1	Experimental constraints on Li isotope fractionation during the interaction
2	between kaolinite and seawater
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16	Corresponding author email: xuzhang@email.com
17	Abstract
18	In this study, to better understand the factors controlling the concentration and isotope
19	composition of lithium (Li) in the ocean, we investigated the behaviour of Li during interaction
20	of kaolinite with artificial seawater. Dissolution of kaolinite in Li-free seawater at acidic
21	conditions (exp. 1) results in a strong preferential release of light Li isotopes, with $\Delta^7 \text{Li}_{aq-kaol} \sim$
22	-19 ‰, likely reflecting both the preferential breaking of ⁶ Li-O bonds over ⁷ Li-O bonds and
23	the release of Li from the isotopically lighter AlO ₆ octahedral sites. Sorption experiments on
24	kaolinite (exp. 2) revealed a partition coefficient between kaolinite and fluid of up to 28, and

25 an isotopic fractionation of -24 ‰. Thermodynamic calculation indicates authigenic smectites 26 formed from the dissolution of kaolinite in seawater at pH 8.4 (exp. 3). The formation of 27 authigenic phase strongly removed Li from the solution (with a partition coefficient between 28 the solid and the fluid equal to 89) and led to an increase of ca. 25% in seawater δ^7 Li. This fractionation can be described by a Rayleigh fractionation model at the early stage of the 29 30 experiment during rapid clay precipitation, followed, at longer reaction time, by equilibrium 31 isotope fractionation during the much slower removal of aqueous Li via co-precipitation and 32 adsorption. Both processes are consistent with a fractionation factor between the solid and the 33 aqueous solution of \sim -20‰. These experiments have implications for interpreting the Li 34 isotopic composition of both continental and marine waters. For instance, the preferential 35 release of ⁶Li observed during kaolinite far-from-equilibrium dissolution could explain the 36 transient enrichments in ⁶Li observed in soil profiles. With regard to the evolution of seawater 37 δ^7 Li over geological time scales, our experimental results suggest that detrital material discharged by rivers to the ocean and ensuing "reverse chemical weathering" have the potential 38 39 to strongly impact the isotopic signature of the ocean through the neoformation of clay minerals. 40

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1. Introduction

42 The formation of authigenic clay minerals during early sedimentary diagenesis was proposed in the sixties as an important control on the concentration of major cations in the 43 44 oceans (Mackenzie and Garrels, 1966; Sillen, 1967). According to this hypothesis, dissolved 45 Na, K, and Mg are removed from seawater by interaction with suspended clays derived from continental weathering and erosion, leading to the consumption of alkalinity and to the release 46 47 of acidity (CO₂). Being the opposite of a weathering reaction on the continents, this process 48 was termed as "reverse weathering". More recently, reverse weathering has been suggested to 49 be a key control on marine pH and climate over Earth history (Isson and Planavsky, 2018).

50 More than half a century after the term "reverse weathering" was first coined, however, we are 51 still lacking key quantitative constraints on this potentially major oceanic sink. This is in part 52 due to the challenges inherent in addressing this question experimentally, which include the 53 slow kinetics of the processes involved and the similarity in mineralogy and chemistry between 54 authigenic clays and allochthonous detrital clays from continental weathering (Odin and Fröhlich, 1988). That said, authigenic clay formation has been empirically observed in 55 56 nearshore settings around tropical deltas (e.g. Rude and Aller, 1994), and Michalopoulos and 57 Aller (1995) showed the plausibility of replicating such processes in laboratory experiments. 58 More recently, field isotope studies have rejuvenated interest in reverse weathering processes 59 (Rahman et al., 2016, 2017; Dunlea et al., 2017; Ramos et al., 2018; Bernhardt et al., 2020) 60 suggesting the significance of authigenic clay formation and reverse weathering for oceanic 61 elemental budgets.

Over the last decade, interest in using lithium (Li) and its isotopes (⁷Li and ⁶Li) as a 62 tracer of weathering processes has risen. Because of the long residence time of Li in the ocean, 63 64 seawater Li isotopes (as recorded by foraminifera) archive global changes occurring at the 65 Earth surface, such as continental weathering (Hathorne and James, 2006; Misra and Froelich, 2012). Reverse weathering, also, has been proposed as a strong control on the Li isotope 66 composition (expressed as δ^7 Li relative to standard reference material L-SVEC: δ^7 Li (‰) = 67 $\left(\frac{(^{7}\text{Li})^{6}\text{Li})_{\text{sample}}}{(^{7}\text{Li})^{6}\text{Li})_{\text{L-SVEC}}} - 1\right) \times 1000$) of the ocean (Misra and Froelich, 2012; Li and West, 2014). For 68 69 instance, the steady-state mass balance model of Misra and Froelich (2012) invokes a fractionation of 16‰ ($\Delta^7 Li = \delta^7 Li_{seawater} - \delta^7 Li_{authigenic-sediments}$) associated with reverse 70 71 weathering in the ocean. However, such a fractionation has not yet been experimentally verified. 72 A number of experimental studies have addressed the behaviour of Li and its isotopes during 73 the alteration of igneous rocks/minerals, focussing primarily on (1) the effect of both low-74 temperature seafloor and high-temperature hydrothermal alteration of oceanic basalts (Seyfried

75 et al., 1984; Berger et al., 1987, 1988; James et al., 2003; Millot et al., 2010); and (2) the 76 partitioning of Li between fluids and solids during silicate weathering on the continents 77 (Pistiner and Henderson, 2003; Vigier et al., 2008; Wimpenny et al., 2010, 2015; Verney-78 Carron et al., 2011; Hindshaw et al., 2019; Pogge von Strandmann et al., 2019). These studies 79 have shown that in low-temperature environments clay minerals readily take up Li from 80 surrounding fluid with a preference for ⁶Li (correspondingly, resulting in the enrichment in ⁷Li 81 of the fluid). This incorporated Li can be hosted at exchangeable sites or chemically bonded 82 into the structural sites, with incorporation into structural sites being the predominant driver of 83 isotopic fractionation toward the enrichment of ⁶Li in the solid (Vigier et al., 2008; Pogge von 84 Strandmann et al., 2019; Hindshaw et al., 2019).

85 A limited number of studies have investigated the Li chemical and/or isotope behaviour 86 during sediment-seawater interaction (Zhang et al., 1998; Pogge von Strandmann et al., 2008; 87 Jones et al., 2012). In the experiments of Zhang et al. (1998), fast adsorption of seawater Li 88 onto clay mineral surfaces was associated with preferential uptake of ⁶Li with fractionation 89 between seawater and solids of 28‰ (seawater-vermiculite) and 21‰ (seawater-kaolinite). 90 However, the experimental procedure of Zhang et al. (1998) was not well documented, and the 91 robustness of the reported isotope measurements has since been questioned (Chan et al., 2006). 92 Jones et al. (2012) conducted a series of experiments consisting of the partial dissolution of 93 riverine/estuarine sediments (derived from Icelandic basalts) in seawater. In these experiments, 94 immersion of riverine sediments in seawater removed a significant amount of Li from the fluid 95 (>70%), but unfortunately Li isotopic fractionation associated with this drawdown was not 96 measured. The field observations of Pogge von Strandmann et al. (2008) on Icelandic estuaries 97 draining basaltic terrains do however indicate that both Li concentration ([Li]) and δ^7 Li of 98 riverine particulate materials derived from continental weathering increase rapidly upon arrival 99 at the river estuary. The authors attribute this behaviour to the formation of secondary minerals

100 following the mixing of river waters with seawater. However, the exact mechanism driving this 101 change in particle [Li] and δ^7 Li upon entry in the estuary is unidentified. Thus if Li isotopes 102 are to be used as a quantitative constraint on global reverse weathering, a better mechanistic 103 understanding of Li isotope fractionation during processes relevant to the reverse weathering 104 (e.g. detrital suspended matter dissolution, Li adsorption onto sediments, and authigenic clay 105 formation) is needed. To fill this gap, we conducted a series of experiments investigating Li 106 isotope fractionation during interaction between seawater and kaolinite which is a typical 107 component of terrigenous sediment material.

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2. Materials and methods

110 <u>2.1 Materials and experiments</u>

Three sets of experiments were conducted at Géosciences Environnement Toulouse 111 112 (GET), with each set investigating the influence of one particular process (or set of processes) 113 relevant to reverse weathering: (1) far-from-equilibrium dissolution of detrital clays in seawater; 114 (2) the adsorption of Li onto detrital clays; (3) close-to-equilibrium interaction between detrital 115 clays and seawater. In these experiments, to control the chemistry of the reactive solution, and 116 to minimize any effect of biological activity, synthetic open-ocean seawater was used in all 117 experiments. This artificial seawater (ASW), with an ionic strength (I) of I = 0.7 M, was 118 synthesised largely following Kester et al. (1967), with some modifications (see Table. 1).

119 Kaolinite was used as representative material of detrital clays produced by continental 120 weathering and delivered by rivers to the ocean. Poorly crystallized kaolinite (reference KGa-121 2) from Washington County (Georgia, USA) was supplied by the Source Clay Repository of 122 the Clay Minerals Society (its surface properties are described in Schroth and Sposito, 1997). 123 The Li content and isotope composition of untreated KGa-2 kaolinite ([Li]_{solid} = 95.94 μ g/g, 124 δ^{7} Li = -0.38 ± 0.72 ‰, 2 s.d, n=12) were determined at the Institut de Physique du Globe de Paris (IPGP) using an Inductively coupled plasma-Quadruple-Mass spectrometer (ICP-Q-MS) and a Thermo Fisher Neptune Plus MC-ICP-MS after acid digestion of powdered aliquots of the solids in HF-HNO₃. The specific surface area of the kaolinite powders, as determined by nitrogen adsorption using the Brunauer-Emmet-Teller (BET) method at GET laboratory, was $22.75 \pm 5 \% \text{ m}^2/\text{g}.$

In experiment (1), designed to study far-from-equilibrium clay dissolution, 20.5 g of the KGa-2 powder were immersed in 501.5 g of Li-free ASW at a constant pH value of 2.7, which allowed the experiment to remain at far-from-equilibrium conditions, and prevented the precipitation of any secondary phases. Seven solution samples were taken periodically over the course of the reaction (~28 days), to measure the change in Li, Al and Si concentrations and δ^7 Li.

136 In experiment (2), designed to characterize Li adsorption onto detrital kaolinite, the 137 KGa-2 powder was first carefully rinsed 12 times with Milli-Q water (18.2 M Ω ·cm) to remove 138 most of the Li located at exchangeable sites or adsorbed at the crystal edges. A suspension 139 made of ~1g of this water-rinsed kaolinite and 30 ml of aqueous solution pre-equilibrated with 140 the same treated kaolinite powder was mixed for several hours in 50 ml PP centrifuge tubes 141 using a tube rotator before Li addition. The aqueous solutions were either ASW or a pure NaCl 142 solution (with the same Na concentration as ASW). Between 71 and ~2,700 µmol/kg of dissolved Li (in the form of LiCl; $\delta^7 \text{Li} = -6.20 \pm 0.01 \text{ }$ %, 2 s.d, n=2) was subsequently added 143 144 to the suspensions and the pH was adjusted to the desired value by addition of small amounts 145 of 1 M NaOH. Each suspension was mixed for 30 minutes to 6 days at a ~constant 20°C 146 temperature and then centrifuged at a speed of 6,500 rpm to separate the aqueous solution from 147 the solid. Sample solutions were collected, filtered with 0.2-µm porosity syringe filters and 148 acidified with distilled HNO₃ for Li isotope and chemical analyses, and the remaining solution 149 volume used for the pH measurement. The Li partition coefficient between the solid and the

fluid (K_d) was calculated according to Equation 1 below, where m_{Li-ads} and m_{Li-aq} correspond to the mass of Li adsorbed on the solid surface and the mass of Li in solution (m_{Li-ads} was determined from the difference between the initial and final (m_{Li-aq}) aqueous [Li]) and m_{kaol} and m_{sln} designate the corresponding mass of kaolinite and aqueous solution, respectively.

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$$K_{d} = \frac{(m_{\text{Li-ads}}/m_{\text{kaol}})}{(m_{\text{Li-aq}}/m_{\text{sln}})}$$
(1)

155 Experiments (3) aimed to investigate the interaction between detrital material and 156 seawater at close-to-equilibrium conditions. Experimental ASW solution was first doped with Li using an ICP standard solution (δ^7 Li_{aq}=52.83 ± 0.28 ‰, 2 s.d) to approximately seawater Li 157 concentration ([Li]_{aq} ~25.9 µmol/kg, or ~180 ppb), and its pH was adjusted using NaOH and 158 159 HCl to pH =8.3. Importantly, this initial ASW solution was devoid of Si and Al, such that only 160 the dissolution of solids was able to provide those elements required for formation of authigenic 161 phases. In this experiment, 20.0 g of KGa-2 powder was immersed in 500.4 g of Li-doped 162 ASW solution. Sampling started 1 day after immersion, with 16 samples taken over the course 163 of the experiment for elemental and Li isotopes analyses. Periodically and after each sample 164 collection, the pH was measured and re-adjusted up to pH~8.4-8.5 using 1M NaOH as required. 165 Experiments (1) and (3) were conducted in polypropylene (PP) beakers hermetically 166 sealed with PVC lids and rubber O-rings to avoid external contamination and to reduce the 167 effects of evaporation. The solutions were continuously mixed using either a Teflon propeller 168 driven by an overhead stirrer or a suspended Teflon-coated magnetic bar attached to a fish-clip (Fig. 1). Before sampling, the stirring system was stopped and the solid in the reactor allowed 169 170 to settle for about 20 minutes. Fluid aliquots ranging from 3 to 25 ml were sampled using a 171 weighed, clean syringe attached to a 0.2-µm pore-size filter. The sampled mass was determined

173 acidified by adding 1 drop of distilled HNO_3 and stored for chemical analyses, while the other

via the mass difference of the syringe before and after sampling. Part of the sampled mass was

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part was kept for Li isotope measurements. The pH of the aqueous solution was measured *in*

situ by inserting a glass combination electrode inside the reactor through an opening made through the lid for this purpose, while the aqueous solution was mixed. The electrode was calibrated against NIST-certified buffers, and as such pH measurements in this study are reported on the NBS-scale and denoted "pH_{NBS}" hereafter (cf. Millero et al., 1993). Although determination of pH in high ionic strength seawater solutions with electrodes calibrated in low ionic strength buffers may introduce systematic measurement error, this effect is unlikely when viewed in the context of the pH range studied (Dickson, 1984; Millero et al., 1993).

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2.2 Fluid chemical and isotopic analyses

The concentrations of dissolved Al and Si were measured via Inductively Coupled 184 185 Plasma Optical Emission Spectrometry (ICP-OES) at the GET laboratory in Toulouse, using a 186 set of calibration standards prepared with the same matrix used for the experiments. The 187 detection limits were determined to be 0.18 and 0.04 μ mol/kg of solution (μ mol/kg_{sln}) for Al 188 and Si, respectively. Additional analyses were conducted via atomic absorption spectrometry 189 (AAS) on selected samples to monitor the possible concentration change of the other cations 190 dissolved in ASW (K, Mg, and Ca). The analytical uncertainty for all the analyzed elements 191 were lower than 2 %.

Measurements of Li concentration and isotope composition were conducted at IPGP. All samples were re-dissolved in 0.5 N HNO₃ and measured by Inductively Coupled Plasma Quadrupole Mass Spectrometry (ICP-Q-MS, Agilent 7900), calibrated using a set of standards with concentrations ranging from 0 to 28.81 μ mol/kg_{sln} (0-200 ppb). The detection limit ranged from 0.14 to 1.44 nmol/kg_{sln} (1-10 ppt) depending on operational conditions. The analytical uncertainty was normally below 2% but could reach up to ~8% for samples with Li concentrations < 0.14 μ mol/kg_{sln} (1 ppb). 199 Prior to Li isotope composition measurements of the aqueous solutions, a double-step 200 separation protocol (details in supplementary materials, Table S1) was performed in order to 201 separate Li from the sample matrix. In the first step, a 0.5-ml sample aliquot containing 20 ng 202 of Li in 1 N HNO₃ was loaded onto a 1-ml column (BioRad, AG50W–X12, 200–400 µm mesh) 203 followed by 4 ml of 1 N HNO₃. In the second step, the eluate of the previous columns was 204 again loaded onto the same (but pre-washed) column and then eluted with 16 ml of 0.2 N HNO₃. 205 The last 8 ml of the elution volume were collected for Li measurement. During each separation 206 session, five reference materials were routinely processed together with samples to check for 207 the quality of this protocol. The Li isotope composition of purified samples was measured at IPGP using a Thermo Fisher Neptune Plus MC-ICP-MS using 10¹¹-ohms amplifiers. Six 208 209 samples (exp. 2) were measured at the German Research Centre for Geosciences 210 (GeoForschungsZentrum GFZ, Potsdam) using a Thermo Neptune Plus MC-ICP-MS and 10¹¹-211 ohms amplifiers. L-SVEC solution was used as a bracketing standard to correct for 212 instrumental mass fractionation, and repeat measurement of the pure Li standard solution 213 IRMM-016 was used to monitor the instrumental stability. Analysis of five known reference 214 materials (Table. S2), NASS-6 (δ^7 Li=30.89 ± 0.48 ‰, 2 s.d, n=7), BHVO-2 (δ^7 Li=4.35 ± 0.18 ‰, 2 s.d, n=5), SRM-2709a (δ^7 Li=-0.68 ± 0.56 ‰, 2 s.d, n=5), TILL-1 (δ^7 Li=6.38 ± 215 216 $0.46 \ \text{\%}, 2 \text{ s.d, n=6}$, and JB-2 ($\delta^7 \text{Li}=4.38 \pm 0.56 \ \text{\%}, 2 \text{ s.d, n=7}$) yielded values in agreement 217 with previously reported values (e.g. Weynell et al., 2017; Kuessner et al., 2020). The analytical 218 uncertainty of δ^7 Li in this study is 0.56 ‰, which is obtained from the greatest standard 219 deviation of reference material measurements.

For samples from experiment (1), Li concentrations (0.61 to 1.03 μ mol/kg_{sln}) were much lower than in seawater (~25.93 μ mol/kg_{sln}) and the corresponding matrix/Li ratios were ~25 to 42 times greater than seawater, making the separation of Li from the matrix impossible with the method described above. Therefore, the samples were split into several aliquots (maximum=12) and processed in parallel through the first step of the protocol. Then, eluates were paired and mixed (such that the number of aliquots was halved), and processed through the same first step of Li separation again. The same procedure was repeated until all initial aliquots were combined into one eluate, then the second step was processed. Such a separation procedure was tested using seawater (NASS-6), and the obtained results (δ^7 Li = 30.86 ± 0.11 ‰, 2 s.d, n=2) are in good agreement with previously reported values (*e.g.* Kuessner et al., 2020).

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2.3 Solid micro-characterization

Kaolinite samples were analysed before and after the experiments using a JSM 7800F
Prime-EDS (JEOL, Ltd.) scanning electron microscope (SEM) at the Castaing Microcharacterization Center in Toulouse to examine the main morphological features of the reacted
solids and detect any mineralogical change due to solid-solution interactions.

235 Lithium bonding environment was characterized for solids from the adsorption 236 experiment (exp. 2) using Nuclear Magnetic Resonance (NMR) at the research unit of 237 CEMHTI (Conditions Extrêmes et Matériaux: Haute Température et Irradiation; CNRS, 238 Orléans). Solid samples from the two adsorption runs that showed the highest amounts of Li 239 sorption onto the kaolinite surface in NaCl and ASW solutions, KL-17 (78.3 µg/g; NaCl 240 solution) and KL-18 (44.3 μ g/g; ASW), were analysed together with one sample of unwashed KGa-2 powder and one of KGa-2 rinsed with Milli-Q water (see above). ⁷Li Magic Angle 241 242 Spinning (MAS) NMR spectra were acquired on a Bruker AVANCE III spectrometer (750 243 MHz – 17.6 T) at a Larmor frequency of 291.5 MHz and a spinning speed of 30 kHz. Around 244 2000 scans were made with a recycling delay of 10s, ensuring complete relaxation of the signal. 245 ⁷Li chemical shifts were referenced relative to a 1 M LiCl solution.

2.4 Thermodynamic calculations

Aqueous solutions' speciation and saturation states with respect to relevant secondary 248 249 phases were calculated from measured aqueous concentrations and pH using the geochemical 250 code PHREEQC v. 3.3 (Parkhurst and Appelo, 2013) and its "LLNL" thermodynamic database. 251 Activity coefficients for dissolved species were calculated using the extended Debye–Hückel 252 equation. The saturation state of the aqueous solution relative to the solid phases of interest is 253 expressed by the saturation index: $SI = Log_{10} (Q/K_{sp})$, where Q defines the ion activity product 254 of the species involved in the hydrolysis of the mineral and K_{sp} is its solubility product value. 255 It must be noted that, given the uncertainty of pH measurements and the possible limitations 256 inherent in the activity coefficient model here used, we do not claim to provide a precise 257 determination of the thermodynamic parameters related to the composition of our ASW solutions. Rather, the results of these thermodynamic calculations should be considered 258 259 qualitative estimates of such parameters.

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3. Results

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3.1 Kaolinite dissolution in Li-free, acidic seawater

262 The results of this experiment (1) are summarized in Table 2 and illustrated in Fig. 2. 263 After an initial rapid dissolution phase with preferential Al release relative to Si, kaolinite 264 dissolution proceeded stoichiometrically, while the fluid remained undersaturated with respect 265 to kaolinite or to any tested Al-Si secondary phase. The absence of newly-formed secondary phases was also confirmed by SEM observations of both fresh and reacted solid KGa-2 266 267 powders that showed no discernible difference in appearance (Figure S1). Aqueous Li 268 concentrations, below the detection limit during the first hours of reaction, continuously increased with time, with the light Li isotope being preferentially released into solution (Fig. 269 270 2). A preferential release of Li relative to Si during the entire course of the experiment was also observed (Fig. 3). Isotopically, whereas bulk kaolinite exhibits an initial $\delta^7 Li_{solid}$ value of -271

272 0.38 ‰, the composition of the first aqueous sample (after ~7 days of experiment) was $\delta^7 Li_{aq}$ = 273 -16.61 ± 0.11‰. With time the $\delta^7 Li_{aq}$ only slightly decreased, reaching a value of -19.03 ± 274 0.20‰ after 28 days of reaction.

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3.2 Li adsorption on kaolinite

276 The results of Li sorption experiments on kaolinite powders are reported in Table 3. It can be seen that the exact nature of the background electrolyte (0.41 M NaCl or ASW) and the 277 278 exposure time had little effect on the value of the Li partition coefficient K_d as defined by Eq. 279 (1). Most K_d observed values are between 0 and 5.7, except one large K_d value (28.2) obtained 280 from a run in which the initial [Li]_{aq} (71.1 µmol/kg) was significantly lower than in the other 281 runs (> 490 μ mol/kg). Adsorbed Li concentrations ranges from 0.2 up to 64 μ g/g, and are positively correlated with fluid pH (Fig. S2a). Li partition coefficients exhibited a slight 282 increase at alkaline pH for solutions used in this study which have relatively low Li aqueous 283 284 concentrations ($\leq 2.7 \text{ mmol/kg_{sln}}$). Also, a linear increase in the amount of Li adsorbed as a function of initial $[Li]_{aq}$ was observed at $9.6 < pH_{NBS} < 11.0$ for Li concentrations varying 285 between 71 and 2,700 μ mol/kg_{sln} (Fig. S2b). 286

Four fluid samples were analysed to determine the isotopic composition of adsorbed Li. These data (Table 4) show that the lighter Li isotope is preferentially adsorbed on the kaolinite surface, with a fractionation between kaolinite surface and aqueous solution ($\Delta^7 \text{Li}_{ads-sln}$) of between -24.2 and -25.8 ‰ (excepting a single value at -14.6 ‰ which we consider to be an analytical artefact of unidentified origin).

The ⁷Li NMR spectra of initial non-treated kaolinite, initial kaolinite rinsed in deionized water and kaolinite recovered from Li adsorption runs KL-17 and KL-18 are shown in Fig. 4. It can be seen that removal of exchangeable or weakly adsorbed Li by water rinsing resulted in a displacement of ⁷Li chemical shift of -0.07 ppm (from -0.10 to -0.17 ppm) whereas Li adsorption on water-rinsed kaolinite (runs KL-17 and KL-18) provoked a displacement of the ⁷Li peak in the opposite direction from -0.17 to -0.08 ppm, which may reflect the adsorption of
Li more weakly bounded than Li substituted in kaolinite octahedral sites (⁷Li peak shift < -0.17
ppm).

300 <u>3.3 Kaolinite interaction with Si- and Al-free and Li-doped seawater at $pH_{NBS} = 8.3 \pm 301$ <u>0.1</u></u>

302 Aqueous Si concentration in experimental seawater increased sharply at the beginning 303 of the run and approached a steady state (~ 28 µmol/kg_{sln}) after 166 days of reaction (Table 5, 304 Fig. 5). At the same time Al concentration remained almost constant, with values $\leq 1 \,\mu mol/kg$ 305 and close to the analytical detection limit. Solution Li concentration (26 μ mol/kg at t = 0) 306 rapidly decreased during the course of the reaction attaining a final concentration of 5.5 307 µmol/kg_{sln}, indicating Li uptake by solids. About 80% of the Li initially present in solution was 308 thus removed during the experiment, corresponding to a partition coefficient K_d between 309 kaolinite and solution of 89.6. This Li removal was accompanied by a strong relative 310 enrichment of the heavy Li isotope in the solution. During the first 39 days, $\delta^7 Li_{aq}$ increased 311 rapidly from 52.8 to 75.4 ‰, and then at a slower rate over the following ~120 days, up to 312 80.2 ‰. Throughout the experiment, solution pH decreased somewhat (Table 5), although 313 NaOH was added in order to maintain relatively stable conditions. PHREEQC calculations 314 indicate that the reacting fluid became undersaturated with respect to kaolinite within a few 315 days, but strongly supersaturated with respect to saponites (SI > 2.0) and mildly supersaturated 316 or close to equilibrium with respect to calcite, gibbsite, and illite (Fig. 6). SEM and Energy-317 dispersive X-ray (EDX) spot analyses of the solid recovered at the end of the run, however, do 318 not indicate any difference in morphology and chemical composition compared to the initial 319 kaolinite (Fig. S3).

4. Discussion

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4.1 Lithium isotope fractionation during kaolinite dissolution in seawater

322 Significant kaolinite dissolution occurred during the experiment in which kaolinite was dissolved in Li-free seawater at pH_{NBS} ~2.7 (Exp. 1). A preferential release of Al and Li over 323 324 Si was observed (Fig. 2a and 3) in accordance with kaolinite dissolution promoted by proton-Al³⁺ exchange reactions (Oelkers et al., 1994; Devidal et al., 1997). Li release, approximately 325 stoichiometric relative to Al (Li/Al = $1.5-1.8 \times 10^{-3}$ mol/mol), was accompanied by a fast and 326 327 strong enrichment of the solution in the lighter Li isotopes ($\delta^7 \text{Li}_{aq} = -16.61$ ‰ after 7 days, Fig. 2b) followed by a much weaker variation with time ($\delta^7 Li_{aq} = -19.03$ ‰ after 28 days) leading 328 329 to significant isotope fractionation between the final aqueous solution and the remaining solid, 330 $\Delta^7 \text{Li}_{\text{sln-kaol}} = -18.68$ ‰. Since kaolinite dissolution in experiment 1 is stoichiometric and our 331 thermodynamic calculations suggest the reacting solution is undersaturated with respect to any secondary mineral, the observed enrichment of the solution in ⁶Li cannot be explained by the 332 precipitation of new solid phases. Instead, lithium isotope fractionation must have occurred 333 334 during dissolution. According to mass balance calculations, 0.17 % of the Li contained in kaolinite was released, whereas only 0.11 % of Si was removed from the solid. The limited 335 336 fraction of Li leached from the starting solid thus results in an insignificant variation of the Li 337 isotopic composition of the solid over the duration of the experiment (~ 0.03 %).

Two different mechanisms could be invoked to explain the observed Li isotope fractionation during early-stage dissolution of kaolinite in seawater: kinetic effects and Li release from different kaolinite sites. Significant kinetic isotope fractionation is known to occur during solid precipitation/dissolution because the rates of desolvation/solvation of light metal isotopes – and thus the breaking rate of light Me-O bonds in the crystal lattice – are faster than those of heavy metal isotopes. Such an effect can in particular result in isotope fractionation during early-stage dissolution (*e.g.* Weiss et al., 2014). Based on molecular dynamics simulation of the exchange rate of water molecules in metal isotopes hydration spheres, Hofmann et al. (2012) proposed that the maximum value of the kinetic fractionation factor, α_{kin} , could be approximated by:

(2)

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$$\alpha_{kin} = \frac{k_{wex,i}}{k_{wex,j}} = \left(\frac{m_i}{m_j}\right)^{-0.049}$$

where $k_{wex,i}$ stands for the water exchange rate constant for the isotope *i* of mass m_i . Application 349 of Eq. (2) to the ⁷Li/⁶Li system yields a maximum value of the kinetic fractionation factor 350 equal to 0.9925 (Δ^7 Li_{fluid-solid} = -7.5 %). This value is consistent with the findings of Verney-351 Carron et al. (2011) who reported a maximum kinetic fractionation, $\Delta^7 \text{Li}_{\text{fluid-glass}}$, of -5.4 ‰, 352 353 during the early stage of dissolution of a Li-enriched synthetic basaltic glass where secondary mineral precipitation did not occur. However, the faster breaking of ⁶Li-O bonds described by 354 355 Eq. 2 (maximum value -7.5 ‰) cannot alone explain the enrichment of the fluid in ⁶Li observed in the present study ($\Delta^7 \text{Li}_{\text{sln-kaol}} = -18.68 \text{ \%}$). 356

357 Alternatively, in exp. (1) Li could have been released from specific crystallographic 358 sites. In kaolinite, Li (a) likely substitutes for Al in octahedral sites, (b) is adsorbed as bidendate 359 inner-sphere complexes on edge octahedra, and to a lesser extent, (c) is located in interlayer 360 sites (Miranda-Trevino and Coles, 2003; Fairén et al., 2015). A part of the Li released to the 361 solution could derive from Li bound to exchangeable sites and/or edge octahedral sites. 362 However, both the stoichiometric Li release relative to Al and the strong enrichment of the solution in ⁶Li during initial non-stoichiometric kaolinite dissolution strongly suggests that Li 363 364 was removed from the AlO₆ octahedral sites where it substitutes for Al, rather than from 365 interlayer sites. These sites are known to be characterized by a strong enrichment in ⁶Li relative to the bulk solid. For example, in the layered silicates synthesized by Hindshaw et al. (2019), 366 367 Li in octahedral sites is about 15 and 21‰ lighter than in the bulk solid and at the exchangeable 368 sites, respectively.

369 Therefore, our preferred interpretation for the observed large Li isotope fractionation during kaolinite dissolution is the preferential release of ⁶Li from octahedral sites, although the 370 impact of a faster breaking rate of ⁶Li-O bonds compared to ⁷Li-O cannot be discounted. It is 371 372 important to notice that in our experiment, kaolinite dissolution was performed in artificial 373 seawater of 0.7 M ionic strength. However, the results of this experiment should also apply to 374 solutions of much lower ionic strength, like those characterizing most continental waters, 375 because in our experiment kaolinite dissolution proceeded at far-from-equilibrium conditions 376 where no sorption or backward reactions (regulated by the composition of the solution) could 377 occur.

378

379

4.2 Li isotope fractionation during adsorption at the kaolinite surface

380 The δ^7 Li values of solution equilibrated with pre-washed KGa-2 in exp. (2) were all 381 higher than that of the initial solution, which is consistent with Li isotopic fractionation during 382 adsorption onto kaolinite. Metal adsorption onto kaolinite surfaces is thought to occur mainly 383 at edge sites (Brady et al., 1996, 1998). Adsorption onto kaolinite edge sites is pH-dependent 384 and particularly predominant when pH is above 7 (Liu et al., 2018), as in our experiments. The 385 observed ⁷Li chemical shift of 0.09 ppm (from -0.17 to -0.08 ppm, Fig. 4) in the NMR analysis 386 of solids from exp. (2) is also consistent with the presence of adsorbed Li onto octahedral AlO_6 387 sites exposed at kaolinite edges. Therefore, we attribute the observed isotope shift of the 388 solutions during exp. (2) to Li adsorption onto kaolinite edge sites inducing preferential uptake 389 of light Li.

The δ^7 Li of the adsorbed fraction, as calculated by isotope mass balance, ranged from -28.30‰ to -19.46‰, corresponding to fractionation factors between solid and fluid between 0.9745 and 0.9856 (Δ^7 Li_{ads-sln} = -25.8 to -14.6 ‰). The measured range of fractionation is relatively large because of the anomalous value found for the experiment KL-18: a replicate of 394 experiment KL-16 but with higher initial Li concentration (2710 vs. 493 µmol/kgsln). If this 395 likely erroneous value is not considered, the mean Li isotope fraction resulting from Li sorption 396 is $\Delta^7 \text{Li}_{ads-sln} = -24$ ‰, a value comparable to those determined by Zhang (2001) from 397 experiments where natural seawater from the Gulf of Mexico was left to interact with kaolinite 398 (-21 ‰), and to that obtained in the present study during the interaction of kaolinite with 399 seawater at $pH_{NBS} \sim 8.3$ (-21‰, see § 4.3). Li in solution is coordinated with 4 water molecules 400 as a tetrahedral aqua ion. The adsorbed Li onto edge sites can be as either outer-sphere 401 complexes (the coordination number of Li remains as 4) or inner-sphere complexes (the 402 coordination number of Li becomes 6) (cf. Liu et al., 2018; Hindshaw et al., 2019). The isotope 403 fractionation of adsorption is mainly associated with the change of coordination number. 404 Therefore, the strong enrichment in ⁶Li of adsorbed lithium confirms that Li increases its 405 coordination number from 4 to 6 upon adsorption and is bounded to kaolinite AlO₆ edge sites 406 in the form of octahedral inner-sphere surface complexes.

407

408 <u>4.3 Li isotope fractionation during kaolinite-seawater interaction</u>

409 In our experiment of seawater-kaolinite interaction at pH_{NBS} 8.3, net dissolution of 410 kaolinite is indicated by increasing dissolved Si concentration through time. No significant 411 release of Al to the solution was observed (Fig. 5a) in contrast to the dissolution of KGa-2 in 412 acidified seawater at far-from-equilibrium conditions (Fig. 2a), suggesting the rapid formation 413 of secondary Al-bearing phases, including clay minerals or their amorphous precursors. 414 Although little evidence for the formation of secondary phases was seen under SEM (Fig. S3), 415 thermodynamic calculations (Fig. 6) suggest that the solution is supersaturated with respect to 416 several secondary phases, in particular Mg-saponite, Na-montmorillonite and gibbsite. As 417 shown in Fig. 5b, this experiment was characterized by a significant removal of Li (~80%) from the initial solution, accompanied by a strong enrichment of ⁷Li in the fluid (~25‰ increase 418

in dissolved δ^7 Li). This is in agreement with previously published results (Zhang et al., 1998; Millot and Girard, 2007) showing that clays preferentially incorporate light Li isotopes. Two main mechanisms can explain the Li uptake and isotopic fractionation observed during our experiment: (1) the adsorption of Li at kaolinite edge octahedral sites as shown by the previous experiment and, (2) the direct Li incorporation in the lattice of newly formed secondary phases, such as saponites.

Depending on the process that controls Li uptake by the solid, the change in Li aqueous isotopic composition in a batch experiment can be described according to either (a) "closed system" equilibrium, in which the Li adsorbed to or incorporated in the solids remains available to isotopic exchange during the progress of the reaction, or (b) Rayleigh distillation, in which the Li adsorbed at the solid surface or incorporated in the precipitating solid is prevented from further isotopic exchange with the solution. The evolution of the Li isotope composition of the aqueous solution for these two behaviours can be expressed as:

432 (a) Closed system equilibrium:
$$\delta^7 Li_{aq}(t) = \delta^7 Li_{aq}(t=0) - 1000 \times (\alpha - 1) \times F$$
 (3a)

433 (b) Rayleigh distillation:
$$\delta^7 Li_{aq}(t) = \delta^7 Li_{aq}(t=0) + 1000 \times (\alpha - 1) \times ln(1-F)$$
 (3b)

434 where $\delta^7 Li_{aq}(t=0)$ and $\delta^7 Li_{aq}(t)$ are the isotopic compositions of the initial solution and of the 435 same solution at time *t*, respectively. In both equations, α is the fractionation factor between 436 the solid and the solution; and *F* stands for the fraction of Li removed from the solution (Eq. 437 3c below), where $[Li]_{aq}(t=0)$ and $[Li]_{aq}(t)$ are the Li concentrations of initial solution and the 438 same solution at time *t*.

439 (c)
$$F = 1 - \frac{[Li]_{aq}(t)}{[Li]_{aq}(t=0)}$$
 (3c)

440 To test the ability of either mechanism to describe the Li isotope fractionation observed in our 441 experiment, in Fig. 7 we have plotted $\delta^7 Li_{aq}(t)$ as a function of *F*, which can be calculated from 442 the Li concentration and solution volume at time *t*. A single linear relationship (Eq. 3a) yielding 443 a fractionation factor α of 0.968 ($\Delta^7 Li_{sol-fluid} = -32\%$) provides a good fit to the entire dataset 444 but does not satisfactorily explain the $\delta^7 Li_{aq}$ change observed during the first part of experiment 445 3 (Fig. 7a). Since $\delta^7 \text{Li}_{aq}$ increases non-linearly during this initial stage and such a fractionation (-32‰) is much larger than any Li isotope fractionation factor yet reported, we discount simple 446 447 "closed system" behaviour. Alternatively, the trend can be reasonably fitted by Eq. (3b) (Fig. 448 7b). However, we note that a systematic deviation between the experimental data and the best 449 fit Rayleigh distillation function exists for high F values (later stage of the experiment; Fig. 450 7b). These observations lead us to conclude that the observed evolution of the fluid Li isotopic 451 composition is the result of a two-stage scenario (Fig. 7b). In the early stage the Li removal 452 from the fluid follows a Rayleigh fractionation process with an estimated fractionation factor of 0.979 (Δ^7 Li_{sol-fluid} = -21‰), indicating a one-way transfer of material from the fluid to the 453 454 solid. In the second stage the evolution of the Li isotopic composition follows a closed-system equilibrium fractionation with a two-way transfer of material to and from the solid, and a 455 456 fractionation factor equal to 0.981 ($\Delta^7 \text{Li}_{\text{sol-fluid}} = -19\%$). Note, the transition to the second 457 reaction stage requires the introduction of a new coordinate reference where the removal of dissolved Li is represented by F', with F' = 0 at the beginning of the new stage. This two-phase 458 459 scenario yields very similar Li isotope fractionation factors for the Rayleigh and closed-system 460 stages, which are in good agreement with the fractionation values reported for Li sorption onto 461 kaolinite and vermiculite by Zhang (2001) and onto kaolinite in our own experiment (section 462 4.2). Additionally, the two-step scenario model (root-mean-square-error (RMSE) = 0.79) better 463 fits the measured data than the closed-system-only model (RMSE=1.0).

Mechanistically, we suggest these two stages in isotope fractionation behaviour reflect two subsequent reactions controlling the Li removal from the fluid. First, Li is rapidly taken up by the precipitating secondary Al-bearing phases such as saponites and gibbsite during the first 7 days of reaction, preventing any isotopic re-equilibration of Li between the solid and the aqueous solution. Subsequently, much slower uptake by secondary phases and/or adsorption at the solid surfaces produces a constant isotope exchange between the two phases. Thus in this interpretation of the data, *both* co-precipitation in secondary phases and adsorption play an important role in the Li removal from the fluid and its isotopic fractionation.

The rapid precipitation of secondary phases is consistent with the fast pH and Li concentration decreases observed during the early stage of the reaction (0-7 days) (Table 5, Fig. 5) and can be exemplified by the following reaction describing the formation of Mg-saponite and gibbsite during kaolinite interaction with seawater:

476
$$1.835 \text{ Al}_2\text{Si}_2\text{O}_5(\text{OH})_{4(s)} + 3.165 \text{ Mg}^{2+} + \text{y HCO}_3^- + (6.33-\text{y}) \text{ OH}^- =$$

477 $Mg_{3.165}Al_{0.33}Si_{3.67}O_{10}(OH)_{2(s)} + 3.34 Al(OH)_{3(s)} + 0.825 H_2O + y CO_{2(g)}$ (4)

478 First, we note that such reaction consumes OH⁻ ions and therefore acidifies the solution, thereby 479 providing an explanation as to why regular addition of NaOH was necessary to keep a relatively 480 constant pH during the experiment. In addition, this reaction leads to the consumption of 481 alkalinity and to the release of CO_2 . As such it is typical of the reverse weathering pathway 482 initially invoked by Mackenzie and Garrels (1966) to illustrate the idea that cations released 483 from the continents by chemical weathering of rocks (and the CO_2 taken up in the process) 484 could eventually be re-sequestered by the neoformation of sedimentary clays in the ocean (and 485 the CO₂ released).

When comparing the Li isotope fractionation resulting from our experiment with that provided by Zhang (2001) for Li sorption on kaolinite, it must be noted that the author derived his value using a Rayleigh fractionation model without taking into account the possible formation of secondary phases. Apart from Li, no information was provided in Zhang (2001)'s study on the evolution of the solution pH and chemical composition, but it is likely that in this experiment the reported Li fractionation factor at least partially reflects Li incorporation in secondary phases.

5. Implications and conclusions

Besides providing experimental constraints on the fundamental properties of the Li isotope system (K_d and isotope fractionation factors), the results of our experimental study have important implications for the global Li cycle as well as its isotope mass balance.

498 First, the fact that both early-stage kaolinite dissolution and Li adsorption onto kaolinite 499 entail significant Li isotope fractionation is noteworthy because kaolinite, among other clay 500 minerals, is a major constituent of soils and, as a result, can greatly affect the isotopic 501 composition of the Li dissolved in soil water. Although Li isotope data on soil solutions are 502 scarce, available data (Lemarchand et al., 2010; Pogge von Strandmann et al., 2012) show an enrichment in ⁶Li with depth in soils' upper layers, which is consistent with the preferential 503 504 release of ⁶Li observed in this study during kaolinite dissolution. Obviously, our experimental 505 results were obtained in very acidic conditions (pH < 3) compared to those usually encountered 506 in soil water, but we contend that a similar Li fractionation during kaolinite dissolution should 507 be expected when mildly acidic rain water, undersaturated with respect to clay minerals, 508 percolate through the topmost soil horizons. During rain storms, this low δ^7 Li signal could even 509 propagate all the way to the river outflow. In most cases, however, this effect cannot dominate 510 the long-term, weighted-average export of dissolved Li from catchments, which is generally 511 characterized by a relatively high δ^7 Li value (*e.g.* Huh et al., 1998; Dellinger et al., 2015; 512 Henchiri et al., 2016; Hindshaw et al., 2019; Murphy et al., 2019), because clay formation and 513 associated ⁶Li uptake outweighs the release of ⁶Li by clay dissolution (Dellinger et al., 2015). 514 We hypothesize that soil and river dissolved Li isotopes recorded during a flood event could show transient, preferential release of ⁶Li through the partial dissolution of kaolinite, thereby 515 516 producing a negative excursion in δ^7 Li in the river water. More generally, such far-from-517 equilibrium conditions might be encountered in catchments where hydrological flow paths are 518 rapid, or when water-mineral contact times are short, like in small catchments affected by

519 landslides. In addition to kaolinite dissolution, the strong Li isotope fractionation during 520 adsorption inferred from our experiments might contribute significantly to short-term 521 variations in the Li isotope signature of soil and river water through fluctuations in the solid-522 to-water ratios in soils and rivers.

523 The results of our study also have implications on the global, longer-term Li cycle. 524 There is probably a large range of possible reactions occurring when riverine material interacts 525 with seawater or sediment pore-water, but the type of reactions that we identified in this study 526 and that occur relatively rapidly (in a couple of weeks in the conditions of our experiments) 527 will act to make the Li isotopic composition of the ocean heavier, even at the very early stage 528 of diagenesis. The Li isotope fractionation observed during two of our experiments (Li 529 adsorption onto kaolinite and interaction between kaolinite and seawater at pH_{NBS} ~8.3) suggest 530 that the detrital clay minerals transported to the ocean by rivers may have a significant impact 531 on the Li chemical and isotopic composition of the ocean, as suggested by Misra and Froelich 532 (2012) and Li and West (2014). With a total flux of suspended matter transported annually by 533 the world rivers to the ocean of 19 Gt (Milliman and Farnsworth, 2013), if one assumes that 534 10% of this flux (a conservative estimate for the global kaolinite+smectite content of the 535 continental detrital flux to the oceans; see Guyot et al. (2007) and Pinet et al. (2019) for the case of the Amazon) is composed of clay minerals exhibiting a Li partition coefficient equal to 536 537 42, (an intermediate value between the values observed in our experiment on kaolinite 538 adsorption ($K_d = 89.6$; see § 3.2) and those reported by Zhang (2001)), the amount of aqueous 539 Li that can be removed from the ocean (taking the modern value for Li concentration in seawater of 180 μ g/kg) is equal to 2.1×10⁹ moles/yr. In comparison, the annual flux of 540 dissolved Li brought into the ocean by rivers is equal to 10×10^9 moles (Gaillardet et al., 2003; 541 Huh et al., 1998; Misra and Froelich, 2012). Therefore, provided that this Li initially adsorbed 542 543 is later locked into newly formed phases, as observed in our experiment of interaction between 544 kaolinite and seawater at $pH_{NBS} = 8.3$, this could result in a significant long-term sink of oceanic, 545 river-derived dissolved Li. Furthermore, the impact of Li scavenging by river suspended matter 546 on the ocean Li isotopic composition can be approximated by the following mass balance 547 equation:

$$\delta' Li_{sw}(initial) = f \times \delta' Li_{sw}(scav) + (1-f) \times \delta' Li_{sw}(final), \tag{5}$$

where $\delta Li_{sw}(initial)$ and $\delta Li_{sw}(final)$ stand for seawater Li isotopic composition before and 549 after Li scavenging by clay minerals, respectively, and f and $\delta^2 Li_{sw}(scav)$ represent the Li 550 551 fraction and Li isotope composition of seawater Li scavenged by clay minerals, respectively. With an ocean mass of 1.36×10^{21} kg and a seawater Li concentration of 26 μ mol/kg_{sln}, the total 552 amount of Li in seawater is equal to 3.53×10^{16} moles. Given an annual flux of Li removed from 553 the ocean by suspended matter equal to 2.1×10^9 moles (hence $f = 5.9 \times 10^{-8}$), and $\Delta^7 \text{Li}_{\text{kaol-sw}} \sim -$ 554 20% (as indicated by both experiments of kaolinite adsorption onto kaolinite and kaolinite-555 seawater interaction at $pH_{NBS} \sim 8.3$), the Li isotopic composition of the ocean could be enriched 556 557 by this process by about 1.2 ‰ over a period of 1 Myr, assuming that the process of Li 558 incorporation into the detrital material is irreversible over these time scales. Froelich and Misra 559 (2012) reported that the present seawater Li isotopic composition is about 9‰ heavier than the 560 late Paleocene (~60 Ma). The isotope effect caused by detrital clays on seawater δ^7 Li, as predicted from our experimental results, is therefore a plausible cause for the Cenozoic rise in 561 562 seawater δ^7 Li, showing that the impact of detrital clay-seawater interactions cannot be 563 neglected on geological time scales (Li and West, 2014).

Finally, with regard to the secular evolution of the seawater δ^7 Li, the fractionating mechanisms investigated in this study bring qualitative arguments to the importance of reverse weathering reactions for controlling the Cenozoic increase of seawater δ^7 Li reported by several authors. Some authors have recently proposed that during the Cenozoic, the development of river floodplains and coastal plains could have helped neoformation of clay minerals on land

and contributed to an increase in the riverine $\delta^7 Li$ (Dellinger et al., 2015; Pogge von 569 570 Strandmann and Henderson, 2015). Alternatively, our experiments suggest that with increasing 571 erosion fluxes due to uplift over the Cenozoic, an increase of detrital clay material supply to the ocean could enhance the neoformation of diagenetic minerals in marine environments, and 572 573 therefore increase seawater δ^7 Li globally (Li and West, 2014). The balance between the 574 importance of neoformation of new clay minerals in floodplains and reverse weathering 575 reactions is still uncertain but both must be considered in interpreting the observed oceanic 576 δ^7 Li curve. Overall, our experiments therefore confirm the potential of Li isotope marine archives as tracers of both continental weathering and marine reverse weathering. 577

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References

Berger G., Schott J. and Loubet M. (1987) Fundamental processes controlling the first stage
of alteration of a basalt glass by seawater: an experimental study between 200 and 320
C. *Earth Planet. Sci. Lett.* 84, 431-445.

Berger G., Schott J. and Guy C. (1988) Behavior of Li, Rb and Cs during basalt glass and
olivine dissolution and chlorite, smectite and zeolite precipitation from seawater:
experimental investigations and modelization between 50 and 300 C. *Chem. Geol.* 71,
297-312.

Bernhardt A., Oelze M., Bouchez J., von Blanckenburg F., Mohtadi M., Christl M. and
Wittmann H. (2020) 10Be/9Be ratios reveal marine authigenic clay formation. *Geophys. Res. Lett.* 47, e2019GL086061.

Brady P. V., Cygan R. T. and Nagy K. L. (1996) Molecular Controls on Kaolinite Surface Charge. *Journal of Colloid and Interface Science* 183, 356-364.

- Brady P. V., Cygan R. T. and Nagy K. L. (1998) Chapter 17 Surface Charge and Metal
 Sorption to Kaolinite. *in* Adsorption of Metals by Geomedia: Variables, Mechanisms,
 and Model Applications, Everett A. Jenne *Ed.*, 371-382, Academic Press.
- 601 Chan L., Leeman W. P. and Plank T. (2006) Lithium isotopic composition of marine
 602 sediments. *Geochem. Geophys. Geosyst.* 7, Q06005.
- 603 Dellinger M., Gaillardet J., Bouchez J., Calmels D., Louvat P., Dosseto A., Gorge C.,
 604 Alanoca L. and Maurice L. (2015) Riverine Li isotope fractionation in the Amazon River
 605 basin controlled by the weathering regimes. *Geochim. Cosmochim. Acta* 164, 71-93.
- 606 Devidal J., Schott J. and Dandurand J. (1997) An experimental study of kaolinite dissolution
 607 and precipitation kinetics as a function of chemical affinity and solution composition at
 608 150°C, 40 bars, and pH 2, 6.8, and 7.8. *Geochimica et Cosmochimica Acta* 61, 5165609 5186.
- Dickson A. G. (1984) pH scales and proton-transfer reactions in saline media such as sea
 water. *Geochimica et Cosmochimica Acta* 48, 2299-2308.
- Dunlea A. G., Murray R. W., Ramos D. P. S. and Higgins J. A. (2017) Cenozoic global
 cooling and increased seawater Mg/Ca via reduced reverse weathering. *Nature Communications* 8, 844.
- Fairén A. G., Losa-Adams E., Gil-Lozano C., Gago-Duport L., Uceda E. R., Squyres S. W.,
 Rodríguez, J.Alexis P., Davila A. F. and McKay C. P. (2015) Tracking the weathering of
 basalts on Mars using lithium isotope fractionation models. *Geochem. Geophys. Geosyst.*16, 1172-1197.
- Gaillardet J., Viers J. and Dupré B. (2003) Trace elements in river waters. *Treatise on geochemistry* 5, 605.
- Guyot J. L., Jouanneau J. M., Soares L., Boaventura G. R., Maillet N. and Lagane C. (2007)
 Clay mineral composition of river sediments in the Amazon Basin. *CATENA* 71, 340356.
- Hathorne E. C. and James R. H. (2006) Temporal record of lithium in seawater: A tracer for
 silicate weathering? *Earth Planet. Sci. Lett.* 246, 393-406.
- Henchiri S., Gaillardet J., Dellinger M., Bouchez J. and Spencer R. G. M. (2016) Riverine
 dissolved lithium isotopic signatures in low-relief central Africa and their link to
 weathering regimes. *Geophys. Res. Lett.* 43, 4391-4399.
- Hindshaw R. S., Tosca R., Goût T. L., Farnan I., Tosca N. J. and Tipper E. T. (2019)
 Experimental constraints on Li isotope fractionation during clay formation. *Geochim. Cosmochim. Acta* 250, 219-237.
- Hofmann A. E., Bourg I. C. and DePaolo D. J. (2012) Ion desolvation as a mechanism for
 kinetic isotope fractionation in aqueous systems. *Proc. Natl. Acad. Sci. USA* 109, 1868918694.

- Huh Y., Chan L., Zhang L. and Edmond J. M. (1998) Lithium and its isotopes in major world
 rivers: implications for weathering and the oceanic budget. *Geochim. Cosmochim. Acta*637 62, 2039-2051.
- Isson T. T. and Planavsky N. J. (2018) Reverse weathering as a long-term stabilizer of marine
 pH and planetary climate. *Nature* 560, 471.
- James R. H., Allen D. E. and Seyfried W. (2003) An experimental study of alteration of
 oceanic crust and terrigenous sediments at moderate temperatures (51 to 350 C): Insights
 as to chemical processes in near-shore ridge-flank hydrothermal systems. *Geochim. Cosmochim. Acta* 67, 681-691.
- Jones M. T., Pearce C. R. and Oelkers E. H. (2012) An experimental study of the interaction
 of basaltic riverine particulate material and seawater. *Geochim. Cosmochim. Acta* 77,
 108-120.
- Kester D. R., Duedall I. W., Connors D. N. and Pytkowicz R. M. (1967) Preparation of
 artificial seawater. *Limnol. Oceanogr.* 12, 176-179.
- Kuessner M. L., Gourgiotis A., Manhès G., Bouchez J., Zhang X. and Gaillardet J. (2020)
 Automated Analyte separation by Ion Chromatography using a Cobot Applied to
 Geological Reference Materials for Li Isotope Composition. *Geostand Geoanal Res* 44,
 57-67
- Lemarchand E., Chabaux F., Vigier N., Millot R. and Pierret M. (2010) Lithium isotope
 systematics in a forested granitic catchment (Strengbach, Vosges Mountains, France). *Geochimica et Cosmochimica Acta* 74, 4612-4628.
- Li G. and West A. J. (2014) Evolution of Cenozoic seawater lithium isotopes: Coupling of
 global denudation regime and shifting seawater sinks. *Earth Planet. Sci. Lett.* 401, 284293.
- Liu Y., Alessi D. S., Flynn S. L., Alam M. S., Hao W., Gingras M., Zhao H. and Konhauser
 K. O. (2018) Acid-base properties of kaolinite, montmorillonite and illite at marine ionic
 strength. *Chemical Geology* 483, 191-200.
- Mackenzie F. T. and Garrels R. M. (1966) Chemical mass balance between rivers and oceans.
 Am. J. Sci. 264, 507-525.
- Michalopoulos P. and Aller R. C. (1995) Rapid Clay Mineral Formation in Amazon Delta
 Sediments: Reverse Weathering and Oceanic Elemental Cycles. *Science* 270, 614-617.
- Millero F. J., Zhang J., Fiol S., Sotolongo S., Roy R. N., Lee K. and Mane S. (1993) The use
 of buffers to measure the pH of seawater. *Marine Chemistry* 44, 143-152.
- Milliman J. D. and Farnsworth K. L. (2013) *River discharge to the coastal ocean: a global synthesis.* Cambridge University Press,

- Millot R. and Girard J. (2007) Lithium isotope fractionation during adsorption onto mineral
 surfaces. In *International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, Lille, France.*
- Millot R., Scaillet B. and Sanjuan B. (2010) Lithium isotopes in island arc geothermal
 systems: Guadeloupe, Martinique (French West Indies) and experimental approach. *Geochim. Cosmochim. Acta* 74, 1852-1871.
- Miranda-Trevino J. C. and Coles C. A. (2003) Kaolinite properties, structure and influence of
 metal retention on pH. *Applied Clay Science* 23, 133-139.
- Misra S. and Froelich P. N. (2012) Lithium Isotope History of Cenozoic Seawater: Changes
 in Silicate Weathering and Reverse Weathering. *Science* 335, 818-823.
- Murphy M. J., Porcelli D., Pogge von Strandmann, Philip AE, Hirst C. A., Kutscher L.,
 Katchinoff J. A., Mörth C., Maximov T. and Andersson P. S. (2019) Tracing silicate
 weathering processes in the permafrost-dominated Lena River watershed using lithium
 isotopes. *Geochim. Cosmochim. Acta* 245, 154-171.
- Odin G. and Fröhlich F. (1988) Chapter C3 Glaucony from the Kerguelen Plateau (Southern Indian Ocean). In *Developments in Sedimentology*. Elsevier, pp. 277-294.
- 686 Oelkers E. H., Schott J. and Devidal J. (1994) The effect of aluminum, pH, and chemical
 687 affinity on the rates of aluminosilicate dissolution reactions. *Geochimica et*688 *Cosmochimica Acta* 58, 2011-2024.
- Parkhurst D. L. and Appelo C. (2013) Description of input and examples for PHREEQC
 version 3--A computer program for speciation, batch-reaction, one-dimensional
 transport, and inverse geochemical calculations. 6-A43, US Geological Survey
- Pinet S., Lartiges B., Martinez J. and Ouillon S. (2019) A SEM-based method to determine
 the mineralogical composition and the particle size distribution of suspended sediment.
 International Journal of Sediment Research 34, 85-94.
- Pistiner J. S. and Henderson G. M. (2003) Lithium-isotope fractionation during continental
 weathering processes. *Earth Planet. Sci. Lett.* 214, 327-339.
- Pogge von Strandmann Philip AE, James R. H., van Calsteren P., Gíslason S. R. and Burton
 K. W. (2008) Lithium, magnesium and uranium isotope behaviour in the estuarine
 environment of basaltic islands. *Earth Planet. Sci. Lett.* 274, 462-471.
- Pogge Von Strandmann, Philip AE, Opfergelt S., Lai Y., Sigfússon B., Gislason S. R. and
 Burton K. W. (2012) Lithium, magnesium and silicon isotope behaviour accompanying
 weathering in a basaltic soil and pore water profile in Iceland. *Earth Planet. Sci. Lett.*339, 11-23.
- Pogge von Strandmann, Philip AE and Henderson G. M. (2015) The Li isotope response to
 mountain uplift. *Geology* 43, 67-70.

- Rahman S., Aller R. and Cochran J. (2016) Cosmogenic 32Si as a tracer of biogenic silica
 burial and diagenesis: Major deltaic sinks in the silica cycle. *Geophys. Res. Lett.* 43,
 708 7124-7132.
- Rahman S., Aller R. and Cochran J. (2017) The missing silica sink: revisiting the marine
 sedimentary Si cycle using cosmogenic 32Si. *Global Biogeochem. Cycles* 31, 15591578.
- Ramos D. P. S., Morgan L. E., Lloyd N. S. and Higgins J. A. (2018) Reverse weathering in
 marine sediments and the geochemical cycle of potassium in seawater: Insights from the
 K isotopic composition (41K/39K) of deep-sea pore-fluids. *Geochim. Cosmochim. Acta*236, 99-120.
- Rude P. D. and Aller R. C. (1994) Fluorine uptake by Amazon continental shelf sediment and
 its impact on the global fluorine cycle. *Continental Shelf Research* 14, 883-907.
- Schroth B. K. and Sposito G. (1997) Surface charge properties of kaolinite. *Clays Clay Miner.* 45, 85-91.
- Seyfried W., Janecky D. and Mottl M. (1984) Alteration of the oceanic crust: implications for
 geochemical cycles of lithium and boron. *Geochim. Cosmochim. Acta* 48, 557-569.
- 722 Sillen L. G. (1967) The ocean as a chemical system. *Science* **156**, 1189-1197.
- Verney-Carron A., Vigier N. and Millot R. (2011) Experimental determination of the role of
 diffusion on Li isotope fractionation during basaltic glass weathering. *Geochim. Cosmochim. Acta* 75, 3452-3468.
- Vigier N., Decarreau A., Millot R., Carignan J., Petit S. and France-Lanord C. (2008)
 Quantifying Li isotope fractionation during smectite formation and implications for the
 Li cycle. *Geochim. Cosmochim. Acta* 72, 780-792.
- Weiss D. J., Boye K., Caldelas C. and Fendorf S. (2014) Zinc Isotope Fractionation during
 Early Dissolution of Biotite Granite. *Soil Science Society of America Journal* 78, 171179.
- Weynell M., Wiechert U. and Schuessler J. A. (2017) Lithium isotopes and implications on
 chemical weathering in the catchment of Lake Donggi Cona, northeastern Tibetan
 Plateau. *Geochimica et Cosmochimica Acta* 213, 155-177.
- Wimpenny J., Gíslason S. R., James R. H., Gannoun A., Pogge Von Strandmann, Philip AE
 and Burton K. W. (2010) The behaviour of Li and Mg isotopes during primary phase
 dissolution and secondary mineral formation in basalt. *Geochim. Cosmochim. Acta* 74,
 5259-5279.
- Wimpenny J., Colla C. A., Yu P., Yin Q., Rustad J. R. and Casey W. H. (2015) Lithium
 isotope fractionation during uptake by gibbsite. *Geochim. Cosmochim. Acta* 168, 133150.

- Zhang L., Chan L. and Gieskes J. M. (1998) Lithium isotope geochemistry of pore waters
 from Ocean Drilling Program Sites 918 and 919, Irminger Basin. *Geochim. Cosmochim.*
- 744 Acta **62**, 2437-2450.
- 745 Zhang L. (2001) Lithium Isotope Geochemistry of Marine Sediments. Ph.D. thesis, Louisiana
 746 State University Historical Dissertations and Theses. 257.

1 FIGURE CAPTIONS

- 2 Figure 1. Sketch of the experimental system used to study KGa-2 (kaolinite) dissolution
- 3 in / interaction with artificial seawater (ASW) solution in experiments (1) and (3).
- 4 Figure 2. Results of experiment (1): kaolinite (KGa-2) dissolution in acidified artificial
- 5 seawater: (a) dissolved Si and Al concentrations; (b) dissolved Li concentration and
- 6 isotope composition, and the isotope composition of KGa-2. The error bars on the
- symbols corresponding to analytical uncertainty, expressed as 2 s.d, are smaller than the
 symbols.
- 9 Figure 3. Preferential release of Li over Si during the dissolution of kaolinite (KGa-2,
- 10 Al₂Si₂O₅(OH)₄) in acidic seawater (pH~2.7; experiment (1)). Diamonds represent the
- 11 amounts of dissolved Si and Li and the solid line represents the Li/Si ratio in the "fresh"
- 12 KGa-2 sample.
- 13 Figure 4. ⁷Li NMR spectra of "fresh" KGa-2, double-deionized water washed KGa-2, and
- 14 kaolinite (KGa-2) collected after Li-adsorption (exposed to Li-rich fluids) in experiment
- 15 **(2).**
- 16 Figure 5. Results of experiment (3): kaolinite (KGa-2) interaction with artificial seawater
- 17 at 25°C and pH 8.3: (a): dissolved Si and Al concentrations; (b): dissolved Li
- 18 concentration and isotope composition. The error bars on the symbols corresponding to
- 19 analytical uncertainty, expressed as 2 s.d, are smaller than the symbols.
- Figure 6. Calculated (using PHREEQC v. 3.3) saturation indexes of the solution of experiment (3) with respect to various secondary phases including gibbsite, boehmite, Mg-saponite, illite, Na-Montmorillonite, and calcite.
- Figure 7. Two scenarios explaining the observed Li isotope fractionation observed in experiment (3): (a) a closed system mass balance in which Li removed from the solution
- 25 is allowed to further equilibrate with the remaining dissolved Li; (b) a two-step scenario
- 26 where a Rayleigh isotopic fractionation in the early stage of the reaction is followed by
- 27 isotopic equilibrium fractionation at the later stage.
- 28



Figure 1



Figure 2





Figure 3



Figure 4



Figure 5





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Figure 7

Table captions

- **Table 1.** Composition of the "artificial seawater" (ASW) prepared for the experiments
- 3 Table 2. Results of experiment (1): dissolution of kaolinite (KGa-2) powder in acid Li-free
- 4 "artificial seawater" solution
- **Table 3.** Results of experiments (2): adsorption of Li onto kaolinite
- **Table 4.** Results of experiments (2): δ^7 Li fractionation during Li adsorption onto kaolinite
- **Table 5.** Results of experiment (3): interaction between kaolinite and Li-doped "artificial
- 8 seawater" solution

Salt	Weight (g)	Concentration (g/kg of water)
NaCl	119.63	23.926
KCl	3.39	0.678
SrCl ₂ •6H ₂ O	0.12	0.024
MgCl ₂ •6H ₂ O	54.16	10.832
C		
$CaCl_2 \cdot 2H_2O$	7.59	1.518
Na ₂ SO ₄	20.04	4,008
NaHCO ₃	0.98	0.196

Diluted in Milli-Q water to 5000 g

Table 1

Sample	elapsed time	pН	Sampled mass	Fluid mass*	[Al] _{aq}	[Si] _{aq}	[Li]aq	Al/Si	δ ⁷ Li	2 s.d.
	(days)		(g)	(g)	(mmol/kg)	(mmol/kg)	(µmol/kg)		(‰)	
G2-1	1.09	2.68	12.1944	489.31	0.29	0.090		3.1		
G2-2	2.25		9.1662	480.14	0.32	0.132		2.4		
G2-3	7.35		18.1016	462.04	0.41	0.212	0.609	1.8	-16.61	0.11
G2-4	10.34		19.8286	442.21	0.43	0.238	0.693	1.7	-16.56	0.13
G2-5	14.31	2.79	17.3749	424.83	0.47	0.278	0.800	1.6	-17.77	0.25
G2-6	21.35	2.78	14.9089	409.93	0.53	0.322	0.910	1.6	-18.32	0.25
G2-7	28.17	2.82	17.0449	392.88	0.57	0.365	1.031	1.5	-19.03	0.20

Note: At the beginning of this experiment δ^7 Li (KGa-2) = -0.38±0.72 ‰

* Fluid mass calculated by subtracting the sampled mass

Sample	рН	Solution	Solution mass g	Kaolinite g	Exposure time (hrs)	[Li] i [*] (µmol/kg)	Δ[Li]** (µmol/kg)	Li (ads) *** (µg/g)	K _d
KLT-02	10.12	NaCl	31.318	1.519	17.3	71.1	-41.1	5.9	28.2
KL-04	6.90	NaCl	30.040	1.001	6.0	715.1	-34.0	7.1	1.5
KL-03	6.91	NaCl	30.065	1.001	3.0	711.3	-43.5	9.1	2.0
KL-02	6.92	NaCl	30.038	1.004	1.5	710.8	-48.2	10	2.2
KL-05	6.94	NaCl	30.103	1.017	8.0	712.3	-31.1	6.4	1.4
KL-01	7.03	NaCl	30.056	1.001	0.6	713.8	-36.1	7.5	1.6
KL-06	7.42	NaCl	30.068	1.087	21.4	518.3	-37.2	7.1	2.1
KL-12	8.45	NaCl	30.053	1.055	148.6	499.8	-43.4	8.6	2.7
KL-07	8.54	NaCl	30.072	1.046	26.1	518.7	-55.4	11.1	3.4
KL-13	9.65	NaCl	30.198	1.034	148.6	498.8	-71.1	14.4	4.9
KL-00	9.95	NaCl	30.125	1.068	20.7	722.0	-120.6	23.6	5.7
KL-15	10.95	NaCl	30.288	1.086	90.6	2701.4	-330.3	63.9	3.9
KL-17	11.58	NaCl	30.955	1.033	90.5	2636.7	-376.3	78.3	5.0
KL-08	6.96	ASW	30.069	1.041	24.0	539.3	-25.9	5.2	1.5
KL-09	7.59	ASW	30.106	1.034	24.0	538.9	-35.5	7.2	2.1
KL-10	7.84	ASW	30.100	1.067	148.7	524.2	-0.9	0.2	0
KL-11	8.29	ASW	30.140	1.024	148.7	527.9	-21.8	4.4	1.3
KL-18	8.77	ASW	30.076	1.118	90.5	2710.3	-237.3	44.3	2.6
KL-16	8.79	ASW	30.280	1.081	90.6	493.3	-77.6	15.1	5.2

* [Li]_i represents initial Li concentration in the solution

** Δ [Li] represents the changes of Li concentration between the end and the start of the experiment, calculated as Δ [Li]=[Li]_{fin}-[Li]_i *** Li (ads) represents the adsorbed Li by each gram of kaolinite, calculated as Li (ads) = Δ [Li] × 6.941 g/mol (molar mass of Li)/ mass of kaolinite

Sample	Starting fluid δ ⁷ Li _i (‰)	Ending fluid δ ⁷ Li _{fin} (‰)	Calculated 8 ⁷ Li-adsorbed (‰) [*]	Δ^7 Li (ads-sln) (‰) ^{**}	α (ads-sln)***
KL-15	-6.19±0.36	-3.23±0.11	-27.44±4.27	-24.21±4.28	0.9761 ± 0.0042
KL-16	-6.20±0.38	-2.69 ± 0.45	-25.01 ± 3.98	-22.32 ± 4.01	0.9779 ± 0.0039
KL-17	-6.19±0.36	-2.51±0.41	-28.30±4.38	-25.79 ± 4.39	0.9745 ± 0.0043
KL-18	-6.19±0.36	-4.92±0.55	-19.43±7.67	$-14.51 \pm 7.69^{\dagger}$	0.9856 ± 0.0076

* Calculated based on isotope mass balance: $\delta^7 \text{Li}_i \times [\text{Li}]_i \times \text{Solution mass} = \delta^7 \text{Li}_{\text{fin}} \times ([\text{Li}]_i + \Delta[\text{Li}]) \times \text{Solution mass} + \delta^7 \text{Li}_i \text{adsorbed} \times |\Delta[\text{Li}]| \times \text{Solution mass};$ [Li]_i, $\Delta[\text{Li}]$, and solution mass for each run are listed in Table 3

** Calculated as Δ^7 Li (ads-sln) = δ^7 Li-adsorbed - δ^7 Li_{fin}

*** Calculated according to the equation Δ^7 Li (ads-sln) = 1000×ln α (ads-sln)

† Likely to be an artefact of unidentified origin

Sample	Time	pН	Sample	Fluid mass ^{**}	[Al]aq	[Si]aq	[Ca]aq	[Mg]aq	[Li]aq	Al/Si	δ ⁷ Li	2 s.d.
	(days)		(g)	(g)	(mmol/kg)	(mmol/kg)	(mmol/kg)	(mmol/kg)	(µmol/kg)		(‰)	
W1-1	1.03	6.48	4.226	496.15	n.d.	1.17E-02			19.37	0		
*	1.1	8.2	-0.74	496.89								
W1-2	3.86	7.99	5.68	491.21	n.d.	7.21E-03	10.76	52.65	15.66	0	64.02	0.10
*	4.8	8.46	-0.3	491.51								
W1-3	6.88	8.25	5.713	485.80	7.90E-04	1.03E-02			12.61	0.1	67.72	0.14
*	7.03	8.42	0.15	485.95								
W1-4	10.92	8.27	4.809	481.14	1.56E-03	1.28E-02	10.93	50.33	11.27	0.1	70.57	0.06
W1-5	19.91	8.28	9.386	471.76	4.20E-04	1.74E-02			9.53	0	72.68	0.25
W1-6	32.04	8.18	7.896	463.86	1.71E-04	1.98E-02	10.70	50.19	8.98	0	74.08	0.16
*	33.76	8.39	-0.1	463.96								
W1-7	39.04	8.25	8.198	455.77	1.67E-04	2.08E-02			7.95	0	75.44	0.30
W1-8	46.92	8.22	8.11	447.66	n.d.	2.24E-02	10.83	51.24	7.85	0	76.45	0.23
W1-9	61.06	8.17	11.1	436.56	1.75E-04	2.21E-02			7.47	0	76.38	0.09
W1-10	74.9	8.09	10.93	425.63	9.17E-05	2.35E-02			7.27	0	78.54	0.07
W1-11	90.02	8.07	12.82	412.81	4.38E-04	2.47E-02			6.86	0	78.79	0.15
W1-12	105.03	8.07	9.961	402.84	n.d.	2.61E-02	10.80	51.69	6.34	0		
W1-13	119.02	8.08	10.05	392.79	1.02E-03	2.73E-02	10.96	51.82	6.09	0		
W1-14	140.06	8.09	12.75	380.04	n.d.	2.46E-02	10.81	51.73	5.53	0	78.29	0.08
W1-15	158.93	8.09	12.14	367.90	n.d.	2.70E-02			5.46	0	80.23	0.21

2.81E-02

0

Table 5

Note: At the beginning of this experiment, δ^7 Li (KGa-2) = -0.38±0.72 ‰, [Li]_{ASW} = 25.9 µmol/kg, δ^7 Li (ASW) = 52.83 ±0.28‰

7.68E-04

n.d. = not detected

W1-16

165.97

8.08

* addition of 1M NaOH to adjust the pH to ~8.3 ** Fluid mass calculated by subtracting the sampled mass

25

342.90