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1 The Li isotope response to mountain uplift

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6 **ABSTRACT**

7 Silicate weathering is a key process by which CO₂ is removed from the atmosphere. It
8 has been proposed that mountain uplift caused an increase in silicate weathering, and led to the
9 long-term Cenozoic cooling trend, although this hypothesis remains controversial. Lithium
10 isotopes are a tracer of silicate weathering processes, which may allow this hypothesis to be
11 tested. Recent studies have demonstrated that the Li isotope ratio in seawater increased during
12 the period of Himalayan uplift (~45 Ma), but the relationship between uplift and the Li isotope
13 ratio of river waters has not been tested. Here we examine Li isotope ratios in rivers draining
14 catchments with variable uplift rates from South Island, New Zealand. A negative trend between
15 $\delta^7\text{Li}$ and uplift shows that areas of rapid uplift have low $\delta^7\text{Li}$, whereas flatter floodplain areas
16 have high $\delta^7\text{Li}$. Combined with U activity ratios, the data suggest that primary silicates are
17 transported to floodplains, where $\delta^7\text{Li}$ and ($^{234}\text{U}/^{238}\text{U}$) are driven to high values due to
18 preferential uptake of ^6Li by secondary minerals, and long fluid-mineral contact times that enrich
19 waters in ^{234}U . In contrast, in mountainous areas, fresh primary mineral surfaces are continuously
20 provided, driving $\delta^7\text{Li}$ and ($^{234}\text{U}/^{238}\text{U}$) low. This is the opposite trend to that expected if the
21 increase in Cenozoic $\delta^7\text{Li}$ in the oceans is driven directly by mountain uplift. These data suggests

22 that, rather than weathering of mountain belts, the increase in seawater $\delta^7\text{Li}$ reflects the
23 formation of floodplains and the increased formation of secondary minerals.

24

25 INTRODUCTION

26 Chemical weathering of silicate rocks is one of two removal processes of carbon from the
27 ocean/atmosphere system (the other being C_{org} burial) and therefore a critical component of long-
28 term climate (Berner, 2003; Kump et al., 2000). Chemical weathering of continental rocks is also
29 one of the main suppliers of material to the oceans, and hence exerts significant influence on
30 ocean chemistry. There is an on-going debate about the factors most significant in controlling
31 chemical weathering rates, with climate – temperature and runoff – (Berner et al., 1983; Gislason
32 et al., 2009; Walker et al., 1981), supply of fresh material (Hilley et al., 2010; Raymo and
33 Ruddiman, 1992; Raymo et al., 1988), or some combination thereof (Li et al., 2014; West et al.,
34 2005) thought to be important in different settings in the modern environment (Jacobson and
35 Blum, 2003). Understanding the controls on weathering is critical to determining the behaviour
36 of the long-term carbon cycle. A climate-dominated control would yield a feedback process that
37 could explain how the long-term climate has maintained itself within relatively narrow bands
38 through Earth history, whereas a supply-dominated cycle has been suggested to link Cenozoic
39 cooling to uplift of the Himalayas (Raymo and Ruddiman, 1992).

40 Marine carbonate strontium isotopes were initially used to examine changes in
41 weathering associated with mountain building, but anomalously radiogenic Himalayan
42 carbonates are thought to dominate the riverine Sr flux (Oliver et al., 2003). Lithium (Li)
43 isotopes are a potential alternative tracer of weathering processes, and may be the only tracer
44 available whose behaviour is solely dominated by silicate weathering processes. Li isotopes are

45 not fractionated by biological processes or plant growth (Lemarchand et al., 2010), and are not
46 affected by carbonate (low temperature or hydrothermal) weathering (Kisakürek et al., 2005;
47 Millot et al., 2010; Reyes and Trompeter, 2012). This gives $\delta^7\text{Li}$ a significant advantage over
48 tracers such as Ca isotopes, which tend to be dominated by carbonate dissolution and formation
49 (Moore et al., 2013). The $\delta^7\text{Li}$ of primary silicate rocks defines a narrow range, with an average
50 for continental crust of $\sim 0 \pm 2\text{‰}$ (Burton and Vigier, 2011; Teng et al., 2004), compared to the
51 high variability in rivers draining these rocks (6–42‰ (Huh et al., 1998; Kisakürek et al., 2005;
52 Millot et al., 2010; Pogge von Strandmann et al., 2006, 2010, 2012; Vigier et al., 2009). Fluvial
53 $\delta^7\text{Li}$ is thus effectively independent of primary lithology, and these highly variable $\delta^7\text{Li}$ in rivers
54 are controlled by weathering processes, particularly by the extent of uptake of Li into secondary
55 minerals, which preferentially remove ^6Li (Pistiner and Henderson, 2003; Wimpenny et al.,
56 2010). Riverine $\delta^7\text{Li}$ therefore reflects the ratio of primary rock dissolution (driving rivers to
57 low, rock-like, $\delta^7\text{Li}$ with high [Li]), relative to secondary mineral formation (driving rivers to
58 high $\delta^7\text{Li}$, and lower [Li]) (Pogge von Strandmann et al., 2010). River $\delta^7\text{Li}$ is thus controlled by
59 the fraction of Li dissolved, relative to the fraction incorporated into secondary minerals. The
60 less Li in solution, the more there is in clays, and the higher the solution $\delta^7\text{Li}$ becomes. This
61 behaviour has also been described as weathering congruency: if riverine $\delta^7\text{Li}$ is low (closer to the
62 primary rock value), then less Li is being taken in secondary clays, and weathering is described
63 as congruent (i.e. direct reflection of rock chemistry by water chemistry) (Misra and Froelich,
64 2012; Pogge von Strandmann et al., 2013). The riverine input to the oceans is combined with the
65 hydrothermal input, and removal by low-temperature clays, to determine the oceanic $\delta^7\text{Li}$ (Misra
66 and Froelich, 2012).

67 Recently, a history of the Li isotope ratio of Cenozoic seawater has been assessed, which
68 shows increasing $\delta^7\text{Li}$ values from ~40Ma to present (Hathorne and James, 2006; Misra and
69 Froelich, 2012). The latter study interprets this increase as due to Himalayan uplift, increased
70 denudation, and more incongruent weathering in the mountain belt (i.e. an increasing amount of
71 clay formation). A problem with this interpretation, however, is that rivers draining the high
72 Himalayas have $\delta^7\text{Li}$ values lower than the global average (Kisakúrek et al., 2005), implying that
73 Himalayan weathering is more congruent, so that Himalayan uplift should have driven seawater
74 $\delta^7\text{Li}$ to lower values rather than higher.

75 In this study, we examine Li isotope ratios in rivers from New Zealand terrains for which
76 uplift rates have been determined, to assess the effect of uplift on riverine Li isotope ratios, and
77 hence the effect of orogeny on riverine $\delta^7\text{Li}$.

78

79 **SAMPLES**

80 Rivers were sampled from multiple catchments around South Island, New Zealand,
81 divided between the East and West of the island (Fig. S1). These samples were collected and
82 analysed for ($^{234}\text{U}/^{238}\text{U}$) (where parentheses indicate activity ratio), and were used previously to
83 define the interaction between weathering, erosion and U activity ratios (Robinson et al., 2004).
84 In general, the individual catchment areas are small, so rivers flow through a narrow range of
85 rainfall and uplift environments. Robinson et al. (2004) developed a hydrologically accurate
86 digital elevation model, which allows estimates of the average rainfall and uplift rate for each
87 catchment, by using digitised rainfall and uplift maps. The western coast has significantly more
88 rainfall than the east (an average of 8000 compared to 1600 mm/yr), and a higher uplift rate (5.8
89 ± 1.5 compared to 1.9 ± 0.8 mm/yr). Overall there is a positive correlation ($r^2 = 0.61$) between

90 uplift and rainfall, and uplift/rainfall ratios are higher in the East. Hydrothermal springs were
91 sampled at Hanmer Springs, to assess the effects of hydrothermal processes, although these
92 springs do not drain into any of the studied rivers. Weathering lithologies have a relatively
93 uniform bulk lithology, dominantly composing Mesozoic greywackes and schists (Rattenbury et
94 al., 2006; Jacobson et al., 2003), with relatively low groundwater contributions (Mongillo and
95 Clelland, 1984). Analytical methods are described in the supplement

96 **RESULTS**

97 Element concentrations are within the range shown by other studies of South Island rivers
98 (Jacobson et al., 2003). Molar Ca/Na (11.8 ± 5.5) co-vary with Mg/Na ratios (0.36 ± 0.16), as
99 expected for rivers draining the continental crust. Lithium concentrations vary between 35 and
100 540 nmol/l, within the range of rivers draining similar terrains in the Mackenzie Basin (Millot et
101 al., 2010). Li isotope ratios ($\delta^7\text{Li}$) vary widely between 7.6 and 34.7‰ (Table S1, Fig. 1a). In
102 general, rivers from the west of the island have lower $\delta^7\text{Li}$ than the eastern rivers, and, overall,
103 there is a negative trend between [Li] and $\delta^7\text{Li}$. Lithium concentrations show positive co-
104 variations with uplift rates, while $\delta^7\text{Li}$ is negatively correlated to uplift (Fig. 1b; $r^2 = 0.67$,
105 significant >99%, Spearman-Rank correlation), as well as less significantly to rainfall ($r^2 = 0.44$).

106 **DISCUSSION**

107 **Lithium Isotopes and Uplift**

108 The observed trend between $\delta^7\text{Li}$ and [Li] (shown as 1/Li in Fig. 1a) is typical for the Li
109 system in rivers (Pogge von Strandmann et al., 2010) and relates to the congruency of
110 weathering: Li isotopes in rivers are controlled by the ratio of primary mineral dissolution to
111 secondary mineral formation (Kisakürek et al., 2005; Pogge von Strandmann et al., 2006, 2012).
112 The range of global rivers extends to lower concentrations and higher $\delta^7\text{Li}$ than the New Zealand

113 rivers, but the latter follow this trend well (Fig. 1a), suggesting that the results of this study can
114 be extrapolated more generally. The similarity between different rivers suggests that, globally,
115 the fractionation caused by clay formation remains similar, allowing behavior approaching
116 mixing.

117 The primary significance of these New Zealand data is the negative relationship between
118 uplift rate and $\delta^7\text{Li}$ (Fig. 1b). This correlation implies that higher uplift rates rapidly provide
119 fresh primary material, resulting in relatively more dissolution of primary rock material relative
120 to secondary mineral formation. The weaker relationship between $\delta^7\text{Li}$ and rainfall suggests that
121 the hydrological cycle is a less important control on silicate weathering. These data show that, in
122 areas of steep relief where there is continuous supply of fresh rock by uplift and rapid runoff,
123 secondary mineral formation is relatively inhibited. In contrast, in the flatter eastern catchments
124 of South Island, uplift and runoff are lower, waters become more supersaturated, and secondary
125 minerals precipitate, driving $\delta^7\text{Li}$ to higher values. These data therefore indicate that $\delta^7\text{Li}$ values
126 are linked to orogenic processes, showing that in mountainous terrains with high uplift rates,
127 chemical weathering processes are relatively congruent. This observation is consistent with those
128 of High Himalayan rivers, which have relatively low $\delta^7\text{Li}$ values (Kisakürek et al., 2005).

129 **Uranium Isotopes and Weathering Regimes**

130 The weathering processes can be further elucidated by comparing ($^{234}\text{U}/^{238}\text{U}$) and $\delta^7\text{Li}$
131 data for these streams, with the two systems providing rather complementary information.
132 Uranium activity ratios are controlled by the ratio of physical erosion to mineral dissolution
133 (Henderson 2002; Andersen et al., 2009; Chabaux et al., 2003; Pogge von Strandmann et al.,
134 2006, 2010, 2011; Robinson et al., 2004). Relatively high physical erosion rates increase mineral
135 surface area, promoting α -recoil of ^{234}U and the leaching of ^{234}U from recoil-damaged lattice

136 sites, and driving riverine ($^{234}\text{U}/^{238}\text{U}$) to high values. In contrast, relatively high dissolution rates
137 will drive river water ($^{234}\text{U}/^{238}\text{U}$) towards the secular equilibrium value of 1, the value of the bulk
138 silicate rock. Unlike $\delta^7\text{Li}$, ($^{234}\text{U}/^{238}\text{U}$) is not expected to be impacted by formation of secondary
139 minerals. These isotope systems are therefore both driven to low values by dissolution, but to
140 high values by different processes: physical erosion or residence time for ($^{234}\text{U}/^{238}\text{U}$), and
141 secondary mineral formation for $\delta^7\text{Li}$. Therefore coupled use of Li and U isotopes in weathering
142 studies can yield complementary information on dissolution vs. clay formation vs. erosion
143 (Pogge von Strandmann et al., 2006, 2010).

144 Rivers from the west coast have ($^{234}\text{U}/^{238}\text{U}$) close to 1, and variable but low $\delta^7\text{Li}$. This
145 implies high dissolution rates and variable and low secondary mineral formation (Fig. 2). The
146 implication is that the high uplift rates in these mountainous catchments result in rapid
147 dissolution of the host rocks, but, due to swift removal of material, rivers rarely reach
148 oversaturation with regard to secondary minerals, which therefore do not form. In contrast, the
149 eastern rivers have higher $\delta^7\text{Li}$ and ($^{234}\text{U}/^{238}\text{U}$) indicating both an increase in secondary mineral
150 formation, and an increase in grain surface area, from physically eroded material transported to
151 the floodplain. Thus eroded grains settle on the flat topography, where the waters dissolving
152 them become oversaturated decreasing the dissolution rate and leading to precipitation of
153 secondary minerals which increases the $\delta^7\text{Li}$.

154 **Consequences for silicate weathering reconstructions**

155 The conclusion that higher uplift drives more congruent weathering, and hence riverine
156 $\delta^7\text{Li}$ to lower values, is consistent with the observation that High Himalayan river $\delta^7\text{Li}$ is almost
157 ubiquitously lower than the global mean (Kisakürek et al., 2005). The weathering of mountain
158 belts should therefore have driven seawater $\delta^7\text{Li}$ lower during the Cenozoic, rather than towards

159 the higher values observed (Misra and Froelich 2012). In contrast, it is the tectonically stable
160 areas such as floodplains, associated with and supplied by high-relief tectonically active terrains,
161 that exhibit incongruent weathering and high clay formation (West et al., 2002; Jacobson and
162 Blum, 2003; Moore et al., 2013), and which drive riverine $\delta^7\text{Li}$ high. The few river $\delta^7\text{Li}$ data that
163 currently exist from the Himalayan floodplain show higher $\delta^7\text{Li}$ relative to rivers of the High
164 Himalayas (Huh et al., 1998), supporting this conclusion. Therefore, while Misra and Froelich
165 (2012) are likely correct that orogeny is responsible for the increase in seawater $\delta^7\text{Li}$ (Wanner et
166 al., 2014), the locus of the dominant Li isotope fractionation is the floodplain and foreland
167 surrounding the mountains, rather than the mountains themselves, possibly coupled to a shift in
168 the oceanic Li sink (Li and West, 2014). This conclusion agrees with modelling of the $\delta^7\text{Li}$
169 record, which suggests a significant increase in retention of Li by clays during the Cenozoic (Li
170 and West, 2014; Wanner et al., 2014). It is possible that this increase in clay retention is linked to
171 Himalayan/Tibetan Plateau and/or Andean uplift (e.g. Hoorn et al., 2010).

172 For a given denudation rate, congruent weathering provides more cations to the ocean
173 than incongruent weathering (where a proportion of cations are retained in clay minerals).
174 Cenozoic uplift increased the surface area available for weathering and might be expected to lead
175 to an increase in the dissolution of silicates and drawdown of CO_2 . The formation of significant
176 floodplains associated with this mountain building would, however, have led to retention of a
177 higher fraction of the released cations on the continents, thus limiting the effectiveness of uplift
178 in driving CO_2 removal. By recording the extent of this cation retention, and thereby the overall
179 congruency of weathering, lithium isotopes are a record of the efficiency of continental
180 weathering in driving CO_2 removal, rather than the overall amount of CO_2 removal.

181 The use of Li isotopes to assess past cation retention is predicated on the assumption
182 that Li is similarly retained in clays as Ca or Mg. In the well-studied example of Iceland, such
183 behavior is indeed seen, with the mobility of Li, Ca and Mg being almost identical, indicating
184 similar clay retention (Gislason et al., 1996; Pogge von Strandmann et al., 2006; Hindshaw et al.,
185 2013). Icelandic data also show that Li and Ca isotopes correlate with one another in rivers
186 where Ca is being removed into clays (Hindshaw et al., 2013), further supporting the use of Li
187 isotopes to assess the retention of cations during clay formation. On a global scale, if weathering
188 of uplifted areas did lead to Cenozoic cooling, then the increase in primary dissolution caused by
189 mountain building must have outweighed the greater retention of cations on the continents
190 recorded by changes in seawater Li isotopes.

191

192 CONCLUSIONS

193 Rivers from South Island, New Zealand, show a strong, negative correlation between the
194 uplift rate of their catchments and their Li isotope ratio. This implies that when uplift rates are
195 high, fresh primary material is continuously supplied for dissolution, leading to highly congruent
196 weathering with a relative absence of secondary mineral formation, and $\delta^7\text{Li}$ that reflects the
197 original rock. In contrast, when uplift rates are lower, in tectonically stable areas, formation of
198 secondary minerals preferentially enriches rivers in ^7Li . The correlation we observe between $\delta^7\text{Li}$
199 and uplift rates is in the opposite sense to that required if uplift of the Himalayas directly caused
200 the increase in seawater $\delta^7\text{Li}$ during the Cenozoic. The results instead indicate that it may have
201 been the formation of large floodplains associated with uplift that explains the increase in
202 seawater $\delta^7\text{Li}$. By recording the congruency of weathering, lithium isotopes may provide a

203 record not of the overall rate of dissolution on the continents, but of the efficiency of this
204 dissolution in driving uptake of CO₂.

205

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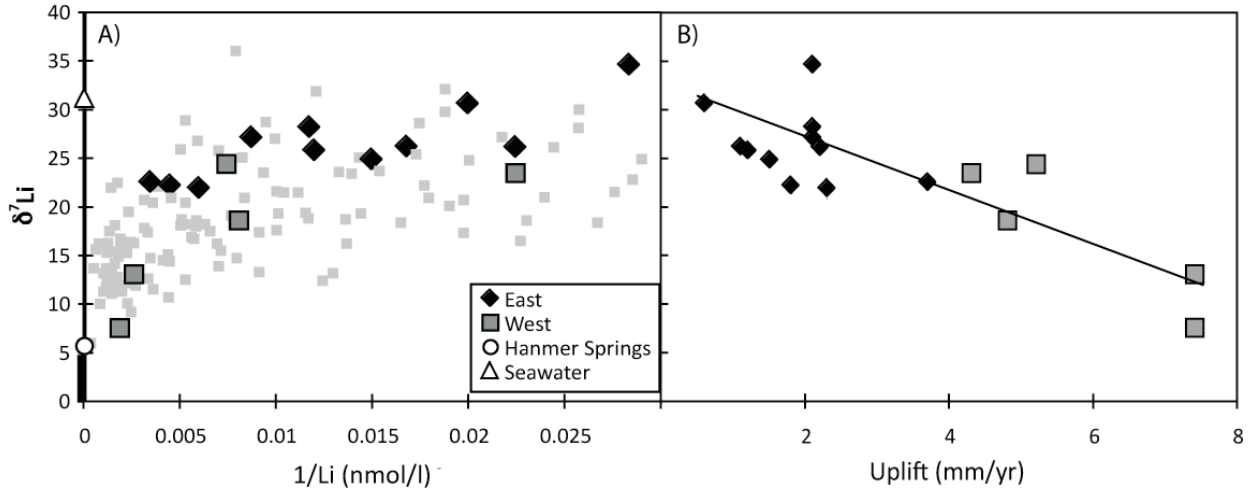
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341 **FIGURE CAPTIONS**

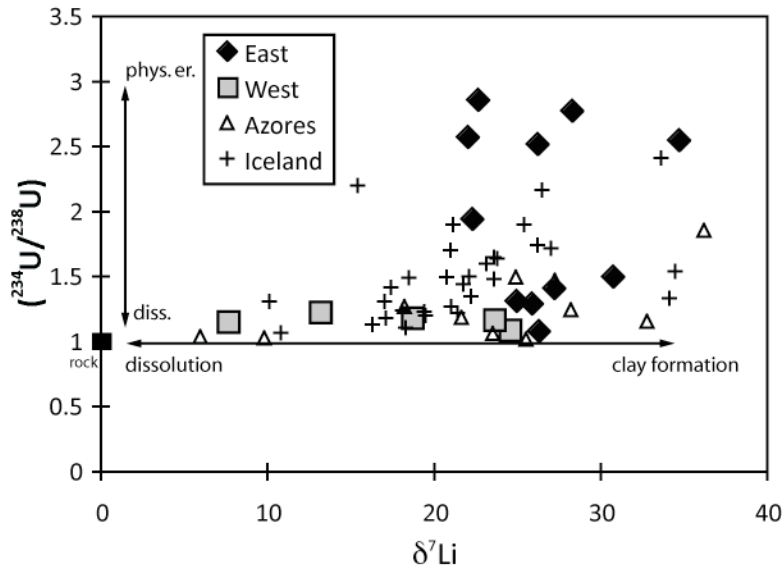
342 Figure 1. A) Li mixing diagram, showing data from this study. The small grey boxes are river
343 studies from other locations (Iceland, Azores, Himalayas, Orinoco, Mackenzies, global large
344 rivers – see text for references). B) Li isotope ratios for New Zealand rivers as a function of local
345 uplift ratios. Low $\delta^7\text{Li}$ values imply relatively greater primary rock dissolution, while high $\delta^7\text{Li}$
346 implies relatively greater secondary mineral formation.

347 Figure 2. Uranium activity ratios compared to lithium isotope ratios. The arrows show the
348 controls associated with both tracers (phys. er. = physical erosion; diss. = dissolution).
349 Additional data are from the Azores (Pogge von Strandmann et al., 2010) and Iceland (Pogge
350 von Strandmann et al., 2006; Vigier et al., 2009).

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