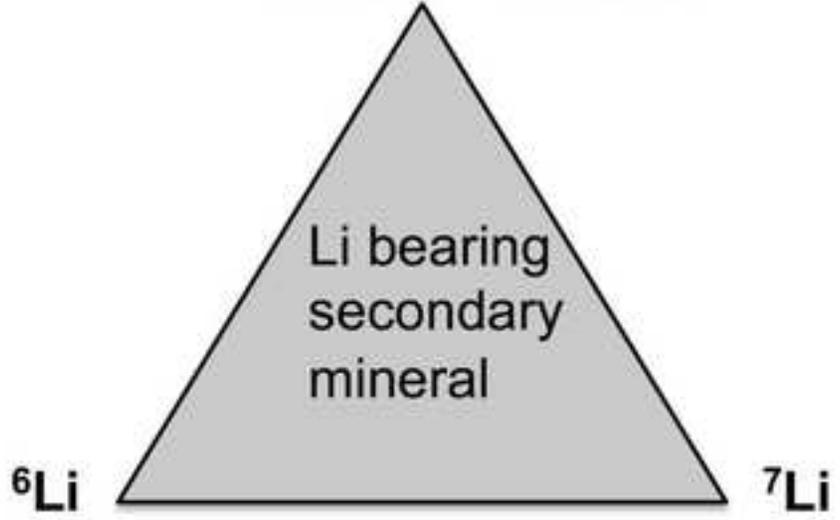


Figure 3  
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Pure (non Li bearing) secondary mineral (e.g., kaolinite, goethite);  
Log(K)=published value (database)

**Pure 2<sup>nd</sup> mineral**



Hypothetical, pure <sup>6</sup>Li mineral phase;  
Log(K)=log([<sup>6</sup>Li<sup>+</sup>]);  
to be calibrated

Hypothetical, pure <sup>7</sup>Li mineral phase;  
Log(K)=log([<sup>7</sup>Li<sup>+</sup>]);  
to be calibrated

Figure 4  
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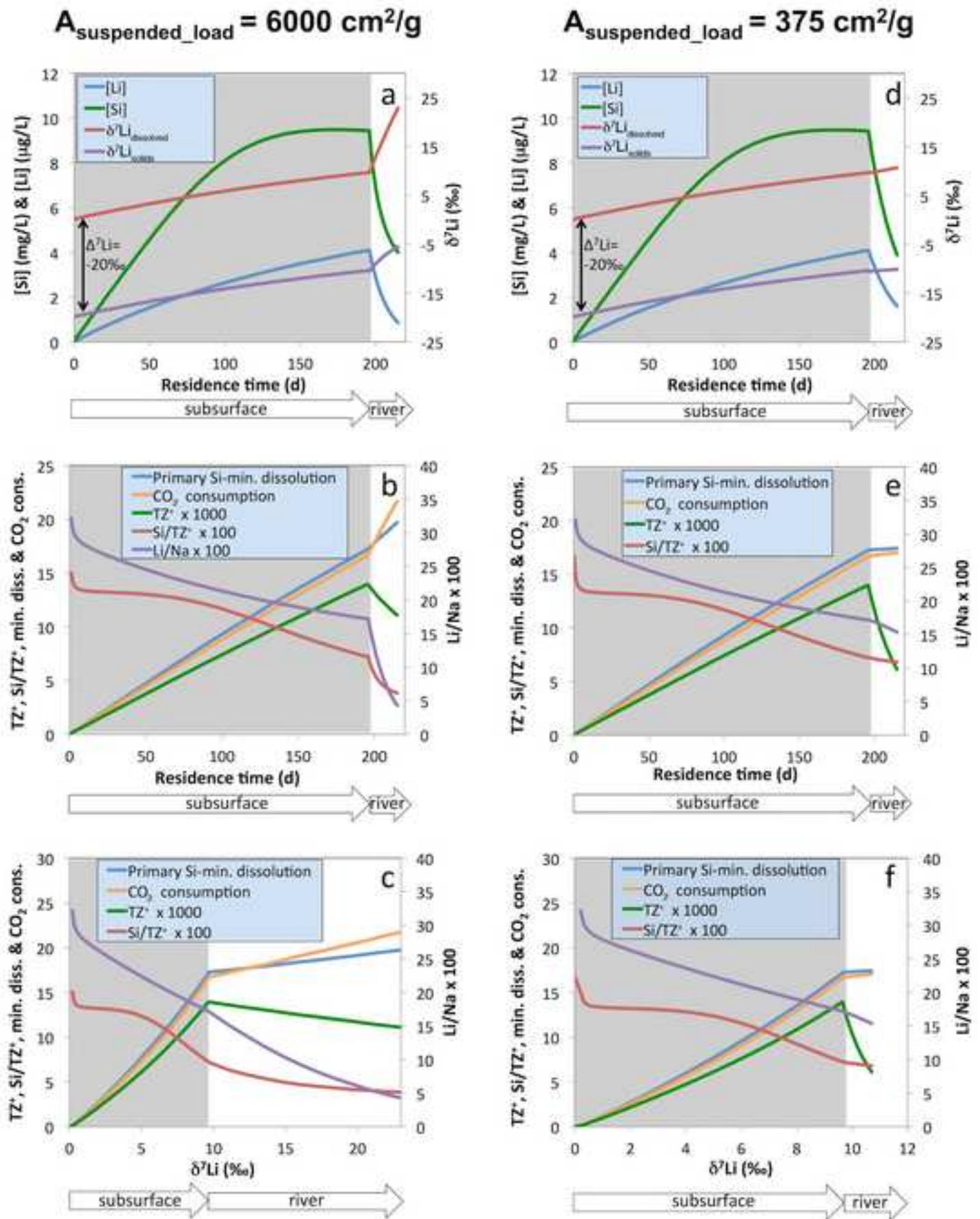


Figure 5  
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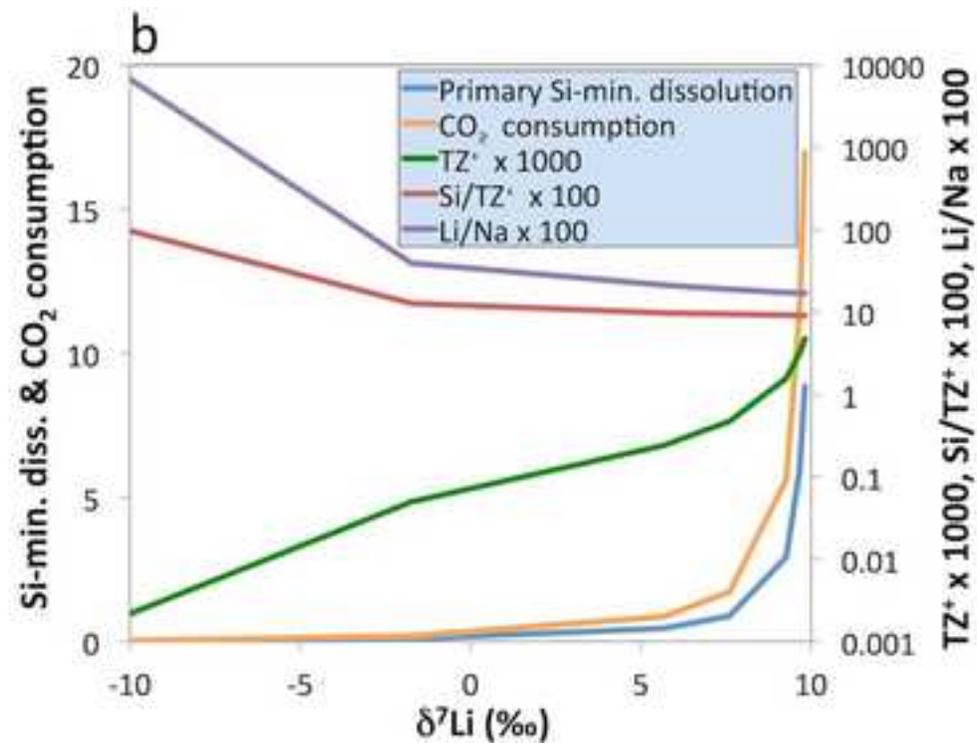
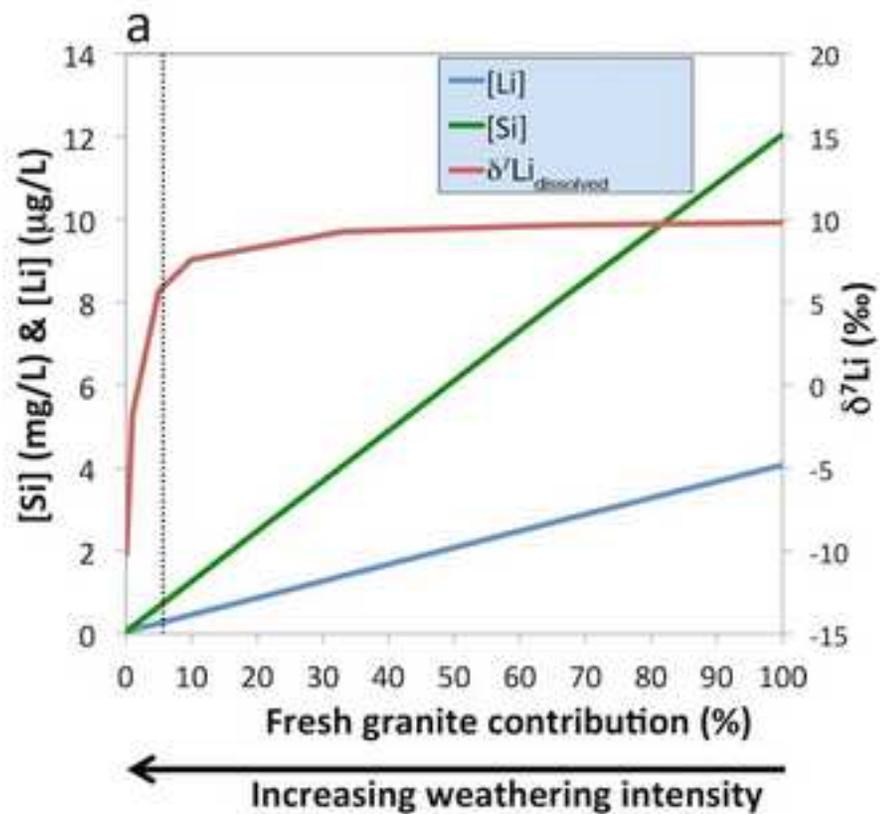


Figure 6  
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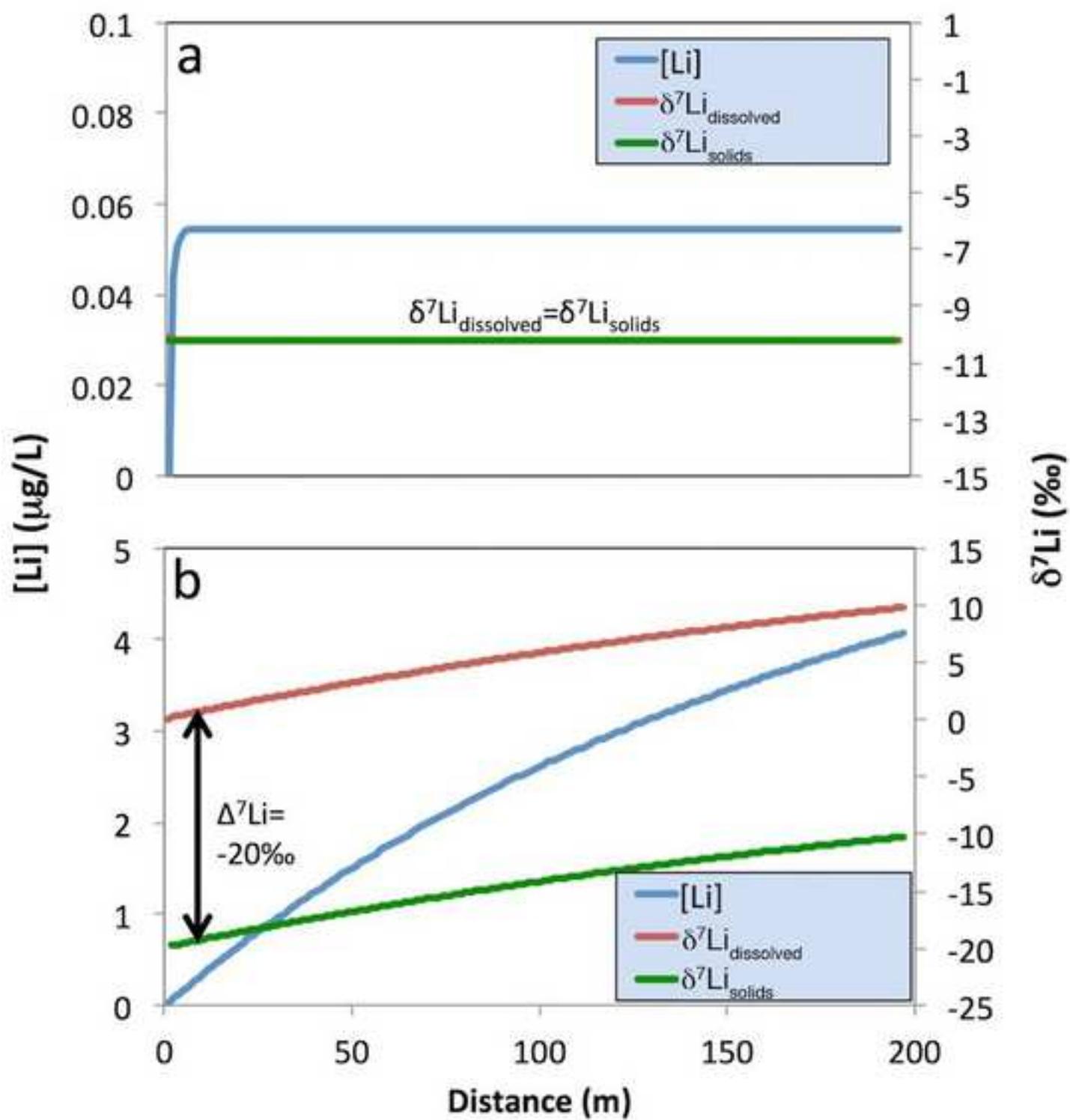
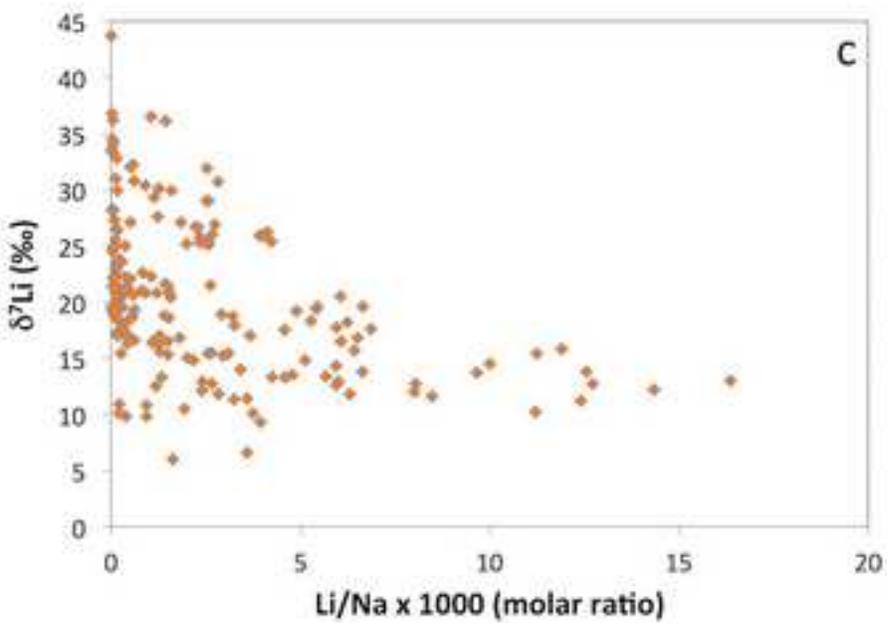
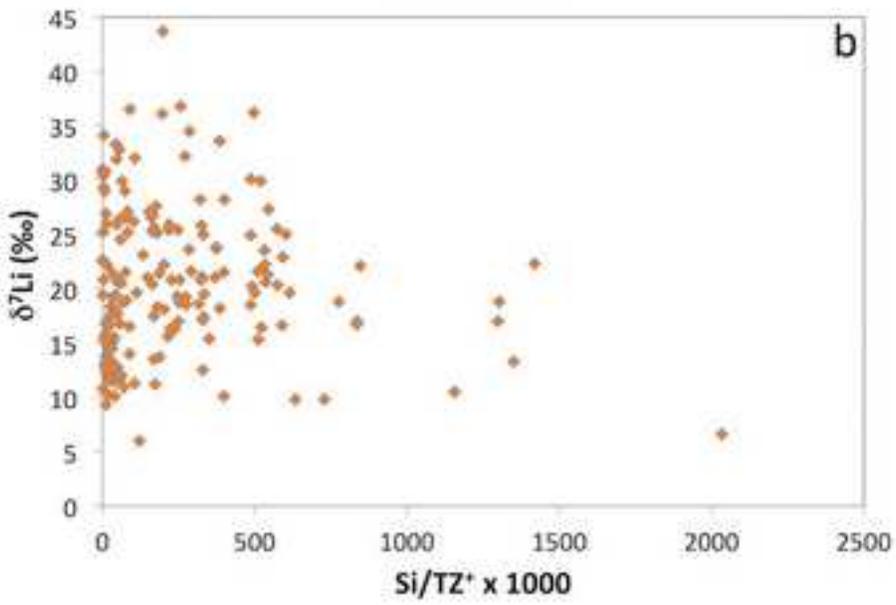
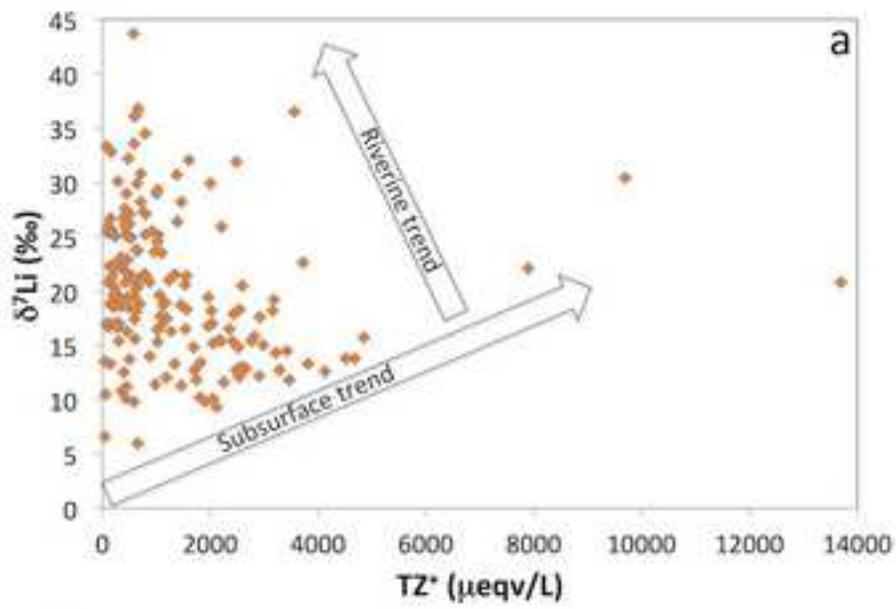


Figure 7

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## Table 1+2

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TABLE 1. INITIAL AND BOUNDARY CONDITIONS

		Simulation of current weathering pattern		Simulation of Paleocene-Eocene boundary weathering pattern	
		subsurface	river	"Fresh Granite"	"Altered Granite"
pH	-	5.63	<sup>d</sup> 8.79	5.37	5.37
HCO <sub>3</sub> <sup>-</sup>	mol/kgH <sub>2</sub> O	<sup>a</sup> 1.51E-5	<sup>d</sup> 4.18E-3	<sup>b</sup> 4.52E-05	<sup>b</sup> 4.52E-05
Na <sup>+</sup>	mol/kgH <sub>2</sub> O	1.0E-10	<sup>d</sup> 3.45E-6	1.0E-10	1.0E-10
K <sup>+</sup>	mol/kgH <sub>2</sub> O	1.0E-10	<sup>d</sup> 1.67E-4	1.0E-10	1.0E-10
Mg <sup>2+</sup>	mol/kgH <sub>2</sub> O	1.0E-10	<sup>d</sup> 2.00E-5	1.0E-10	1.0E-10
Ca <sup>2+</sup>	mol/kgH <sub>2</sub> O	1.0E-10	<sup>d</sup> 2.22E-3	1.0E-10	1.0E-10
Al <sup>3+</sup>	mol/kgH <sub>2</sub> O	1.0E-10	<sup>d</sup> 8.31E-7	1.0E-10	1.0E-10
<sup>6</sup> Li <sup>+</sup>	mol/kgH <sub>2</sub> O	<sup>c</sup> 7.68095e-11	<sup>d</sup> 4.5097E-8	<sup>c</sup> 7.68095e-11	<sup>c</sup> 7.68095e-11
<sup>7</sup> Li <sup>+</sup>	mol/kgH <sub>2</sub> O	<sup>c</sup> 9.23191E-10	<sup>d</sup> 5.4726E-7	<sup>c</sup> 9.23191E-10	<sup>c</sup> 9.23191E-10
SiO <sub>2(aq)</sub>	mol/kgH <sub>2</sub> O	1.0E-10	<sup>d</sup> 3.36E-4	1.0E-10	1.0E-10
O <sub>2(aq)</sub>	mol/kgH <sub>2</sub> O	2.5E-4	2.5E-4	2.5E-4	2.5E-4
Fe <sup>2+</sup>	mol/kgH <sub>2</sub> O	1.0E-10	<sup>d</sup> 6.59E-19	1.0E-10	1.0E-10
CO <sub>2(s)</sub>	vol frac (of solids)	0.01	0.01	0.01	0.01
Albite	vol frac (of solids)	0.304	0.304	0.304	0.304
Anorthite	vol frac (of solids)	0.076	0.076	0.076	0.076
Orthoclase	vol frac (of solids)	0.29	0.29	0.29	0.29
Quartz	vol frac (of solids)	0.31	0.31	0.31	0.31
Annite	vol frac (of solids)	0.04	0.04	0.04	0.04
Li-phlogopite	vol frac (of solids)	0.01	0.01	0.01	0.01
Kaolinite	vol frac (of solids)	0.0	0.0	0.0	0.004 <sup>e</sup>
<sup>6</sup> Li (kaolinite)	vol frac (of solids)	0.0	0.0	0.0	0.00031020 <sup>e</sup>
<sup>7</sup> Li (kaolinite)	vol frac (of solids)	0.0	0.0	0.0	0.00368979 <sup>e</sup>
Goethite	vol frac (of solids)	0.0	0.0	0.0	0.0003 <sup>e</sup>
<sup>6</sup> Li (kaolinite)	vol frac (of solids)	0.0	0.0	0.0	0.00002326 <sup>e</sup>
<sup>7</sup> Li (kaolinite)	vol frac (of solids)	0.0	0.0	0.0	0.00027673 <sup>e</sup>
Porosity	-	0.1	0.99	0.1	0.1

<sup>a</sup>Calculated by assuming equilibrium with pCO<sub>2</sub> of 370 ppmV (log(pCO<sub>2</sub>)=-3.43)<sup>b</sup>Calculated by assuming equilibrium with pCO<sub>2</sub> of 1200 ppmV (log(pCO<sub>2</sub>)=-2.92)<sup>c</sup>Specification corresponds to an initial <sup>δ</sup>Li of 0.0‰<sup>d</sup>Read out from downstream boundary of aquifer model run<sup>e</sup>Read out from model run with "fresh granite" domain only

Table 2. SIMULATED SILICATE WEATHERING REACTIONS

Mineral phase	<sup>e</sup> log(K)	<sup>f</sup> k (mol/m <sup>2</sup> /s)	<sup>g</sup> A <sup>fresh</sup> granite <sup>g</sup> (cm <sup>2</sup> /g)	A <sup>altered</sup> granite <sup>g</sup> (cm <sup>2</sup> /g)	A <sup>river simulation*</sup> (cm <sup>2</sup> /g)	Hydrolysis reaction
CO <sub>2(s)</sub> <sup>a</sup>	-11.25	1.00e-04	100	100	100	CO <sub>2(s)</sub> + H <sub>2</sub> O = H <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup>
Albite <sup>c1</sup>	1.41	2.75e-13	1	0	6000 or 375 <sup>h</sup>	NaAlSi <sub>3</sub> O <sub>8</sub> + 4H <sup>+</sup> = Na <sup>+</sup> + 3SiO <sub>2(aq)</sub> + Al <sup>3+</sup> + 2H <sub>2</sub> O
Anorthite <sup>c1</sup>	24.52	7.59e-10	1	0	6000 or 375	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> + 8H <sup>+</sup> = Ca <sup>2+</sup> + 2SiO <sub>2(aq)</sub> + 3Al <sup>3+</sup> + 4H <sub>2</sub> O
Orthoclase	-0.20	3.89E-13	1	0	6000 or 375	KAlSi <sub>3</sub> O <sub>8</sub> + 4H <sup>+</sup> = K <sup>+</sup> + 3SiO <sub>2(aq)</sub> + Al <sup>3+</sup> + 2H <sub>2</sub> O
Quartz	-4.05	2.46e-13	1	0	6000 or 375	SiO <sub>2(s)</sub> = SiO <sub>2(aq)</sub>
Annite <sup>c2</sup>	18.31	7.76e-12	2.4	0	6000 or 375	FeCaSi <sub>2</sub> O <sub>6</sub> + 4H <sup>+</sup> = Ca <sup>2+</sup> + Fe <sup>2+</sup> + 2SiO <sub>2(aq)</sub> + 2H <sub>2</sub> O
Li-phlogopite <sup>b,c2</sup>	37.428	2.82E-13	2.4	0	6000 or 375	K <sub>1.144</sub> Mg <sub>2.856</sub> Li <sub>0.144</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub> + 10H <sup>+</sup> = 1.144K <sup>+</sup> + 2.856 Mg <sup>2+</sup> + 0.01104322 <sup>6</sup> Li <sup>+</sup> + 0.13295678 <sup>7</sup> Li <sup>+</sup> + Al <sup>3+</sup> + 3SiO <sub>2(aq)</sub>
Kaolinite <sup>S3</sup>	7.55	6.6e-14	6824	6824	6000 or 375	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> + 6H <sup>+</sup> = 2Al <sup>3+</sup> + 2SiO <sub>2(aq)</sub> + 5H <sub>2</sub> O
<sup>6</sup> Li (Kaolinite) <sup>d, c3</sup>	-2.60877392	6.6e-14	6824	6824	6000 or 375	<sup>6</sup> Li = <sup>6</sup> Li <sup>+</sup>
<sup>7</sup> Li (Kaolinite) <sup>d, c3</sup>	-2.6	6.6e-14	6824	6824	6000 or 375	<sup>7</sup> Li = <sup>7</sup> Li <sup>+</sup>
Goethite <sup>S4</sup>	-8.3710	1.15e-8	6824	6824	6000 or 375	Fe(OH) <sub>3</sub> + 2H <sup>+</sup> = 0.25O <sub>2(aq)</sub> + 1.5H <sub>2</sub> O + 1Fe <sup>2+</sup>
<sup>6</sup> Li (Goethite) <sup>d, c4</sup>	-2.60877392	1.15e-8	6824	6824	6000 or 375	<sup>6</sup> Li = <sup>6</sup> Li <sup>+</sup>
<sup>7</sup> Li (Goethite) <sup>d, c4</sup>	-2.6	1.15e-8	6824	6824	6000 or 375	<sup>7</sup> Li = <sup>7</sup> Li <sup>+</sup>

<sup>a</sup>Hypothetical solid CO<sub>2(s)</sub> phase to fix pCO<sub>2</sub> (= model CO<sub>2</sub> source). Different values were defined to fix pCO<sub>2</sub> to 1200 ppmV (log(K)=-10.739) and 370ppmV (log(K)=-11.252)

<sup>b</sup>Corresponds to a phlogopite Li concentration of 2400 ppm to get an initial bulk granite Li conc. of 24 ppm according to Economos (2009) (at a phlogopite vol fraction of 0.01), and a δ<sup>7</sup>Li value of 0.0 ‰

<sup>c</sup>Endmember of solid solution x.

<sup>d</sup>Li isotopic endmember of defined solid solution (Fig. 3).  $K_{6Li}/K_{7Li} = 0.98 = \Delta^7Li_{\text{solution-kaolinite}} = -20\text{‰}$ . Log(K) was calibrated to get maximum Li concentration in goethite and kaolinite of about 200 ppm.

<sup>e</sup>With the exception of kaolinite, which was defined according to Yang and Steefel (2008), equilibrium constants log(K) were defined according to Reed and Palandri (2006).

<sup>f</sup>Reaction rate constants *k* were defined according to Palandri & Kharaka (2006)

<sup>g</sup>Reactive surface areas of primary silicate minerals (feldspars, quartz, biotite) were calibrated to get a Li concentration larger than the global average riverine Li conc. (0.265 μmol/L) at the downstream aquifer model boundary ("mixing", Fig. 2). Reactive surface areas of secondary minerals (e.g., kaolinite, goethite) were set to 6824 cm<sup>2</sup>/g according to Dobson et al. (2003).

<sup>h</sup>River simulations were run for two different reactive surface area to simulate the effects of a varying suspended river load on riverine δ<sup>7</sup>Li values. 6000 cm<sup>2</sup>/g allowed matching the current global average riverine δ<sup>7</sup>Li values after a simulated river residence time of 20 d.