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► **To cite this version:**

Pierre Maffre, Yves Godd ris, Nathalie Vigier, Jean-S bastien Moquet, S bastien Carretier. Modelling the riverine $\delta^{7}\text{Li}$ variability throughout the Amazon Basin. *Chemical Geology*, 2020, 532, pp.119336. 10.1016/j.chemgeo.2019.119336 . hal-02378976

HAL Id: hal-02378976

<https://hal.science/hal-02378976>

Submitted on 21 Dec 2021

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1 **Modelling the riverine $\delta^7\text{Li}$ variability throughout the Amazon Basin**

2

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13

14

15 **Keywords**

16 Lithium isotopes, weathering, Amazon, model

17

18

19 **Abstract**

20

21 The present study investigates the processes controlling the elementary and isotopic cycle of
22 the lithium over the Amazon basin. A numerical model is developed to simulate two major
23 processes that have been proposed as key controls of the river lithium isotopic composition:
24 weathering reactions inside the regolith, accounting for secondary phase formation, and
25 interactions between riverine water and secondary phases in floodplain. Both processes
26 generate fractionation of lithium isotopes (“batch” fractionation and “Rayleigh” distillation
27 respectively) that potentially control the riverine isotopic composition of the Amazon and its
28 tributaries.

29 A study of the model parameters shows that two different regimes are impacting the lithium
30 isotopic composition of the rivers within the Amazon catchment. In the South (Madeira and
31 its tributaries), the lithium isotopic signature of river waters can be explained by lithium
32 release and fractionation during weathering reactions in the regolith, followed by “Rayleigh
33 distillation” in the floodplain increasing progressively the lithium isotopic composition, in
34 agreement with a previously published hypothesis. In contrast, the lithium isotopic
35 composition of rivers located in the northern part of the Amazon watershed (Solimoes and
36 tributaries) cannot be simulated by the model assuming the same processes than in the
37 southern part. Model optimization suggests that the nature of the material being eroded and
38 weathered is important. In the North, fresh source rocks of volcanic origin releases large
39 amount of Li and promotes rapid smectite precipitation, allowing the riverine $\delta^7\text{Li}$ to rise
40 before flowing through floodplains. This result suggests that the environments able to
41 generate high riverine $\delta^7\text{Li}$ (higher than 25‰) are complex and not firmly identified yet.

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45 1. Introduction

46

47 The lithium isotopic composition ($\delta^7\text{Li}$) of river waters is a potential tracer of continental
48 weathering processes (e.g. Huh et al., 1998; Vigier et al., 2009; Millot et al., 2010b; Dellinger
49 et al., 2014, 2015; Pogge von Strandmann et al., 2017). Indeed, the isotopic composition of
50 dissolved riverine lithium is the result of complex interactions between solids and the water
51 flowing through the Critical Zone. The dissolution of primary minerals releases lithium in
52 solution without significant isotopic fractionation (Pistiner and Henderson, 2003; Wimpenny
53 et al., 2010a; Verney-Carron et al., 2011). Precipitation of secondary clay minerals retains
54 about 80 to 90% of the lithium released by rock and mineral leaching, and this incorporation
55 occurs with a strong isotopic fractionation ranging from 10‰ to 25‰ at low temperature (e.g.
56 Pistiner and Henderson, 2003; Vigier et al., 2008; Millot et al., 2010a; Dupuis et al., 2017), in
57 favor of the light ^6Li isotope. As a result, river dissolved phases are systematically enriched
58 in ^7Li in small and large watersheds (e.g. Kısakürek et al., 2005; Huh et al., 1998; Dellinger et
59 al., 2014; Pogge von Strandmann et al., 2017).

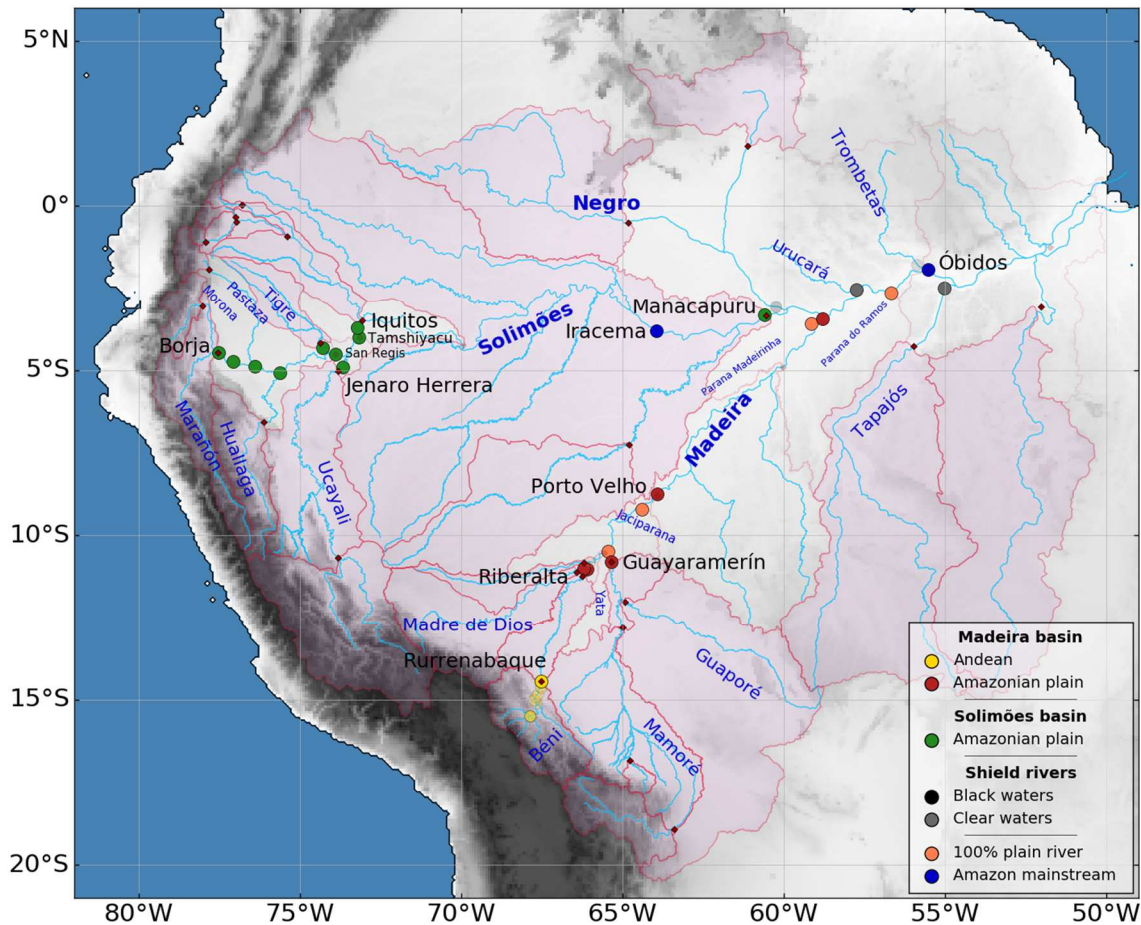
60 A consensus, based on both observational and modelling studies (Stallard and Edmond,
61 1983; Riebe et al., 2004; West et al., 2005; Gabet and Mudd, 2009; West, 2012), emerged
62 for defining two major weathering poles: some areas are characterized by a “weathering-
63 limited” regime where primary minerals are not completely weathered before being eroded
64 away. In those regions, dissolution rates of fresh minerals are the limiting process. The
65 export of dissolved species is relatively fast, soil residence time is small and secondary clay
66 formation remains limited. Generally, tectonically-active mountain ranges belong to this pole
67 (e.g. West et al., 2005). If the corresponding soil thickness is small, the lithium isotopic
68 composition of the runoff (superficial waters) is expected to be maintained at a low value,
69 close to the continental source rocks (Dellinger et al., 2015; Bouchez et al., 2013; Pogge von
70 Strandmann and Henderson, 2015). Other areas, mostly located in the plains, lowlands or
71 cratons, are characterized by the supply-limited regime where residence time of minerals
72 within the regolith is long enough to completely remove primary phases at the surface. In
73 these regions, the time of water-rock interactions is longer and secondary phase formation is
74 facilitated. Thus, in these flat regions, removal of dissolved Li by secondary mineral formation
75 is expected to increase the runoff $\delta^7\text{Li}$ values.

76 Given the isotopic composition of the continental rocks (1.7‰ on average, Teng et al., 2009)
77 and accounting for the known values of lithium isotopic fractionations (around 20‰), the
78 maximum $\delta^7\text{Li}$ value that river waters can reach (assuming an equilibrium process) is close
79 to 22‰. However, a non negligible amount of rivers display much higher $\delta^7\text{Li}$ values,
80 reaching 30 to 40‰ (Huh et al., 1998, 2001; Kısakürek et al., 2005; Vigier et al., 2009; Millot
81 et al., 2010b; Wimpenny et al., 2010b). For large basins, it has been hypothesized that the

82 high values reached in low relief area and in floodplains could be the result of a continuous
83 isotopic fractionation similar to a Rayleigh distillation (Vigier et al., 2009; Bagard et al., 2015;
84 Dellinger et al., 2015; Pogge von Strandmann et al., 2017). In floodplains, the dissolved
85 lithium released upstream continuously interacts with secondary mineral phases, reducing
86 the dissolved lithium load while enriching it in ^7Li . Thus, the elevated $\delta^7\text{Li}$ values of the
87 downstream tributaries of the Madeira and Solimões rivers (Amazon Basin, Dellinger et al.,
88 2015) can be explained by Rayleigh distillation law, based on correlations between the river
89 isotopic ratio and its dissolved Li concentration. However, in the specific case of the
90 Solimoes high $\delta^7\text{Li}$ values are also observed close to the outlet of the Andes, potentially
91 suggesting the existence of enrichment in ^7Li before the water flows through floodplains.
92 High values for mountain rivers have been compiled by Schmitt et al. (2012). Conversely
93 more recent contributions have reported low $\delta^7\text{Li}$ values in mountaineous rivers (Millot et al.,
94 2010; Pogge von Strnadmann et al., 2017). These contradictory results do not allow drawing
95 a general picture, and suggest the existence of a variety of processes impacting the riverine
96 $\delta^7\text{Li}$ that are not fully understood yet.

97
98 In the present contribution, we build a comprehensive numerical model simulating the lithium
99 elemental and isotopic behaviour at the continental scale. The model accounts for both
100 secondary mineral precipitation in regolith and for continuous interactions between river
101 water and secondary phases in floodplains. As a test for the ability of these two processes to
102 explain the first order pattern of the riverine $\delta^7\text{Li}$, we simulate the elemental and isotopic
103 mass balance over the Amazon. The Amazon contributes significantly to the global dissolved
104 and suspended fluxes delivered to the oceans. It includes both “supply limited” and
105 “weathering limited” domains and extended areas of permanent or seasonal floodplains.
106 These characteristics make the Amazon catchment an ideal laboratory to simulate the
107 processes impacting the riverine lithium dissolved load and its isotopic composition. The
108 Amazon watershed is monitored by the HYBAM observatory providing high-frequency
109 measurements of water discharge, suspended and dissolved load at 40 stations distributed
110 within the catchment (see Fig. 1, and Appendix A). Erosion and weathering fluxes are known
111 at the geomorphologic domains scale (Moquet et al., 2011, 2016). Moreover, the lithium
112 isotopic composition and elemental concentrations are available at various measurement
113 sites (Dellinger et al., 2015).

114



115
 116 **Figure 1:** Map of the Amazon tributaries (blue lines) showing the monitoring stations where
 117 riverine $\delta^7\text{Li}$ has been measured (Dellinger et al., 2015) (colored circles), the HYBAM
 118 monitoring stations (dark grey diamonds) and corresponding watersheds (light red shades).

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123 2. River water $\delta^7\text{Li}$ in the Amazon Basin

124

125 Dellinger et al. (2015) published a detailed database for the Amazon watershed, gathering 39
 126 sample sites, from the Andes to the outlet in the Atlantic Ocean. Measured Li isotopic
 127 composition of river waters range from 2‰ to 33‰ and can be explained by considering
 128 three types of waters contributing to the Amazon main flow: the white, clear, and black
 129 waters. “Black” waters are characterized by high organic matter content and low $\delta^7\text{Li}$ (2‰ to
 130 10‰), close to the bedrock values. Dellinger et al. (2015) suggest that the high organic acid
 131 content of the black waters promotes a complete dissolution of the secondary phases. This
 132 weathering congruency drives the $\delta^7\text{Li}$ of the black waters close to the continental bedrock

133 values, explaining the low riverine $\delta^7\text{Li}$. This process was also evidenced for some rivers
134 draining the Congo basin (Henchiri et al., 2016). The “white” waters are characteristic of the
135 Andes and floodplains, with highly variable $\delta^7\text{Li}$ (from 4 to 33%). White waters contribute for
136 more than 70% of the dissolved lithium released to the ocean by the Amazon River. Finally,
137 the last water pool is flowing on the Amazonian shield (clear waters) and contributes for less
138 than 10% to the dissolved lithium flux of the Amazon river. Based on their measurements,
139 Dellinger et al. (2015) do not observe a significant seasonality in the $\delta^7\text{Li}$, except for the
140 N egro and Madeira rivers, with maximum differences about 9.2‰ and 6.5‰ respectively.

141
142 In the present contribution, we only focus on the white and clear waters. Modelling organic
143 matter content and dissolution by organic acid is beyond the capacity of this study. In white
144 and clear waters, $\delta^7\text{Li}$ below about 20‰ have been explained by Dellinger et al. (2015) by an
145 equilibrium fractionation occurring inside the weathering profiles. Primary mineral dissolution
146 releases Li with a low isotopic signature, and the subsequent formation of secondary
147 minerals increases the $\delta^7\text{Li}$ of the circulating water. Higher values plots along a Rayleigh
148 distillation line, leading these authors to postulate that continuous interactions between water
149 and secondary minerals occur in flood plains and allow the water $\delta^7\text{Li}$ to rise above the limit
150 of the equilibrium fractionation.

151
152 The objective is to calculate the isotopic composition of the waters draining the Amazon
153 watershed. Given that the two processes suspected to control the Amazon Li isotopic
154 signature are geographically distributed over the watershed, it is mandatory to build a
155 spatially resolved model. The simulated values are then compared to the available data at
156 various locations over the watershed.

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160 **3. Model description**

161

162 **3.1. Overall design of the model**

163

164 We built a spatially resolved numerical model of the Li elemental and isotopic behaviour over
165 the Amazon watershed. The model is designed as a tool to test the “floodplain” hypothesis. It
166 requires the knowledge of the erosion and weathering fluxes. Both are calculated using
167 published models (Gabet and Mudd, 2009; West, 2012; Maffre et al., 2018) and a corrective
168 factor is applied to match the spatially-distributed data. Those fluxes are then injected into a
169 numerical model simulating (1) the lithium isotopic and elemental behaviour inside the

170 regoliths (vertical 1D model, referred in the text as the “regolith component”), (2) and the
 171 impact of lateral floodings on the Li terrestrial cycle. (1D ramified model referred as
 172 “floodplain component”). As described below, each grid cell is divided into a floodplain
 173 fraction where lateral movements of water modify the elemental and isotopic composition of
 174 dissolved lithium. The remaining part of the grid cell is assumed to behave as a regolith,
 175 which controls the Li composition of the draining waters. Then both components are mixed.

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178 3.2. Modeling Li isotopes in weathering profiles: the regolith component

179

180 The backbone of the regolith component consists of a set of 4 equations (Eq. 1 to Eq. 4). The
 181 specific release of Li by primary mineral dissolution $F_{diss}(Li)$ (mol/m²/yr) on each grid element
 182 (0.5°lat x 0.5°long) of the Amazon watershed is set proportional to the main cation release,
 183 itself calculated according to the steady state weathering model of West (2012):

184

$$185 \quad F_{diss}(cat) = \chi_{cat} \cdot E \cdot \left\{ 1 - \exp \left[-K \cdot \exp \left(-\frac{E_A}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right) \cdot (1 - e^{-k_w q}) \cdot \frac{(h/E)^{\sigma+1}}{\sigma+1} \right] \right\}$$

186 (1)

187

188 χ_{cat} is the abundance of cations in rocks (in mol/m³), E_A is here the activation energy for rock
 189 dissolution and K , k_w and σ three parameters (see Table 1). h is the local regolith thickness
 190 and E the physical removal of material by erosion. Both are spatially distributed over the
 191 watershed, E comes from the reconstruction of Ludwig and Probst (1998). We assume a
 192 constant lithium/cation ratio of source rocks (χ_{Li}/χ_{cat}) equals to 1.2×10^{-4} (Teng et al., 2009).

193

194 $F_{sp}^{reg}(Li)$ is the specific uptake of Lithium by secondary mineral phases within the regolith
 195 (mol/m²/yr). We assume that the ratio $F_{sp}^{reg}(Li)/F_{diss}(Li)$ depends on the residence time of
 196 the water inside the regolith, written as $\varphi h/q$, where q is the vertical water drainage
 197 (precipitation minus evapotranspiration, m yr⁻¹), h the regolith thickness (m) and φ the
 198 regolith porosity. (m³/m³). To describe mathematically the dependence of $F_{sp}^{reg}(Li)/F_{diss}(Li)$
 199 on the water residence time, we choose a Michaelis function, so that $F_{sp}^{reg}(Li)/F_{diss}(Li)$ is
 200 equal to zero for a null water residence time and to 1 (all lithium is retained in secondary
 201 phases) for infinite water residence time:

202

$$203 \quad F_{sp}^{reg}(Li) = \frac{1}{1 + \frac{\tau_0}{\varphi h/q}} F_{diss}(Li) \quad (2)$$

204

205 The regolith thickness h is calculated using the Gabet and Mudd (2009) model describing the
206 evolution of a regolith under the combined effect of regolith production and erosion.
207 According to this model, the regolith production decreases exponentially with the regolith
208 thickness. Following Carretier et al. (2014), we made the equation for regolith production rate
209 dependent on temperature and runoff. For each grid cell, the steady state thickness h of the
210 regolith can be calculated according to:

211

$$212 \quad h = h_o \cdot \ln \left(k_{rp} \cdot q \cdot \exp \left(-\frac{E_A^{rp}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right) / E \right) \quad (3)$$

213

214 where h_o is the decay depth and k_{rp} is the soil production constant, T is the mean annual
215 temperature, q is the water drainage, E_A^{rp} the apparent activation energy for the regolith
216 production, R the ideal gas constant and k_{rp} a scaling constant (see Table 1).

217

218 The specific flux of lithium leaving the regolith and reaching the hydrographic network
219 $F_{leach}(\text{Li})$ (mol/m²/yr) is the difference between the specific flux of Li released by primary
220 mineral dissolution and the specific flux of Li retained by secondary phases.

221

$$222 \quad F_{leach}(\text{Li}) = F_{diss}(\text{Li}) - F_{sp}^{reg}(\text{Li}) \quad (4)$$

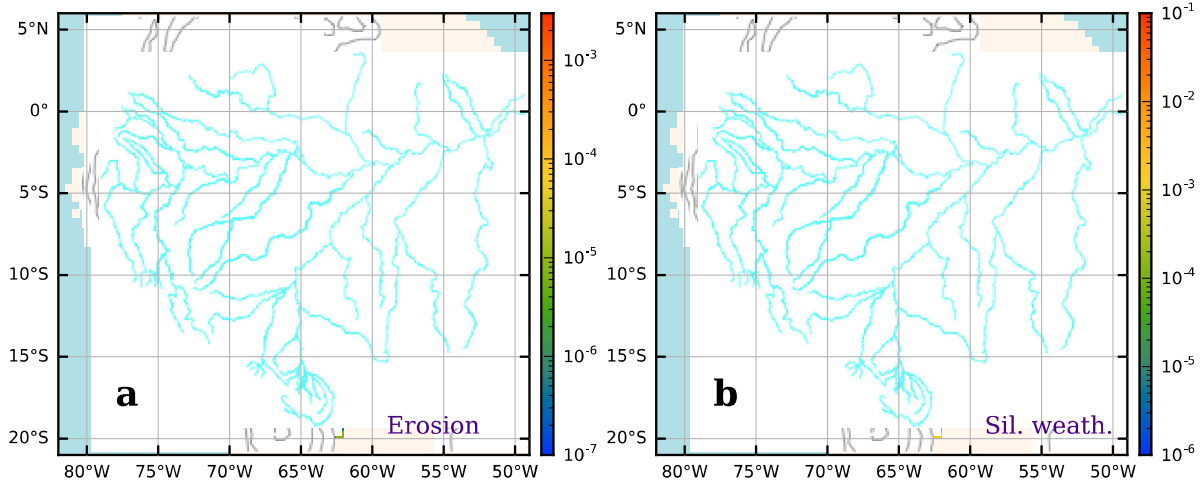
223

224 The system of equations 1 to 4 defines $F_{sp}^{reg}(\text{Li})$, $F_{diss}(\text{Li})$, $F_{leach}(\text{Li})$ and h , for each grid cell
225 of the Amazon watershed.

226

227 Practically, the model is fed with the output of two published models giving the spatial
228 distribution of the weathering flux F_{diss} (main cations) and of the physical erosion E
229 (respectively West, 2012; Ludwig and Probst, 1998). To limit the propagation of the
230 uncertainties brought by these models into the lithium model, we applied corrective factors to
231 the calculation of F_{diss} and E . Over each monitored sub-basin of the Amazon, we use the
232 HYBAM database to correct the calculated fields of erosion and cation release by silicate
233 dissolution. The weathering and erosion are multiplied by a corrective factor, so that they fit
234 the measured values at the outlet of the sub-basin, once integrated over the sub-basin. The
235 erosion and weathering fields shown on Fig. 2 (a and b respectively) are the corrected ones.
236 The details of this correction procedure can be found in Appendix A.

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Figure 2: (a) Erosion rates (m/y) and (b) silicate weathering rates (major cation flux in kg/m²/y) over the Amazonian basin. The erosion field is taken from Ludwig and Probst (1998), the weathering field is computed with Eq. 1. Both are corrected with HYBAM data (see section 3.4 and Appendix A). The grey areas correspond to locations where the erosion or weathering rates are equal to zero. Weathering rate goes down to zero when the erosion does, or because the regolith thickness falls down to zero. Blue lines show the main rivers; the white arrows show water routing in the model grid; black contours are elevation isolines (500m, 1000m, 2000m, 4000m and 6000m).

Regarding isotopes, lithium is assumed to follow an equilibrium fractionation occurring during the precipitation of secondary phases, primary phases being congruently dissolved (Bouchez et al., 2013; Dellinger et al., 2015). The isotopic mass balance is written as:

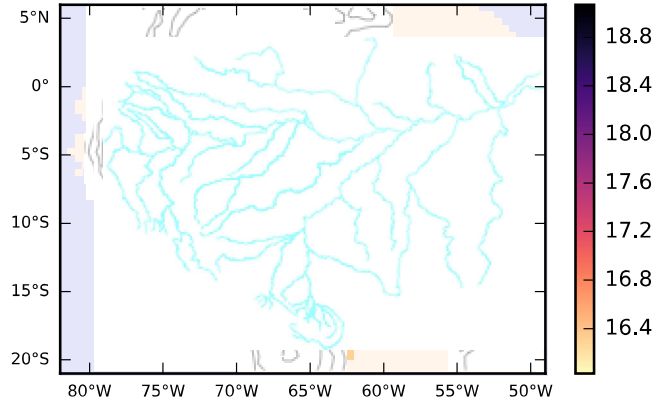
$$\delta_{riv}^7Li = \delta_{rock}^7Li + \frac{F_{sp}^{reg}(Li)}{F_{diss}(Li)} \Delta_{land} \quad (5)$$

δ_{riv}^7Li is the δ^7Li value of waters leaving the regolith, δ_{rock}^7Li is the δ^7Li value of the source rocks (1.7‰, Teng et al., 2004, 2009), and Δ_{land} the corresponding isotope fractionation factor during the incorporation of dissolved Li into secondary phases. This fractionation factor is mainly controlled by temperature (Vigier et al., 2008) and, to a lesser extent, by chemistry (Li and West, 2014; Dupuis et al., 2017). Here the fractionation factor is made dependent on temperature through a T⁻² fit (T being the temperature, in K) supported by both experimental measurements and ab-initio computation at various temperatures (Dupuis et al., 2017).

$$\Delta_{land} = \frac{1.63 \cdot 10^6}{T^2} - 2.04 \quad (6)$$

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The calculated value of Δ_{land} is equal to 17‰ at 20°C, a value consistent with Dellinger et al. (2015) observations and with laboratory experiments (Hindshaw et al, 2019). In the model, it decreases to 16‰ in the warmest places and increases to 19‰ in the coldest. (Fig. 3).



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Figure 3: Li isotopic fractionation occurring during the precipitation of secondary phases Δ_{land} over the Amazon catchment (‰) as computed by Eq. 6.

277 3.3. Modelling Li isotopes in floodplains: the floodplain component

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The vertical “regolith” component is coupled to the second component: an horizontal ramified 1-D reactive transport model that simulates the Li isotopic and elemental budgets of the main rivers of the Amazon catchment, assumed at steady-state (all time derivatives are set to zero). This model component is designed to calculate the impact of lateral flooding. If x is the river coordinate (increasing from head to mouth) and $F_{riv}(\text{Li})(x)$ is the flux of lithium carried by the river at coordinate x (in mol/yr), the elementary mass budget can be written as:

$$286 \quad \frac{dF_{riv}(\text{Li})}{dx} = w \left(F_{diss}(\text{Li}) - F_{sp}^{flood}(\text{Li}) \right) \quad (7)$$

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where w is the river width, and $F_{diss}(\text{Li})$ and $F_{sp}^{flood}(\text{Li})$ are respectively the specific dissolved and retention lithium fluxes (in mol/m²/y) within floodplains. As river water enters in contact with sediments containing primary minerals, we calculate the supply of Li by mineral dissolution using the same methodology than the one used for the regolith component (which is applied to the fraction of the grid cell not flooded). Conversely, the retention of lithium by

293 secondary phases is now written F_{sp}^{flood} , to distinguish it from F_{sp}^{reg} . The reason for this is that
 294 F_{sp}^{flood} might be a different process than the precipitation of secondary minerals, or that it can
 295 be limited by other factors than the production term $F_{diss}(Li)$. To our knowledge, no study has
 296 proposed a mathematical relation to quantify it. The incorporation of lithium on clays (or other
 297 secondary minerals, such as aluminium hydroxides) is still poorly understood. It is yet
 298 unclear whether riverine water can exchange lithium with clays already formed or lithium can
 299 only be integrated in clays at the time they precipitate. In the absence of such information,
 300 we tested the two possibilities, assuming basic mathematical equations. In the first case, the
 301 Li riverine concentration is the only control:

$$302 \quad F_{sp}^{flood}(Li) = k_{sp}[Li]_{riv}^a \quad (8)$$

303
 304 Where k_{sp} and the exponent a are two adjustable parameters. They can be seen
 305 respectively as the kinetic constant and the order of the reaction. Eq. (8) will be referred in
 306 the following as the case #1, and can be interpreted as a case where secondary phases are
 307 pre-existing in the sediment and that Li is removed by adsorption or any similar process,
 308 limited by the available amount of lithium supplied by the rivers.
 309

310
 311 In the second case, F_{sp}^{flood} is supposed to be limited by the local rate of secondary phases
 312 precipitation, this last being proportional to the local rate of primary mineral dissolution. But
 313 the difference with the vertical “regolith” component is that, even if the removal of lithium in
 314 the flooded part of the grid cell is controlled by the precipitation of secondary minerals, it
 315 must exceed the supply of lithium by the local primary mineral dissolution to allow the
 316 dissolved riverine δ^7Li to increase. This is made possible by the supply of dissolved lithium
 317 from upstream flows. Mathematically speaking, the maximal value for F_{sp}^{flood} is set equal to
 318 $K_m F_{diss}(Li)$ where K_m is the lithium storing capacity of secondary phases with respect to
 319 primary phases. In other words, if 1 mole of primary minerals contains 1 mole of Li, the
 320 secondary minerals formed from that minerals could contain at most K_m mole of Li. K_m has
 321 to be greater than 1 to make possible a net uptake of lithium in floodplain at position x from
 322 the river head. In addition, we supposed a kinetic limitation at low lithium concentrations.
 323 With again a Michaelis-like relation, these conditions can be written as follows:

$$324 \quad F_{sp}^{flood}(Li) = \frac{K_m F_{diss}(Li)}{1 + \frac{K_m F_{diss}(Li)}{k_{sp}[Li]_{riv}}} \quad (9)$$

325
 326

327 k_{sp} is here the kinetic constant. Eq. (9) will be referred as the case #2. The theoretical
 328 behaviour of the floodplain model is explored in Appendix B.

329

330 Given the local fractionation rule ($\delta_{sp}^7\text{Li}(x) = \delta_{riv}^7\text{Li}(x) - \Delta_{land}$), the isotopic budget of the
 331 local riverine $\delta^7\text{Li}$ becomes:

332

$$333 \quad F_{riv}(\text{Li}) \frac{d\delta_{riv}^7\text{Li}}{dx} = w F_{diss}(\text{Li}) (\delta_{rock}^7\text{Li} - \delta_{riv}^7\text{Li}) + w F_{sp}^{flood}(\text{Li}) \Delta_{land} \quad (10)$$

334

335 where $\delta_{riv}^7\text{Li}$ is the $\delta^7\text{Li}$ value of riverine water at the distance x from the head of the river,
 336 $\delta_{sp}^7\text{Li}$ the $\delta^7\text{Li}$ of locally formed secondary phases and $\delta_{rock}^7\text{Li}$ is the isotopic ratio of the
 337 source rocks. w is the width of the flooded area connected to the river at the distance x from
 338 the river head. It can be interpreted as the characteristic distance reached laterally by floods.
 339 We assume that riverine water and overbank water are instantaneously mixed, so the system
 340 behaves like a homogenous channel of width w . Yet, w varies along the river course,
 341 according to the lateral extension of the flood plains.

342

343 The complete ramified model is built accounting for the hydrographic network. The whole
 344 river basin is discretized on a latitude-longitude mesh (the resolution is $0.5^\circ \times 0.5^\circ$). Each cell
 345 of the mesh is connected to a unique downstream cell according to the hydrographic
 346 network. If L is the length of the river course within a single cell, Eq. 7 and 10 are integrated
 347 between 0 (where the river enters the cell) and L (where the river leaves the cell).

348

349 3.4. Coupling *regolith* and *floodplain* components

350

351 The cells of the model spatial grid are sorted from upstream to downstream. Then the
 352 integration of the two model components is performed cell by cell according to the following
 353 steps:

354 1) Running the *regolith* model component (Eq. 2 and 5) and compute $F_{riv}(\text{Li})\langle hillslope \rangle$
 355 and $\delta_{riv}^7\text{Li}\langle hillslope \rangle$

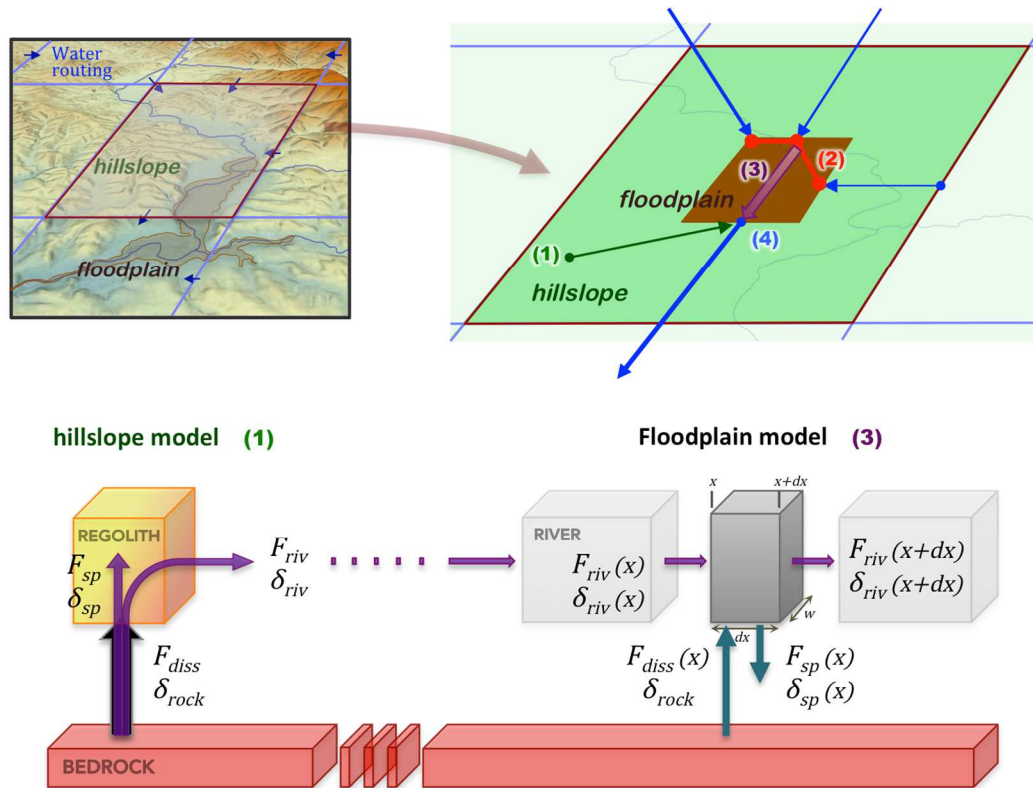
356 2) Averaging the outputs of all upstream cells ($F_{riv}(\text{Li})$ and $\delta_{riv}^7\text{Li}$) to initialize *the plain*
 357 model

358 3) Integrating the *floodplain* model (Eq. 7 and 10) from $x = 0$ to $x = L$ and compute
 359 $F_{riv}(\text{Li})\langle floodplain \rangle$ and $\delta_{riv}^7\text{Li}\langle floodplain \rangle$

360 4) Weighting the *weathering* and *plain* outputs by the ratio unflooded or flooded surfaces
 361 to the total grid cell surface, to compute the values of $F_{riv}(\text{Li})$ and $\delta_{riv}^7\text{Li}$ leaving the cell

362

363 These steps are illustrated in Fig. 4. The numerical solving of the coupled model is detailed
 364 in Appendix C.
 365



366
 367
 368 **Figure 4:** Schematic representation of the *hillslope* lithium model, *floodplain* model and their
 369 coupling. Cells are connected by the hydrographic network (blue arrows). The upper-right
 370 scheme summarizes the four steps of the model coupling: 1) running the *hillslope* model; 2)
 371 initializing the *floodplain* model; 3) integrating the *floodplain* model; 4) mixing (see section
 372 3.3). The lower scheme is a simplified 1D representation of the *hillslope* and *floodplain*
 373 models. It illustrates the mass and isotopic budget of the *hillslope* box model and of an
 374 infinitesimal slice (between x and $x+dx$) of the *floodplain* model.

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380 3.5. Boundary conditions and parameterizations.

381
 382 The model parameters are listed in Table 1 and the main variables in Table 2 (next two
 383 pages).

385 **Table 1:** List of model parameters.

386

Parameter	Description	Units	Value	Reference
h_o	Characteristic depth of regolith production exponential decay	m	2.73	Best fit in Maffre et al. (2018)
k_{rp}	Scaling constant of regolith production	-	2e-3	Adapted from Maffre et al. (2018)'s best fit
E_A^{rp}	Activation energy at $T_o = 25^\circ\text{C}$ for regolith production	J/K/mol	48200	Oliva et al. (2003)
E_A	Activation energy at $T_o = 25^\circ\text{C}$ for mineral dissolution	J/K/mol	1000	Best fit in Maffre et al. (2018)
k_w	Runoff sensitivity constant of mineral dissolution	m^{-1}yr	0.076	West (2012)
σ	Time-dependence exponent of mineral dissolution	-	-0.1	West (2012)
K	Scaling constant of mineral dissolution	-	5e-4	Best fit in Maffre et al. (2018)
χ_{cat}	Main cation abundance in unweathered bedrock	mol/m^3	4750	Best fit in Maffre et al. (2018)
$\chi_{\text{Li}}/\chi_{\text{cat}}$	Li abundance with respect to main cations in bedrock	-	1.2×10^{-4}	Teng et al. (2009)
$\delta_{\text{rock}}^7\text{Li}$	Li isotopic ratio of bedrock	‰	1.7	Teng et al. (2004; 2009)
φ	Regolith porosity	-	0.2	Arbitrary (see current section)
τ_o	Li half-retention residence time in regolith	yr	0.8	calibrated
k_{sp}	Scaling constant for Li retention in floodplain	-		explored
a	Exponent of Li retention in floodplain (eq. to reaction order)	-		explored
K_m	Li retention/dissolution saturating ratio in floodplain	-		explored
w	Flooding width (eq. to width of inundated area)	m	Spatially distributed	Martinez and Le Toan (2007)

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393 **Table 2:** List of model main variables.

394

Variable	Description	Units
T	Surface air temperature	K
q	"Total" runoff (ie: precipitation minus evapo-transpiration)	m/y
E	Erosion rate	m/y
h	Regolith thickness	m
$F_{diss}(\text{Li})$	Specific flux of lithium dissolved from primary phases (same value in <i>hillslope</i> and <i>floodplain</i> components)	mol/m ² /y
$F_{sp}^{reg}(\text{Li})$	Specific flux of lithium retained in secondary phases in hillslopes	mol/m ² /y
$F_{sp}^{flood}(\text{Li})$	Specific flux of lithium retained in secondary phases in floodplains	mol/m ² /y
$\delta_{riv}^7\text{Li}$	Li isotopic ratio of water (either leaving the regolith of riverine water)	‰
$F_{riv}(\text{Li})$	Flux of lithium carried by riverine water	mol/y

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397

398 The required climatic fields, including temperature (T) and runoff (q), the erosion field (E), the
399 water routing and the distribution of flooded areas are taken from global databases,
400 reconstructions or remote sensing cartography.

401

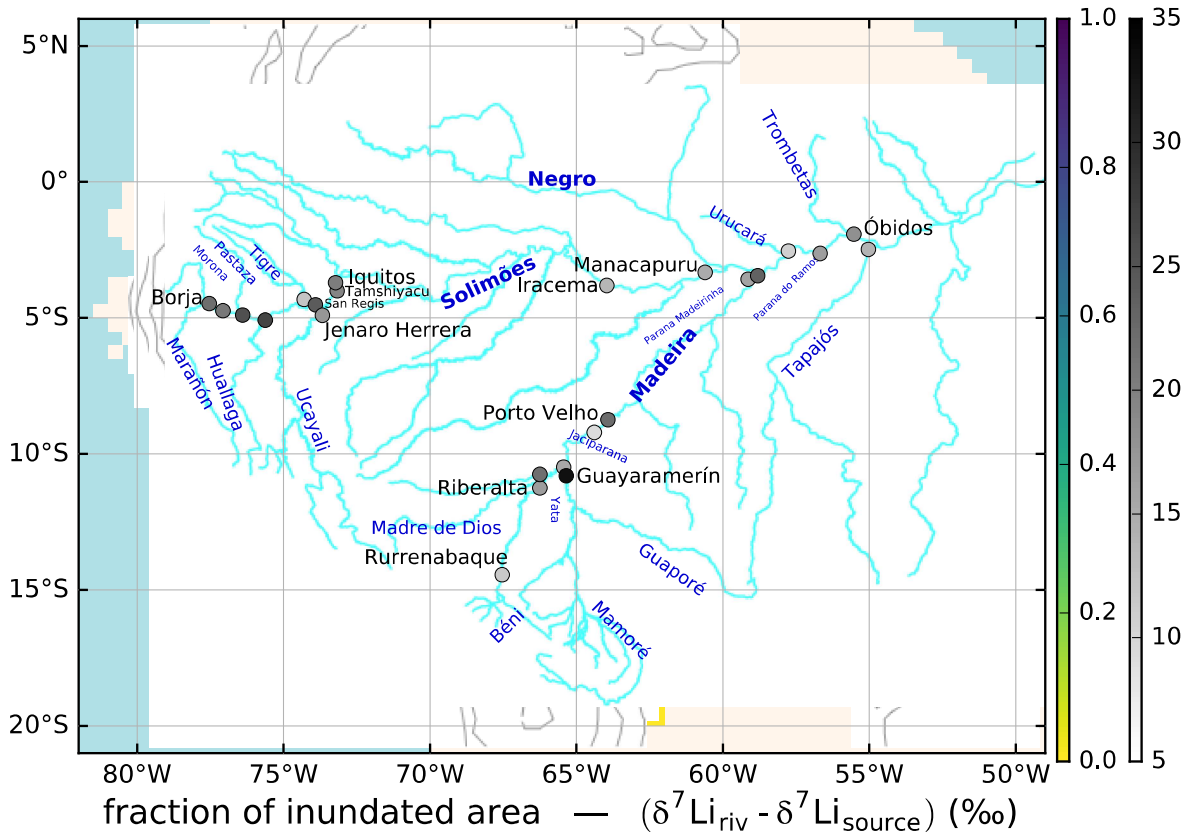
402 Water routing has been taken from the Global Runoff Data Center at its original resolution
403 $0.5^\circ \times 0.5^\circ$.

404

405 The erosion field is taken from Ludwig and Probst (1998), still at its original resolution
406 $0.5^\circ \times 0.5^\circ$, and the climatic fields have been taken from the Climate Research Unit database
407 and interpolated on the $0.5^\circ \times 0.5^\circ$ grid. The erosion field is shown on Fig. 2a.

408

409 This “floodplain” model component formulation depends *a priori* on both the “channel width”
410 w , and the length of integration L . L depends on the size of each cell of the model grid and
411 on the river sinuosity inside the cell. w represents the characteristic distance between the
412 river bed and the characteristic flood distance. A careful study of Eq. 7 and 10 shows that the
413 integrated values actually only depends on the products Lw . In other words, an integration
414 path n times shorter gives exactly the same results if the width is n times wider. Then, it is
415 meaningless to seek for the exact value of L and w in each cell. The product Lw is actually
416 the area (in m^2) of the flooded continental surface that interacts with riverine water. It can be
417 described as the average inundated area A_{flood} . In practice, we arbitrarily set L to the square
418 root of the cell area: $L = \sqrt{A_{cell}}$, and then $w = A_{flood}/L$. The distribution of the inundated
419 areas is estimated from satellite remote sensing. We apply the method developed by
420 Martinez and Le Toan (2007) to two multi-temporal GRFM (Global Rain Forest Mapping)
421 mosaics (100m resolution) derived from the J-ERS satellite Synthetic-Aperture Radar (SAR).
422 One mosaic corresponds to the 1995-1996 dry season and the other corresponds to the wet
423 season of the same hydrological year. This hydrological year is representative of the median
424 climate condition of the Amazon basin (Abril et al., 2014). The map gathers the class
425 “occasionally flooded” and “permanently flooded” defined by Martinez and Le Toan (2007),
426 and account for both the open water bodies areas and flooded areas under vegetation. We
427 thus consider the maximum extension of the floodplains for a standard hydrological year.
428 Given the small number of hydraulic buildings and due to the low topographic gradients, this
429 map can be considered as reproducible from one year to the other. The distribution of
430 inundated areas are estimated from satellite remote sensing. We converted the high-
431 resolution ($\sim 100m$) contours of the inundated zones into a proportion of inundated area (in
432 m^2/m^2) on each cell of the model mesh: A_{flood}/A_{cell} (Fig. 5 and Appendix A).



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Figure 5: Map of the fraction of inundated area in each cell of the model grid (yellow to blue scale) and $\delta^7\text{Li}$ riverine minus the $\delta^7\text{Li}$ of the source rock (‰) from Dellinger et al. (2015; circles colored by the $\delta^7\text{Li}$ value, grayscale). The blue lines show the path of the main rivers; the white arrows show the water routing through the model grid; black contours are elevation isolines (500m, 1000m, 2000m, 4000m and 6000m). Names of the monitoring stations are written in black, river names in blue. When the station name is not specified, monitoring was done at the river outlet.

The last 4 parameters (τ_o , k_{sp} , a and K_m) do not have a value *a priori*, so we conducted an exploration.

One should notice that combining equations 2 (*hillslope* model) and 3 (regolith thickness) leads to:

$$450 \quad \frac{F_{sp}^{reg}(\text{Li})}{F_{diss}(\text{Li})} = \left(1 + \frac{\tau_o}{\phi h_o} \cdot q / \ln \left(k_{rp} \cdot q \cdot \exp \left(-\frac{E_{rp}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right) / E \right) \right)^{-1}$$

451 This means that, once k_{rp} and E_A^{rp} fixed, the only thing that matters for the lithium retention
452 ratio is the ratio $\tau_o/\phi h_o$. In other words, there is no way to know the individual influences of
453 h_o , ϕ and τ_o on the model. Then, we set the value of ϕ —regolith porosity— to 0.2 and only
454 focus on τ_o (wich is the water residence time for which the dissolved $\delta^7\text{Li}$ reaches half of its
455 maximum value, cf. Eq. 2).

456

457 Concerning the last “free” parameters, we conducted an exploration of the two-dimensional
458 parameter space for each case (k_{sp} and a , 1st case, Eq. 8; or k_{sp} and K_m , 2nd, Eq. 9).

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461 4. Results

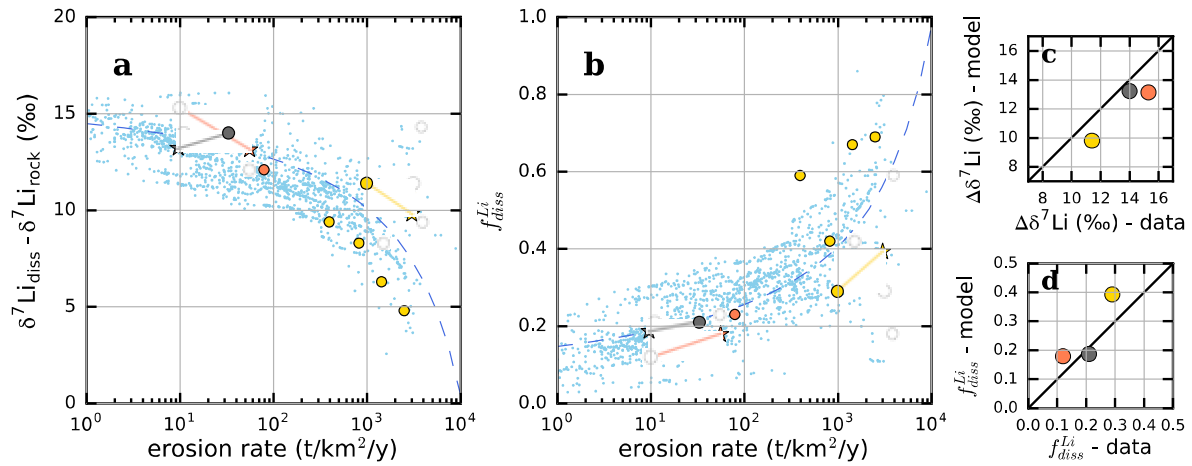
462

463 4.1. Hillslopes

464

465 We first test the efficiency of the *regolith* model component, in simulating the effect of batch
466 fractionation on the lithium isotopic composition of the rivers. Accordingly, the *regolith*
467 component has been run alone without using the *floodplain* component. We compare our
468 model results to a selection of data points documented by Dellinger et al. (2015) as the result
469 of batch fractionation only. As erosion decreases from the Andes to the Amazonian plain, the
470 regolithic cover becomes thicker (Eq. 3), the residence time of water becomes longer and
471 consequently river $\delta^7\text{Li}$ should increase as more lithium is retained in secondary phase
472 precipitation (Eq. 2 and 5). Such trends have been observed in the field by Dellinger et al.
473 (2015) for 8 points of their database. Being the sole free parameter of our batch fractionation
474 model, the half-retention residence time τ_o has been tuned so that two conditions are
475 verified: (1) the model $\delta_{riv}^7\text{Li} - \delta_{rock}^7\text{Li}$ versus the physical erosion matches the
476 corresponding scatterplot of the data from Dellinger et al. (2015, Fig. 3a in their contribution),
477 (2) the scatterplot of the simulated ratio $F_{sp}(\text{Li})/F_{diss}(\text{Li})$ versus physical erosion also
478 matches the data scatterplot of Dellinger et al. (2015, Fig. 3b in their contribution). This is
479 illustrated on Fig. 6 a and b. Here, only 3 of the 8 measurement sites can be precisely
480 located within the model hydrographic network (the 5 others come from rivers too small to be
481 accurately reproduced at the model resolution). We found that a τ_o value of 0.8 years leads
482 to an acceptable match between model output and field data. The direct implication of this
483 result is that our model formalism simulates correctly the batch fractionation process in the
484 field. It might not be the unique solution, but all other parameters have been fixed to
485 previously published values.

486



487
 488 **Figure 6:** Comparison between the Dellinger et al. (2015) lithium data with the model output
 489 (without considering the potential role of inundated areas). Only the *hillslope* model is
 490 activated. Only “batch” fractionation is simulated : (a) scatterplot of the ($\delta_{\text{riv}}^7\text{Li} - \delta_{\text{rock}}^7\text{Li}$) versus
 491 erosion rate for data (circles colored accordingly to Dellinger et al. (2015), see Fig. 1) and
 492 model output. (b) fraction of dissolved lithium leaving the weathering system, $f_{\text{diss}}^{\text{Li}}$ (Eq. 11)
 493 versus the erosion rate. The blue dots are the values calculated for each grid cell element.
 494 The stars display the model-calculated values for the three measurements stations that have
 495 been localized in the model hydrographic network. They are connected to the corresponding
 496 measured value by a solid line of the same color. The light colored circles correspond to
 497 rivers which are too small to be modeled using our typical resolution (see section 2 for more
 498 details) (c) and (d) scatterplots of data (x axis) versus model (y axis) for (c) the riverine $\delta^7\text{Li}$
 499 and (d) the fraction of dissolved lithium leaving the weathering system, $f_{\text{diss}}^{\text{Li}}$. Only the 3
 500 stations localized in the model hydrographic network can be used here.

4.2. Coupling “regolith” and “floodplain” model components

506
 507 Both lithium model components are now coupled. We use the value of the parameter τ_o
 508 calculated in the previous section. Contrary to the regolith model displaying only one free
 509 parameter (τ_o), the floodplain model has 2 free parameters (k_{sp} and a for case #1; k_{sp} and
 510 K_m for case #2), requiring a parameter optimization procedure.

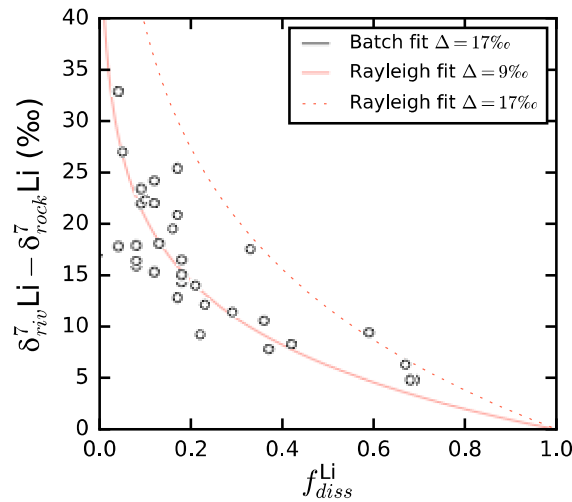
511
 512 We first test the case where Eq. 8 is used to compute $F_{sp}(\text{Li})$ and the parameter optimization
 513 is performed by considering the entire river database. It is referred as case #1. The full model

514 is able to reproduce the two distinct trends observed by Dellinger et al. (2015) when plotting
 515 $\delta_{riv}^7\text{Li}$ versus f_{diss}^{Li} (the ratio of the river flux of lithium at a given measurement site versus the
 516 upstream integrated fluxes of Li released by rock weathering):

$$517 \quad f_{diss}^{\text{Li}}(x) = \int_{\text{upstr. } x} (F_{diss} - F_{sp}) / \int_{\text{upstr. } x} F_{diss} = F_{riv}(x) / \int_{\text{upstr. } x} F_{diss} \quad (11)$$

518 This is illustrated in Fig. 7 for parameterization case #1. The same result is also observed for
 519 the other parameterization (Eq. 9) (not shown). The grid cell where the “*regolith*” component
 520 of the numerical model is dominant plots along the batch fractionation line (black line in Fig.
 521 7), with a fractionation factor Δ_{land} close to Dellinger et al. (2015)’s fit (17‰). The fact that
 522 data plot on a $\Delta=9\text{‰}$ Rayleigh distillation trend is more surprising. The *floodplain* model
 523 component never simulates pure Rayleigh distillation except in areas where weathering rate
 524 is close to zero (corresponding to a $F_{diss}(\text{Li})$ equal to zero).

525



526

527 **Figure 7:** scatterplot of the riverine $\delta^7\text{Li}$ riverine minus the $\delta^7\text{Li}$ of the source rocks (y axis) as
 528 a function of the lithium riverine remaining fraction (f_{diss}^{Li} , Eq. 11, x axis). The Batch

529 fractionation and Rayleigh distillation trends are represented by the black and red lines
 530 respectively. Colored circles are the Dellinger et al. (2015) data. Blue dots are model points.

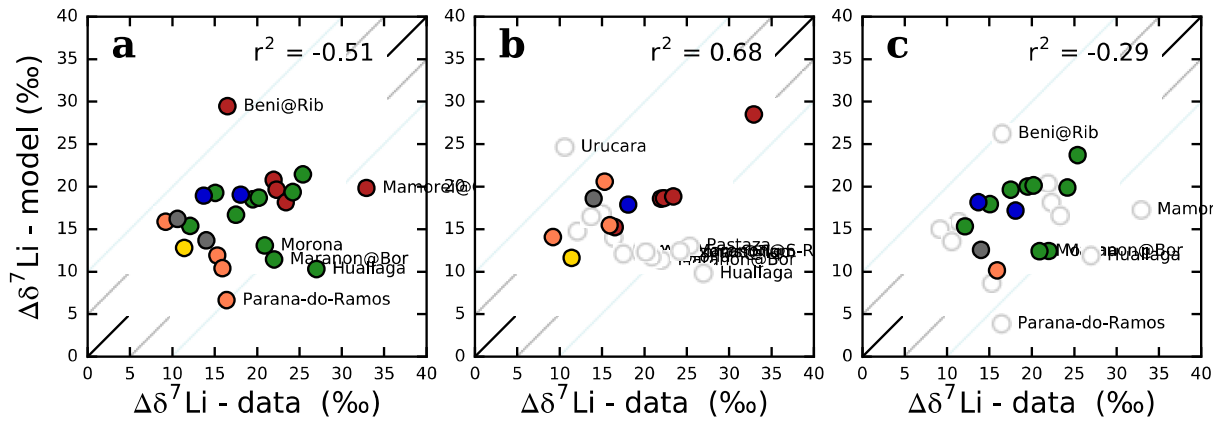
531 Only the case #1 is considered here: Eq. 8 for $F_{sp}(\text{Li})$ with parameters optimised over the
 532 whole dataset (see section 4.6).

533

534

535 The highest $\delta_{riv}^7\text{Li}$ are calculated for rivers flowing through inundated areas (see for instance
 536 Fig. 9, best-fit parameters of case #1). This result does not depend on the chosen
 537 parameterization for $F_{sp}(\text{Li})$. The calculated isotopic composition of the dissolved Li in the
 538 Madeira river increases progressively during its journey through a large floodplain (Fig. 5).
 539 The highest $\delta_{riv}^7\text{Li}$ are found downstream of the inundated area between 12°S and 15°S, and

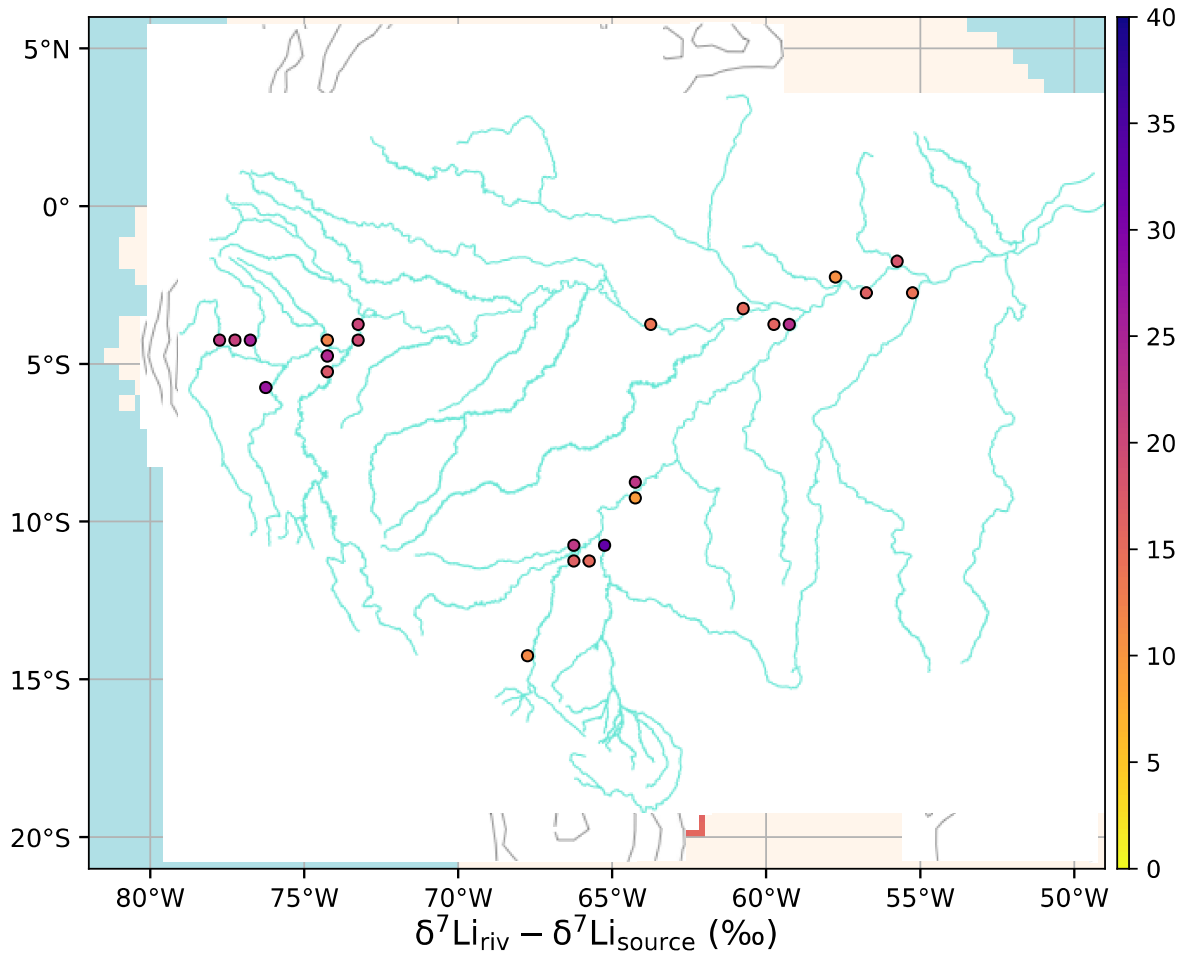
540 the lower $\delta_{riv}^7\text{Li}$ are found when the Béni river leaves the Andes. In the northern region of the
 541 Amazon watershed, the Solimões river seems to display an opposite trend: the highest
 542 measured $\delta_{riv}^7\text{Li}$ are found at the entrance of the inundated area (25‰ and more), very close
 543 to the Andes (Huallaga, Pastaza, Morona, Marñón at Borja), and $\delta_{riv}^7\text{Li}$ is lower downstream
 544 (Tamshiyacu, Iquitos) or for longer river path (Ucayali). Conversely, the model predicts
 545 values of 15‰, with a maximum of 20‰ at the feet of the Andes, before entering the
 546 floodplain.
 547



548
 549 **Figure 8:** Data-model scatterplots when the model is run with the best-fit parameters for 3
 550 cases: (a) Eq. 8 for $F_{sp}(\text{Li})$ and optimization using all stations (case #1); (b): Eq. 9 for $F_{sp}(\text{Li})$
 551 and optimization on the Madeira only (case #2-M); (c) Eq. 8 for $F_{sp}(\text{Li})$ and optimization on
 552 the Solimões only (case #1-S). On (b) and (c), the stations not used for the parameter
 553 optimization are drawn in transparency. The names of the stations where the misfits are
 554 greater than 7‰ (for δ_{riv}^7 riv) are specified. Colour code follows Dellinger et al. (2015; see
 555 Fig. 1). Madeira tributaries are in yellow, red and orange (except Parana do Ramos),
 556 Solimões tributaries are displayed in green. On each panel, the bold line is the 1:1 line, the
 557 lighter lines denote the $\pm 5\%$ and $\pm 10\%$ mismatch. The coefficient of determination (r^2 , see
 558 also Appendix D) is specified on each panel.
 559
 560
 561

562 The optimization of the model parameters has been conducted using all the river samples
 563 available in Dellinger et al. (2015). Doing so, the model fails to explain the whole dataset at
 564 the scale of the Amazon basin. None of the tested combinations of parameters leads to a
 565 positive coefficient of determination (r^2), meaning that the mismatch between data and
 566 model is always greater than the variability of the data (Appendix D). The “best-fit” case
 567 shown in Fig. 8a ($r^2 = -0.51$) is actually a compromise between the two incompatible river’s

568 behaviours. In this configuration, the $\delta_{riv}^7\text{Li}$ of three Solimões tributaries are largely
569 underestimated (by 15‰, 10‰ and 8‰ respectively): the Huallaga, the Marañón at Borja,
570 and the Morona. This is because the “distillation rate” —given by the k_{sp} — is too low with
571 respect to their small path through the inundated area. In parallel, the Béni at Riberalta $\delta^7\text{Li}$
572 value is overestimated by ~15‰ for the exactly opposite reason (rate of distillation too high
573 with respect to its long path). The Mamoré at Guayaramerín is underestimated by ~10‰
574 despite its very long path though inundated areas. This paradoxical behaviour is in fact due
575 to a distillation so efficient that the lithium concentration of the Mamoré becomes lower than
576 the Guaporé’s one at their confluence, although the Guaporé is providing a Li weathering flux
577 several orders of magnitude lower than the Mamoré, and is actually negligible in term of
578 chemical flux (see Fig. 2). The calculated isotopic signature of the Guaporé —much lower
579 than the Mamoré’s one— becomes dominant at the confluence of both rivers. The last outlier
580 is the Parana do Ramos that is abnormally low with respect to all the rivers flowing in the
581 plain. This is a consequence of a weathering increase shortly before the confluence with the
582 Amazon mainstream (see Fig. 2b). The *floodplain* model responds to this increase of
583 weathering with a drop in $\delta^7\text{Li}$. This can be seen on the map of modelled $\delta^7\text{Li}$ with the “best-
584 fit” parameters (Fig. 9).
585



586

587 **Figure 9:** Map of $\delta^7\text{Li}$ riverine minus the $\delta^7\text{Li}$ of the source rock (‰) when the model is run
 588 with the best-fit parameters of case #1 (Eq. 8 for $F_{sp}(\text{Li})$ and optimization on all stations).

589 Circles shows the Dellinger et al. (2015) monitoring stations and are colored by the
 590 measured $\delta^7\text{Li}$ riverine minus the $\delta^7\text{Li}$ of the source rock. The blue lines show the path of the
 591 main rivers, the white arrows show water routing in the model grid, black contours are
 592 elevation isolines (500m, 1000m, 2000m, 4000m and 6000m).

593

594

595

596 If we use Eq. 9 for computing $F_{sp}(\text{Li})$ (case #2), the results are not significantly improved
 597 (see Appendix D, best r^2 is -0.47). The best fit is found for higher K_m value (around 20). For
 598 such high values, Eq. 9 becomes equivalent to Eq. 8 in the linear case ($a = 1$).

599

600

601 4.3. Local optimizations:

602

603 The model output shows that lithium data from the Madeira and the Solimões cannot be
604 explained by a single mechanism, or at least, both systems cannot be described by a single
605 parameter combination. The “global” optimization performed in the previous section
606 represents a compromise where none of the river trend is correctly simulated (Fig. 8a).
607 Because of this apparent incompatibility, we performed a separate parameter optimization for
608 each basin. We optimized the parameters by minimizing the mismatch between the model
609 and the data, considering the points of the Madeira only (case -M), or those of the Solimões
610 only (case -S). We added—in both cases—the point downstream the confluence (Óbidos,
611 Tapajós and Parana Madeirinha). We removed—in both optimizations—two data points: the
612 Urucará and the Parana do Ramos. The Urucará is a shield river with a $\delta^7\text{Li}$ overestimated
613 by the model. Dellinger et al. have shown that shield rivers are impacted by clay dissolution
614 under the corrosive action of organic acids, leading to low $\delta^7\text{Li}$. This is the case for the Negro
615 and Trombetas rivers, and we assume that it is also the case for the Urucará rivers, given its
616 location between the Negro and Trombetas. This clay dissolution process is not simulated
617 here, and we removed the Urucará from the optimization procedure. We removed the Parana
618 do Ramos because of the plausible artefact already mentioned (increase of weathering rate
619 before its mouth). Finally, for the optimization on the Solimões, we removed the data point of
620 the Huallaga. Indeed, this river displays a very high $\delta^7\text{Li}$ (27‰) despite the quasi-absence of
621 inundated area along its path. It has been shown that this river is affected by the dissolution
622 of evaporites (Dellinger et al., 2015; Moquet et al., 2011), with potentially high $\delta^7\text{Li}$ (Huh et
623 al., 1998).

624
625 For the optimization on the Madeira, the results are improved when using Eq. 9 for $F_{sp}(\text{Li})$
626 (case #2-M). The best fit is reached for low K_m , around 6–7 ($r^2 = 0.68$). This corresponds to
627 a regime where $F_{sp}(\text{Li})$ is limited by $F_{diss}(\text{Li})$ (see Appendix D). As shown in Fig. 8b, the Béni
628 is no longer overestimated nor the Mamoré underestimated. The Parana do Ramos is well
629 predicted too though the optimization did not try to reduce its misfit. However, as expected,
630 most of the points from the Solimões are now underestimated.

631
632 When the optimization is performed on the Solimões tributaries, none of the two equations
633 for $F_{sp}(\text{Li})$ (Eq. 8 or 9) yields reasonable results: r^2 remains negative in both cases. Eq. 8
634 (case #1-S) gives the “best” result (-0.29, shown in Fig. 8c). As in case #1, r^2 reaches a
635 plateau for high values of α (greater than 2, see Appendix D), making this optimization less
636 reliable. The Morona and Marañón at Borja are still underestimated. The Huallaga too but
637 that was expected because the parameter optimization does not try to reduce its mismatch
638 and this river is likely impacted by evaporite dissolution. Yet, for the first two, the

639 contributions from the dissolution of evaporites cannot be invoked as no significant dissolved
640 flux from evaporites has been reported (Moquet et al., 2011). The behaviour of those three
641 tributaries cannot be explained by the model coevally with the other points of the Solimões.
642 Moreover, the data-model scatterplot of the current optimization (case #1-S, Fig. 8c) is very
643 close to the one obtained with the whole dataset (case #1, Fig. 8a), and displays the same
644 outliers: Béni at Riberalta, Mamoré at Guayaramerín and Parana do Ramos—in addition to
645 the three Solimões tributaries.

646

647 While using Eq. 9 for $F_{sp}(\text{Li})$ (case #2-S), r^2 is constantly increasing with K_m for the tested
648 range (1–100, see Appendix D), as if the limitation by F_{diss} was inappropriate for this dataset.
649 Indeed, Eq. 9 is equivalent Eq. 8 with $a = 1$ when K_m approaches infinity.

650

651 In an attempt to refine our modelling, we have constrained independently the range of
652 parameters needed to explain the high $\delta^7\text{Li}$ values exhibited by the three Solimões
653 tributaries. Then we test them for the whole dataset. For this, we first minimized the
654 mismatch of these three points only (Appendix D), using Eq. 8 for $F_{sp}(\text{Li})$. The results show
655 that these three datapoints can be fitted by our modelling with a very low a (~ 0.3) and a very
656 high k_{sp} . The k_{sp} value obtained here cannot be compared directly with other optimizations
657 because it is directly correlated to a . Indeed, as $[\text{Li}]_{riv}$ is lower than 1, increasing the
658 exponent a requires to increase k_{sp} in order to keep the same order of magnitude for the
659 product $k_{sp}[\text{Li}]_{riv}^a$. For this reason, the plausible parameters plot along a straight line in
660 $\{a, \log k_{sp}\}$ space, with a roughly similar slope in all optimizations (see Appendix D). One way
661 to compare the k_{sp} of the different optimizations is to compare the intercept: for the minimum
662 tested a (0.2), the values of k_{sp} we get are $\sim 3 \cdot 10^{-2}$ for cases #1 and #1-M, $\sim 5 \cdot 10^{-2}$ for
663 case #1-S and $\sim 1 \cdot 10^1$ in the current optimization (Appendix D). By doing the same
664 comparison at $a = 1$, we get a factor of 50. In conclusion, we see that explaining the values
665 of the Marañón at Borja, the Huallaga and the Morona requires a kinetic of Li incorporation
666 on secondary phases about 100 times faster compared to the three other optimizations. In
667 that case, almost all the other rivers display an unrealistic $\delta^7\text{Li}$, generally overestimated
668 (Appendix D).

669

670

671 5. Discussion

672

673

674 The spatial fluctuations of river $\delta^7\text{Li}$ values along the course of the Madeira and its tributaries
675 (Béni, Madre de Dios, Mamoré...) can be simulated by a batch fractionation in the regolith
676 coupled to a Rayleigh distillation occurring in the plain flooded areas (case #2-M, Fig. 8b).
677 Importantly, the model results show that the fit is better in the case #2 (Eq. 9 for F_{sp}) than in
678 the case #1 (Eq. 8 for F_{sp}). Things are more complicated regarding the Solimões and its
679 tributaries. High dissolved $\delta^7\text{Li}$ are rapidly reached at the feet of the Andes, well before the
680 river reaches extensive flooded areas, a feature that our model cannot reproduce. The three
681 highest riverine $\delta^7\text{Li}$ values have been measured in the Huallaga at mouth, in the Marañón at
682 Borja and in the Morona at mouth. Among the Solimões monitoring stations, these three
683 stations are the closest to the Andean range, the Huallaga having the highest measured $\delta^7\text{Li}$.
684 If these high values are caused by “Rayleigh” distillation in the floodplain, reaching high $\delta^7\text{Li}$
685 so upstream requires a kinetics of the interactions between water and the mineral phases
686 (k_{sp}) 100 times more efficient compared to the other locations in the Amazon watershed.
687 Furthermore, optimization of the model parameters using the Solimoes data shows that the
688 best fit is obtained when Eq. 8 is used to describe the interaction between water and
689 secondary phases in floodplains.

690

691 A contrasting behaviour between the Northern and the Southern parts of the Amazon
692 watershed is thus identified. The isotopic signature of the Solimoes pole is best explained
693 when the removal of lithium in floodplains (1) is a function of the amount of lithium carried by
694 the upstream rivers (Eq. 8), (2) is not limited by the local dissolution of primary minerals, and
695 (3) is operating at a fast rate (k_{sp}). Conversely, the isotopic signature of the Madeira is best
696 explained when the floodplain interactions (1) are not only limited by the dissolved lithium
697 carried by rivers, (2) but also by the release of lithium by the dissolution of fresh minerals
698 incorporated in floodplain sediments, and (3) operate at a slower rate.

699

700 The suspended solids carried by the Solimoes and the Madeira derives from rocks of
701 different original chemical composition (Viers et al., 2008). The lithology drained by the
702 headwaters differs between the Solimoes and Madeira watersheds. The Andean headwaters
703 of the Madeira drain shales, that are recycled sediments, depleted in cations but enriched in
704 lithium and most of all, weakly weatherable. In contrast, in the Solimões river basin
705 weathering budget is significantly influenced by igneous rocks (Dellinger et al. 2015),
706 including a large contribution from volcanic rocks weathering. Weathering rate is doubtlessly
707 not the same for these two basins (Moquet et al., 2011). We can speculate that because of
708 lithological contrasts, the weathering of sediments eroded in the range occurs in the first

709 tenths of kilometres of the alluvial plain in the Solimões basin, whereas it occurs over larger
710 distance in the Madeira basin (Bouchez et al., 2011).

711

712 The sediment load of the Solimoes and tributaries contains coarse solids supplied by the
713 erosion of volcanic rocks exposed in the Andes, and includes the input of young basaltic
714 products owing to the volcanic activity in Ecuador. The presence of unweathered minerals in
715 the Solimoes suspended solids is probably the consequence of weathering conditions limited
716 by unfavourable climate in the magmatic area from which they derive (Bouchez et al., 2011).
717 Conversely, the suspended solids of the Madeira river and tributaries derive from Paleozoic
718 sediments that originate from a cratonic rocks, and that have been impacted by several
719 weathering cycles (Veizer and Janssen, 1979). The Chemical Index of Alteration ranges from
720 0.3 to 0.55 for the Madeira sediments, and is always below 0.3 for the Solimoes (Roddaz et
721 al., 2014).

722

723 In the case of the Solimoes river and tributaries, the absence of limitation on the supply of
724 lithium by local dissolution of minerals suggest that the sediments exported from the Andes
725 contains easily weatherable materials. The model output suggest that the lithium is released
726 and then removed at a fast rate owing to the fast dissolution rate of volcanic materials mixed
727 in the sediments (Dessert et al., 2003). Those sediments also contain large amounts of
728 smectite clay mineral, part of it being mechanically transported from uplands (Guyot et al.,
729 2007; Dellinger et al., 2014). But smectite abundance in sediments is also rapidly rising with
730 the distance from the mountain range, suggesting precipitation of smectite minerals (Guyot et
731 al., 2007). The lithium might thus be supplied by upstream rivers, without being limited by
732 local dissolution of primary minerals, and the abundance of clay minerals may result in both
733 batch and “Rayleigh” distillation close to the Andes, before the water flows through large
734 floodplains. In the Madeira, the sediments eroded upstream and accumulating in the Madeira
735 floodplains are much more depleted in cations owing to their lithological origin. As a result,
736 the lithium isotopic composition starts to rise during secondary mineral-water interactions
737 only within extensive floodplains. The dimension of the flooded systems, and the residence
738 time of water inside these flood plains, may compensate for the limitation in lithium supply by
739 primary mineral dissolution inside the flood plain, allowing secondary phases to precipitate
740 and the riverine $\delta^7\text{Li}$ to rise above the maximum value allowed by “batch” fractionation.

741

742

743 **6. Limitations**

744

745 Our results are highly dependent on the reliability of the calculated weathering field, where it
746 is considered that leaching or dissolution (in undersaturated conditions) is congruent
747 ($F_{diss}(Li)$ is set proportional to weathering rate). This seems reasonable based on recent
748 experimental investigations (e.g. Pistiner and Henderson, 2003; Verney-Carron et al., 2011;
749 Wimpenny et al., 2010a; Ryu et al., 2014). Moreover, we assumed a uniform weathering rate
750 inside each cell, even if the cell is partly flooded. However, the weathering rate could be
751 higher or lower in the flooded part of the grid cell, compared to the weathering contribution of
752 the non-flooded part of the grid cell. The release of lithium by weathering may depend on the
753 nature of deposited sediments, being more or less weatherable. Therefore, the dissolution
754 rates within the flooded area of the model remains poorly constrained. If the weathering rates
755 in flooded area differ significantly from the weathering rate outside the flooded area, nothing
756 can be said about the relative efficiency of Eq. 9 versus Eq. 8.

757
758 The processes at play within the floodplains are not fully identified. Here we propose a
759 simple formalism to describe those processes (Eq. 8 and 9), and we postulate, in agreement
760 with Dellinger et al. (2015) that the enrichment of riverine waters occur in the flood plains.
761 Yet the enrichment in 7Li of the water depends probably also on the nature of the sediments
762 being stored (as we discussed above), on their reactivity, and on the size and geometry of
763 the aquifer. Here we only account for the lateral extension of the flooded area to modulate
764 the residence time of water.

765
766 The climate is not uniform over the Amazon watershed. The Solimões flows under a tropical
767 rainforest climate, with very low seasonality, whereas the Madeira, located southward, has a
768 tropical monsoon climate with more pronounced seasonal contrast. Although no clear
769 seasonal fluctuations in the riverine isotopic composition have been reported up to now,
770 seasonal precipitations may explain a lower lithium uptake rate, because flooding areas are
771 inundated only for a few months a year. Yet, alternate wet and dry period could also lead to
772 more intense distillation via strong evaporation in varseas disconnected from river paths
773 during the dry season. The influence of seasonality is far from being understood.

774
775 Another possibility is that Rayleigh distillation does not take place only in inundated areas,
776 but within the whole basin. Several studies have highlighted high δ^7Li values in mountainous
777 rivers (Burton and Vigier, 2012; Schmitt et al., 2012). Some of these high values cannot be
778 explained by batch fractionation as underlined in the introduction. Recent δ^7Li values
779 published for mountainous rivers are rather low. While these new data suggest that high δ^7Li
780 in mountains might be an exception rather than a common feature, high values must still be
781 explained. Colluviums are a possible site for lithium distillation in mountains: if river waters

782 flow through colluviums, a reactive transport concept would makes sense: lithium would
783 dissolve upstream, and be incorporated into colluviums, leading to a pseudo-distillation just
784 like in *floodplain* model, although shorter residence time of the waters are expected
785 compared to the floodplain environments. The existence of such a “distillation” process along
786 the groundwater path has been postulated and simulated by Bohlin and Bickle (2019) for
787 kinetically-limited weathering environment. Still we need to further understand why colluvium
788 would play a more important role in the Solimões Li cycle and not in the Madeira one.

789

790

791 **7. Conclusions**

792

793 In the present study, we explore the processes controlling the elementary and isotopic cycle
794 of the lithium in a continental-scale watershed: the Amazonian basin. We build a numerical
795 model specifically designed to simulate the processes at play in vertical weathering profiles,
796 and coupled it to an horizontal reactive-transport model. The model is able to simulate the
797 impact of the formation of weathering profiles on the lithium isotopic composition of the
798 rivers, as well as the role of floodplains. The model takes advantage on the existence of
799 spatially distributed sites where the riverine lithium has been monitored, from the Andes to
800 the outlet in the Atlantic ocean.

801

802 We identify two different regimes in the Amazon basin. In the southern part of the basin
803 (Madeira basin), the evolution of the riverine lithium isotopic composition can be explained by
804 the production of lithium by weathering reactions inside the regolith, with a fractionation
805 occurring during the precipitation of secondary mineral phases. Then, interactions between
806 the water and the secondary mineral phases within floodplains generate a Rayleigh
807 distillation process explaining high isotopic values for dissolved riverine lithium. This scenario
808 was previously proposed by Dellinger et al. (2015) based on river sampling. In the Northern
809 part of the watershed (Solimões and tributaries), this scenario cannot account for the lithium
810 isotopic composition of the tributaries of the Amazon. Indeed, the Huallaga, Marañón at Borja
811 and Morona display high isotopic values well before they flow through the inundated area in
812 the flood plain. An in-depth study of the model parameters suggests that the nature of the
813 bedrock eroded in the North of the Andes (fresh volcanic materials) and transported
814 downstream may impact strongly the $\delta^7\text{Li}$ of the tributaries of the Solimoes. We suggest that
815 the efficient weathering of this material directly at the feet of the Andes, together with
816 reported precipitation of smectites, allows the riverine $\delta^7\text{Li}$ to rise upstream of the floodplains.
817 But, in its present state, the model failed at reproducing the measured upstream high isotopic
818 values without accelerating the kinetics of the reactions up to non-reasonable values. In

819 addition, we suggest that two other factors should be explored in more detailed in future
820 modelling: the amplitude of the climatic seasonal fluctuations (less pronounced in the
821 Northern part of the watershed), and the possibility for Rayleigh distillation processes in
822 uplands when water flows through colluvions or along the flow path of the groundwaters.

823

824 Our study shows that the lithium continental cycle is not fully understood yet, at least for the
825 biggest watershed on Earth. More data are obviously needed to constrain models. More
826 sampling of the riverine $\delta^7\text{Li}$, especially in the mountainous tributaries, would help at
827 identifying where the isotopic ratios increases. We also think that data relative to the lithology
828 must be gathered, including rock type, dissolution rates, lithium content and isotopic
829 signature. This has implications on the interpretation of the oceanic lithium isotopic
830 composition in terms of past weathering. The variability of the lithium isotopic signature at the
831 outlet of the same mountain range (the Andes) suggests that the role of mountains on this
832 tracer is not well-constrained yet, and consequently their impact on the global carbon cycle
833 and other major chemical species are still to be refined.

834

835 **8. Acknowledgments**

836

837 The authors thank Jérôme Gaillardet, Jacques Schott, Martin Roddaz, Jean-Loup Guyot,
838 Mathieu Dellinger for helpful discussions. Two anonymous reviewers greatly help at
839 improving this manuscript.

840

841

842 **9. Declaration of interest**

843

844 The authors declare they have no conflict of interest.

845

846

847 **10. Funding**

848

849 This research was supported by the ANR INTOCC.

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851

852

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1022
1023

1024 **Appendix A: stations and measurements of HYBAM database — correction method**

1025

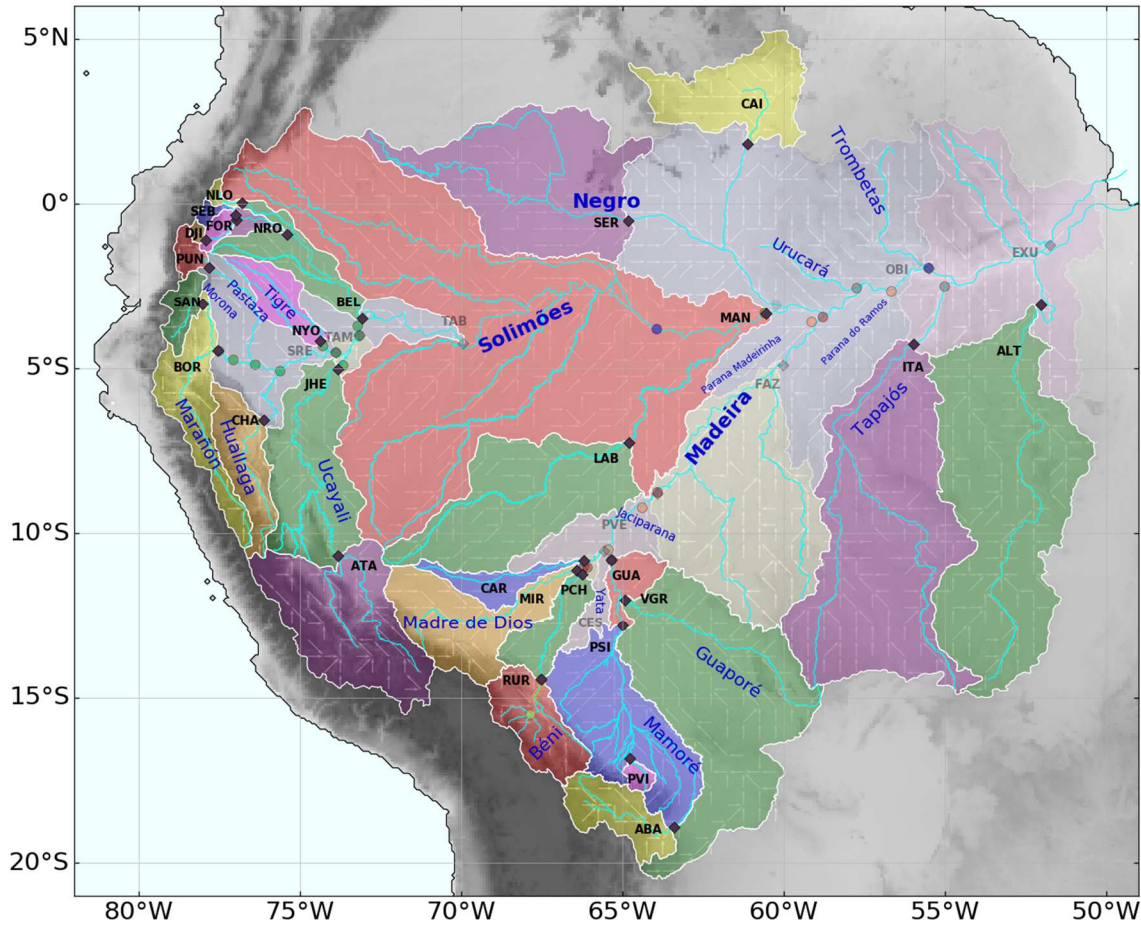
1026 The HYBAM (HYdrologie du Bassin AMazonien) observatory monitors daily discharge,
1027 monthly chemical compositions of rivers and the carried suspended load (with a ten-days
1028 frequency) over a network of hydrological stations distributed in the Amazonian basin from
1029 the Andes to the outlet. These time series are freely available from the HYBAM observatory
1030 website (<http://www.ore-hybam.org/>).

1031 We use the erosion flux (sediment transport) and dissolved cation flux released by silicate
1032 weathering reconstructed by Moquet et al. (2011) for the 26 Andean basins of the Amazon.

1033 The silicate weathering fluxes are corrected for atmospheric inputs. (Moquet et al., 2011).

1034 Ten additional stations have been added to the present study (Moquet et al., 2016), using the
1035 same correction procedure for the atmospheric input than Moquet et al. (2011). For each
1036 sampling station, we subtract the flux from the upstream stations in order to get fluxes from
1037 non-overlapping areas. The map of these non-overlapping watersheds and their
1038 corresponding stations is shown in Fig. A1. Eight watersheds have been removed from the
1039 present analyses because the subtraction procedure gave aberrant fluxes due to the
1040 proximity of the upstream and downstream stations considered to calculate the sub-basin
1041 flux (CES, EXU, FAZ, OBI, PVE, SRE, TAB, TAM). Their watersheds and names appears in
1042 transparency on Fig. A1.

1043



1044
 1045 **Figure A1:** Map of the Dellinger et al. (2015) stations (colored circles), the HYBAM stations
 1046 (black diamonds) and the corresponding watersheds (colored shades). Those put in
 1047 transparencies have been used in the correction procedure, because the fluxes difference
 1048 (upstream minus downstream) was lower than the fluxes uncertainties. The abbreviations of
 1049 HYBAM stations follow Moquet et al. (2016).

1050
 1051
 1052 These measured fluxes are used to correct both the erosion and weathering fields used by
 1053 the model. First, the watershed are converted into the regular $0.5^\circ \times 0.5^\circ$ model grid as follow:
 1054 for each station k , for each cell of the grid $\{i, j\}$ (ie: cell located at the j^{th} column and the i^{th}
 1055 row), we computed the area common to the watershed k and the grid cell $\{i, j\}$: $A_{i,j}^k$. The total
 1056 area of the cell is $A_{i,j}^{\text{tot}}$.

1057
 1058 The modeled erosion flux at the station k is then:

1059
 1060

$$F_k = \sum_{i,j} E_{i,j} A_{i,j}^k$$

1061

1062 where $E_{i,j}$ is the erosion rate field as used by the lithium model.

1063 F_k^{dat} is the erosion flux measured at the station k . The simplest way to correct the erosion

1064 $E_{i,j}$ would be to multiply each cell of the considered watershed by the ratio of the measured

1065 erosion flux at station k versus the model integrated erosion flux at the same station. The

1066 correction would thus be uniform over one given watershed:

1067

$$1068 \quad E_{i,j}^{corr} = E_{i,j} \cdot (F_k^{dat} / F_k)$$

1069

1070 The problem is that many cells intercept several watersheds. They would see their erosion

1071 rate corrected several times, and these corrections are incompatible. We overcame this

1072 issue by correcting *iteratively* the whole erosion field.

1073 Starting with:

1074

$$E_{i,j}^0 = E_{i,j}$$

1075 We iterated as follow:

1076

$$F_k^n = \sum_{i,j} E_{i,j}^n A_{i,j}^k$$

1077

$$E_{i,j}^{n+1} = E_{i,j}^n \prod_k (F_k^{dat} / F_k^n)^{A_{i,j}^k / A_{i,j}^{tot}}$$

1078 The exponent $A_{i,j}^k / A_{i,j}^{tot}$ ensures that cells not intercepting the watershed k will not be

1079 modified by F_k^{dat} , and also provides a smoother transition for cells at the boundary between

1080 several watersheds. Note that the order of the stations (k) used for the computation has no

1081 importance because the terms of the product are interchangeable.

1082

1083 This process converges toward a stable corrected field $E_{i,j}^\infty$ that verifies —for each k — the

1084 relation $F_k^\infty = \sum_{i,j} E_{i,j}^\infty A_{i,j}^k = F_k^{dat}$. In practice, 10 iterations are sufficient to get close to this

1085 equality.

1086

1087 The corrected erosion field is used to compute the silicate cations dissolution field (Eq. 1),

1088 which is then corrected by the HYBAM measurements of silicate cations using exactly the

1089 same method. Finally, the lithium dissolution is computed with this corrected cation

1090 dissolution rate assuming a constant lithium-cation ratio in source rock:

1091

$$1092 \quad F_{diss}(\text{Li}) = \frac{\chi_{\text{Li}}}{\chi_{\text{cat}}} F_{diss}^{corr}(\text{cat})$$

1093

1094 Note that the field of cation dissolution rate computed in Maffre et al., (2018) —with
1095 optimization only on HYBAM data— was already in agreement with data ($r^2 = 0.45$), most of
1096 rivers misfit the data by less than an factor 2.

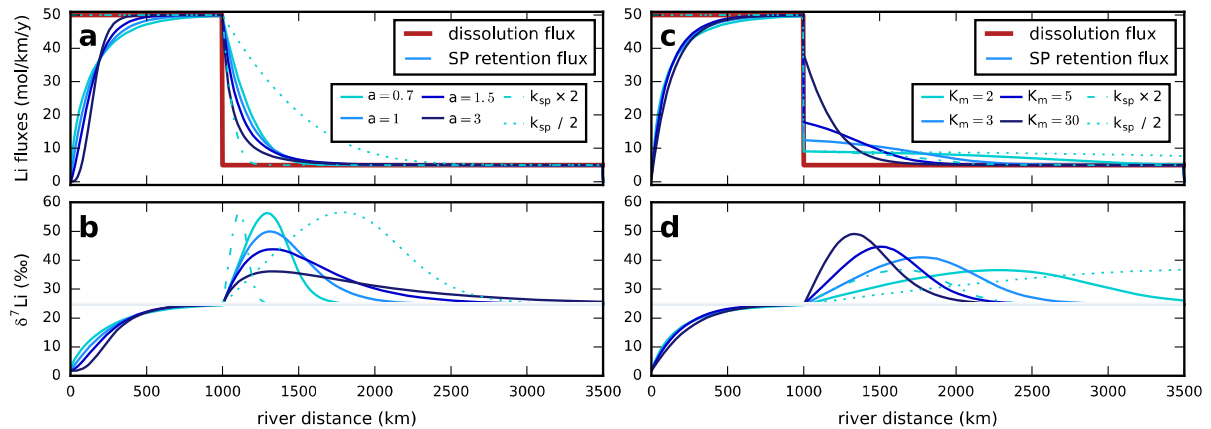
1097 **Appendix B: theoretical behaviour of the “floodplain” model**

1098

1099 Fig. B1 shows an idealized case where the floodplain model is run alone, on a 1D river
 1100 profile with constant water discharge and constant width w . The parameters and the lithium
 1101 dissolution flux (F_{diss} , forcing of the model) have been set arbitrarily to illustrate the model
 1102 behaviour. F_{diss} is set constant over the first 1000 km of the river flow. The model is
 1103 initialized (at $x = 0$) with no lithium in the water (except when k_{sp} is modified, it is initialized
 1104 with equilibrium conditions). Whatever the equation chosen for $F_{sp}(\text{Li})$, or the parameter
 1105 values, the model reaches the equilibrium: lithium concentration increase until F_{sp} balances
 1106 F_{diss} (Fig. B1 a and c), and concurrently, $\delta^7_{riv}\text{Li}$ increases from bedrock value ($\delta^7_{rock}\text{Li}$)
 1107 towards its equilibrium value: $\delta^7_{rock}\text{Li} + \Delta_{land}$ (Fig. B1 b and d).

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1110

1111 **Figure B1:** Examples of the 1D *floodplain* model response to a prescribed decreasing step
 1112 of the supply of dissolved Li by chemical weathering of the bedrock (red thick line in panels a
 1113 and b). This flux is reduced by 90% at 1000km, after the river reached its equilibrium state (in
 1114 all cases). The model is initialized with no lithium in river water, and the $\delta^7\text{Li}$ of source rock is
 1115 set at 0‰. Moreover, a constant flood width w (30km) and water discharge ($20 \text{ km}^3/\text{y}$) along
 1116 the river has been chosen for these examples. (a) and (b): lithium fluxes (mol/km/y):
 1117 dissolution ($F_{diss}(\text{Li})$, prescribed, red line) and retention in secondary phases ($F_{sp}(\text{Li})$, all blue
 1118 lines). (c) and (d): riverine $\delta^7\text{Li}$. (a) and (c) correspond to case #1 (Eq. 8 for $F_{sp}(\text{Li})$), (b) and
 1119 (d) to case #2 (Eq. 9 for $F_{sp}(\text{Li})$). In all panels, the different solid blue lines correspond to
 1120 different values for the second parameter (a for case #1, panels a and c; K_m for case #2,
 1121 panels b and d). The kinetics constant k_{sp} is modified with the second parameter in order to
 1122 keep the same response time. For the dashed and dotted curves, the kinetics constant k_{sp}
 1123 has been multiplied or divided by 2 with respect to the “reference” case (solid curve of the
 1124 same color) without changing the second parameter. For this cases only, the model is

1125 initiated with equilibrium values because response time has changed. When k_{sp} is divided by
1126 2, the equilibrium would not have been reached before the perturbation at 1000km.

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1131 At $x = 1000\text{km}$ (once the river is at steady state), we force F_{diss} to decrease by -90% , an
1132 arbitrary value chosen to generate a significant response of the model. This drop in F_{diss} is
1133 expected when the river leaves the mountain range (or the foreland) and reaches the
1134 floodplain —though rivers are not necessarily at steady-state at that moment. The imbalance
1135 between F_{sp} and F_{diss} leads to a net uptake of Li, until F_{sp} decreases and balance F_{diss} again.
1136 This uptake (F_{sp} greater than F_{diss}) triggers first a rise of $\delta_{riv}^7\text{Li}$ before it decreases towards its
1137 steady state value. This behaviour is independent of the equation used to simulate F_{sp} and of
1138 the chosen parameterization. The intensity of the peak directly depends on the intensity of
1139 the drop in F_{diss} , it also depends on the “second” parameter: a (“reaction order”, first case,
1140 Eq. 8, Fig. B1a–b) or K_m (saturating SP/diss ratio, second case, Eq. 9, Fig. B1c–d), but it is
1141 almost insensitive to the kinetics constant k_{sp} .

1142

1143 In the first case (case #1), low values for a generate a pronounced $\delta_{riv}^7\text{Li}$ peak, but rapidly
1144 relaxing to equilibrium. Conversely, high values for a generate low peak, with the maximum
1145 slightly delayed and relaxation to equilibrium much slower. a also controls the symmetry of
1146 the peak: it is symmetrical for $a = 1$, decreasing faster than increasing for $a < 1$ and
1147 decreasing slower than increasing for $a > 1$ (Fig. B1b). In the second case (case #2), the low
1148 K_m generates low, delayed and asymmetrical peak (decreasing faster than increasing). At
1149 high K_m , the model becomes equivalent to the first case with $a = 1$ (Fig. B1a).

1150

1151 In both cases, modifying the kinetics constant k_{sp} make the peak sharper or wider without
1152 changing its shape, or intensity. This behaviour is theoretically expected if we have $F_{sp} \gg$
1153 F_{diss} and in the second case $K_m F_{diss} \gg k_{sp}[\text{Li}]_{riv}$ —meaning F_{sp} is not saturated by F_{diss} .
1154 With these conditions, rescaling k_{sp} by a factor n is equivalent to rescaling x by a factor $1/n$.

1155

1156 **Appendix C: numerical resolution of lithium models.**

1157

1158 Cells of the model mesh are first ordered from upstream to downstream along the specified
1159 drainage network and then treated in that order, so that their incoming water fluxes and
1160 material are known. In the drainage network we used, each cell is connected to a unique
1161 downstream cell, and the following equations involve this assumption. Once the sorting
1162 complete, the four integration steps are computed cell by cell in the following order. (*H*
1163 denotes *hillslope* model and *F floodplain* model):

1164

1165 1. Running the *hillslope* model (Eq. 2 and 5) and computing $F_{riv}(\text{Li})_H$ and $\delta_{riv}^7\text{Li}_H$

1166

1167 2. Averaging the output of all upstream cells which are directly connected to the considered
1168 cell, to initialize the *floodplain* model:

1169

1170
$$F_{riv}(\text{Li})_F(0) = \sum_{upstream} F_{riv}(\text{Li})_{out}$$

1171

1172
$$\delta_{riv}^7\text{Li}_F(0) = \sum_{upstream} \delta_{riv}^7\text{Li}_{out} \cdot F_{riv}(\text{Li})_{out} / F_{riv}(\text{Li})_F(0)$$

1173

1174
$$Q_F = \sum_{upstream} Q_{out} + q \cdot A_{flood}$$

1175

1176 *out* stands for “leaving the cell”. $\delta_{riv}^7\text{Li}_F(0)$ and $F_{riv}(\text{Li})_F(0)$ are the initial value of the
1177 *floodplain* model $\delta_{riv}^7\text{Li}$ and $F_{riv}(\text{Li})$. *q* denotes here the runoff and *Q* is the water discharge.

1178 The discharge within the considered cell floodplain (Q_F) is the sum of the discharges coming
1179 from the upstream cells plus the runoff generated by rainfall on the inundated part of the
1180 considered cell: $q \cdot A_{flood}$.

1181

1182

1183 3. Integrating the *floodplain* variables $F_{riv}(\text{Li})_F$ and $\delta_{riv}^7\text{Li}_F$ (Eq. 7 and 10) from $x = 0$ to $x =$
1184 *L*.

1185

1186 We assumed that the integration length is equal to the square root of the cell area ($L =$
1187 $\sqrt{A_{cell}}$). As mentioned in the main text, the precise value of *L* does not matter, as long as $w \cdot$

1188 $L = A_{flood}$.

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Equation 7 ($F_{riv}(Li)_F$) is solved using the 4th-order Runge-Kutta method. Q_F , w and $F_{diss}(Li)_F$ being constant in a cell, the equation is then a non-linear differential equation with (locally) constant coefficients.

Equation 10 is solved analytically with the approximation that $F_{riv}(x)$ and $F_{sp}(x)$ are constant between 0 and L . Regarding F_{sp} we consider $F_{sp} = \frac{1}{w} \frac{dF_{riv}}{dx} - F_{diss}$ where $\frac{dF_{riv}}{dx}$ is computed with the Runge-Kutta 4th-order method. Regarding F_{riv} , if $F_{riv}(0)$ is null, we take the value $F_{riv}(L)$, otherwise the harmonic mean between $F_{riv}(0)$ and $F_{riv}(L)$ (because Eq. 10 is divided by F_{riv}):

$$\overline{F_{riv}} = \begin{cases} F_{riv}(L) & \text{if } F_{riv}(0) = 0 \\ 2/(1/F_{riv}(0) + 1/F_{riv}(L)) & \text{otherwise} \end{cases}$$

Equation 10 becomes:

$$\frac{d\delta_{riv}^7}{dx} = -\frac{wF_{diss}}{\overline{F_{riv}}} \delta_{riv}^7 + \frac{w(F_{diss}\delta_{rock}^7 + F_{sp}\Delta_{land})}{\overline{F_{riv}}} := a\delta_{riv}^7 + b$$

And the analytical solution is:

$$\delta_{riv}^7(L) = \begin{cases} (\delta_{riv}^7(0) - b/a)e^{-aL} + b/a & \text{if } a > 0 \\ \delta_{riv}^7(0) + bL & \text{if } a = 0 \end{cases}$$

4. Mixing *hillslope* and *floodplain* outputs to compute the values leaving the cell.

At this step we define the *out* values, ie: value “leaving” the current cell towards the downstream cell. They are the result of the mixing of *hillslope* and *floodplain* output within the current cell:

$$F_{riv}(Li)_{out} = F_{riv}(Li)_H + F_{riv}(Li)_F(L)$$

$$\delta_{riv}^7 Li_{out} = (\delta_{riv}^7 Li_H \cdot F_{riv}(Li)_H + \delta_{riv}^7 Li_F(0) \cdot F_{riv}(Li)_F(L)) / F_{riv}(Li)_{out}$$

$$Q_{out} = (A_{cell} - A_{flood})q + Q_F$$

1222 **Appendix D: Parameter exploration and the model optimizations.**

1223

1224 One of the key processes of the model is the calculation of the lithium flux being removed
1225 from the water by secondary phase precipitation $F_{sp}(\text{Li})$. In the absence of firm constraints,
1226 two mathematical expressions are tested (Eq. 8 and Eq. 9). Each equation has two
1227 parameters for which we tested a large range of values. For each tested combination of the
1228 two parameters, we ran the complete lithium model and assessed the modelled $\delta_{riv}^7\text{Li}$ with
1229 respect to the data by computing the coefficient of determination:

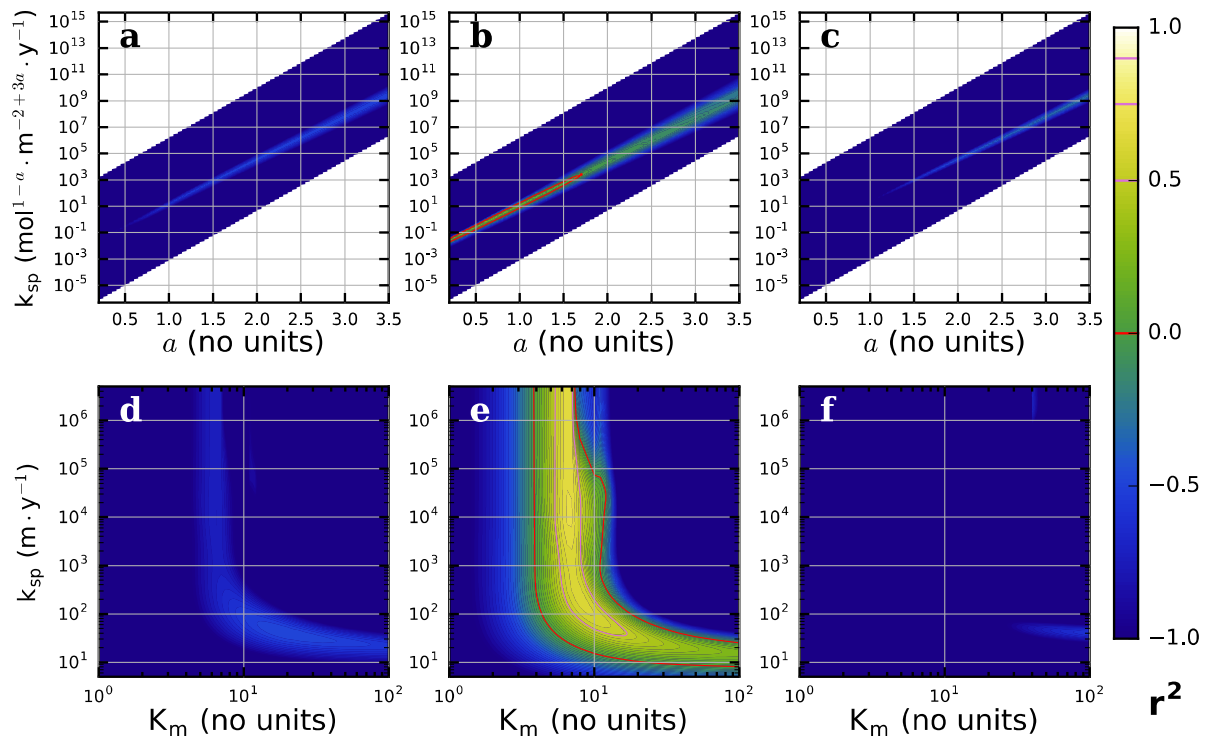
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$$r^2 = 1 - \frac{\sum[\Delta\delta_{model}^7 - \Delta\delta_{data}^7]^2}{\sum[\Delta\delta_{data}^7 - \overline{\Delta\delta_{data}^7}]^2}$$

1231 Where $\Delta\delta_{data}^7$ stands for “measured $\delta_{riv}^7\text{Li}$ minus estimated $\delta^7\text{Li}$ of source rock” and $\Delta\delta_{model}^7$
1232 for “modelled $\delta_{riv}^7\text{Li}$ at the corresponding location minus $\delta_{rock}^7\text{Li}$ ”. In the model, $\delta_{rock}^7\text{Li}$ is
1233 uniform and set to 1.7‰. $\overline{\Delta\delta_{data}^7}$ is the unweighted arithmetic average of $\Delta\delta_{data}^7$.

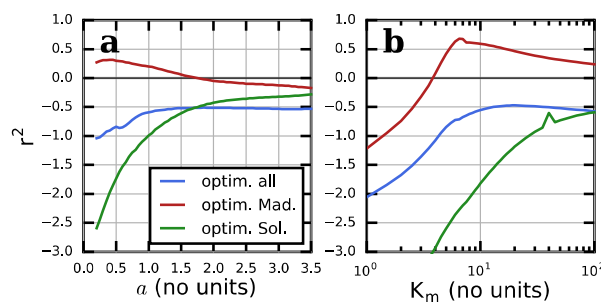
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1235 When using Eq. 8 to compute $F_{sp}(\text{Li})$, the value of k_{sp} depends strongly on the value of the
1236 exponent a . Indeed, as $[\text{Li}]_{riv}$ is lower than 1, k_{sp} should increase exponentially with a to
1237 maintain a “realistic” value of $k_{sp}[\text{Li}]_{riv}^a$. This appears clearly on Fig. D1a–c showing the r^2
1238 as a function of k_{sp} and a . For this reason, we did not explore the whole space of parameter:
1239 the white regions in Fig. D1a–c correspond to combinations of k_{sp} and a that have not been
1240 tested. Hence, the parameter optimization can be grasped looking at a only, as on Fig. D2a
1241 showing for a given a the maximum r^2 for all values of k_{sp} .

1242



1243
 1244 **Fig. D1:** Exploration of the parameters of Eq. 8 (a–c) (case #1) and Eq. 9 (d–f). (case #2).
 1245 Each panel shows the data-model coefficient of determination (r^2) as a function of the two
 1246 parameters: k_{sp} and a (a–c) and k_{sp} and K_m (d–f). We remind that a is equivalent to a
 1247 reaction order, K_m is the saturating SP/diss ratio and k_{sp} is the kinetics constant in both
 1248 equations. r^2 is computed using: (a and d) all stations (resp. case #1 and case #2); (b and e)
 1249 The Madeira stations (resp. case #1-M and case #2-M); (c and f) The Solimões stations
 1250 (resp. case #1-S and case #2-S).
 1251



1252
 1253 **Fig. D2:** Parameter exploration of Eq. 8 (a–c) or Eq. 9 (d–f). Each panel show the data-
 1254 model coefficient of determination (r^2) as a function of a (a) and K_m (b). For each given
 1255 value of (a or K_m) the k_{sp} leading to the best r^2 has been chosen, and this best r^2 is shown on
 1256 the y axis. Colour code indicates the stations that have been selected to compute the r^2 .
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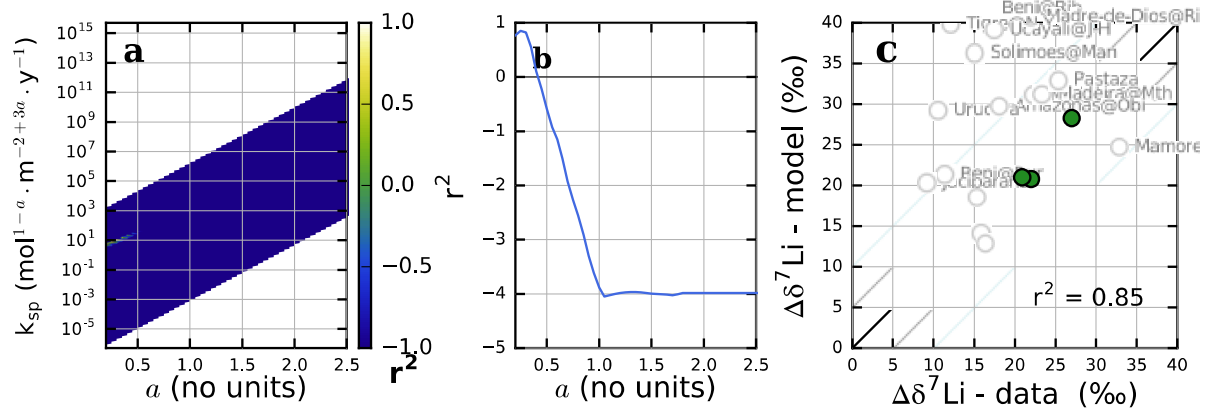
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When using the whole dataset (case #1, blue curve on Fig. D2a), the best r^2 is found for $a = 1.5$, and for higher a , it stays almost at the same value. When using only the Madeira stations (case #1-M, red curve on Fig. D2a), the best fit is for low a (0.4). When using only the Solimões stations (case #1-S, green curve on Fig. D2a), the result of the optimization is worse than with the whole dataset. r^2 reaches a plateau for a above 2.

Eq. 9 is slightly more complex to interpret. Fig. D1d–f shows the r^2 as a function of k_{sp} and K_m . The model displays two regimes depending on the value of K_m . For low K_m , F_{sp} is strongly limited by F_{diss} , and weakly by $[Li]_{riv}$. This means that δ_{riv}^7Li —and consequently r^2 — are almost independent on the value of k_{sp} . Conversely, for high K_m , F_{sp} becomes limited by $[Li]_{riv}$ and not by F_{diss} , which means that the r^2 depends on k_{sp} but very weakly on K_m . In this regime, Eq. 9 becomes equivalent to Eq. 8 with $a = 1$. Fig. D2b shows for a given K_m the maximum r^2 of all values of k_{sp} .

When using the whole dataset (case #2, Fig. D1d and blue curve on Fig. D2b), there is a plateau for intermediate values of K_m (between 10 and 50) where the maximum r^2 is found. This corresponds roughly to the transition between the two regimes. When using only the Madeira stations (case #2-M, Fig. D1e and red curve on Fig. D2b), the best regression is clearly for low K_m (between 5 and 6), in the first regime. When using only the Solimões stations (case #2-S, Fig. D1f and green curve on Fig. D2b), r^2 increases continuously within the tested range of K_m , so it is not possible to strictly define a best regression.

A last optimization has been conducted where we minimize the misfits of only the three “main” outliers of the Solimões system: the Huallaga, the Marañón at Borja and the Morona. Optimizing 2 parameters with 3 data points does not really make sense, this should rather be seen as a test of the model limits: is there a range of parameter able to produce the high δ^7Li observed in these 3 rivers despite their very short path in inundated area? Only the case with Eq. 8 is discussed here. There is actually a narrow range of a (between 0.2 and 0.4) for which the r^2 computed with this 3 points is positive (Fig. D3b). Such low a leads to high and narrow “peaks of δ^7Li ” along river paths (see Fig. B1). In addition, it also requires a kinetics constant k_{sp} around 50 to 100 times higher than for the other optimizations (Fig. D3a). Besides, Eq. 9—that cannot generate such high and narrow peaks— never produces positive r^2 for those 3 points (not shown). Finally, the parameters best explaining these 3 rivers generate unrealistic values for almost all the other rivers (Fig. D3c).



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Fig. D3: Parameter exploration of Eq. 8 and optimization (according to r^2) on only three Solimões tributaries: Huallaga, Marañón at Borja and Morona. (a) same as Fig. D1. (b) same as Fig. D2 (c) same as Fig. 8.