

The Li isotope response to mountain uplift

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ABSTRACT

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

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

INTRODUCTION

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

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

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

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

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

SAMPLES

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

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

RESULTS

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

DISCUSSION

Lithium Isotopes and Uplift

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

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

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

Uranium Isotopes and Weathering Regimes

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

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

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

Consequences for silicate weathering reconstructions

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

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

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

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

CONCLUSIONS

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

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

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FIGURE CAPTIONS

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

Figure 2. Uranium activity ratios compared to lithium isotope ratios. The arrows show the controls associated with both tracers (phys. er. = physical erosion; diss. = dissolution).

Additional data are from the Azores (Pogge von Strandmann et al., 2010) and Iceland (Pogge von Strandmann et al., 2006; Vigier et al., 2009).

