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Lithium and Lithium Isotopes in Earth's Surface Cycles

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ABSTRACT

Lithium and its isotopes can provide information on continental silicate weathering, which is the primary natural drawdown process of atmospheric CO_2 and a major control on climate. Lithium isotopes themselves can help our understanding of weathering, via globally important processes such as clay formation and cation retention. Both these processes occur as part of weathering in modern surface environments, such as rivers, soil pore waters, and groundwaters, but Li isotopes can also be used to track weathering changes across major climate-change events. Lithium isotope evidence from several past climatic warming and cooling episodes shows that weathering processes respond rapidly to changes in temperature, meaning that weathering is capable of bringing climate back under control within a few tens of thousands of years.

Keywords: weathering; thermostat; palaeo-climate; oceans; clay formation

INTRODUCTION

Lithium and its isotopes have been used to examine Earth's surface processes since the pioneering work of Lui-Heung Chan in the late 1980s (see reviews in Tomascak et al. 2016 and Penniston-Dorland et al. 2017). However, it is only since the advent of the multi-collector inductively coupled plasma mass spectrometer (MC–ICP–MS) that lithium isotopic analyses have become sufficiently precise for a variety of Earth and ocean science applications. Over the last 30 years, analyses of river waters, seawater, pore waters, groundwaters and these waters' associated rocks, secondary minerals, and soils have shown that Li isotopes exhibit

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very strong fractionation at the Earth's surface, primarily due to processes occurring during chemical weathering of rocks.

Weathering is one of the fundamental processes operating at the Earth's surface. Weathering of silicate minerals is the primary mechanism by which CO_2 is removed from the atmosphere, and, hence, likely the dominant natural process that controls climate (and could mitigate climate change). Investigating weathering processes, though, has proven difficult, especially for the geological past. Many interpretations of other tracers of continental weathering are often geologically ambiguous. This ambiguity has opened the door for the use of a suite of 'non-traditional' metal stable isotopes, including lithium. Lithium has two key advantages as a weathering tracer: it is only affected by silicate weathering, which is the specific process that removes CO_2; it is apparently unaffected by biological function. Therefore, a significant amount of work has gone into trying to use lithium to provide information on how exactly the silicate weathering process acts to control Earth's climate, most notably to investigate the timescales on which these processes operate.

THE BASICS OF LITHIUM AT EARTH'S SURFACE

Lithium is the third lightest chemical element, and the lightest alkali metal. It is a trace element in silicate rocks, having a concentration of 1.39 ± 0.10 (2σ) μg/g in the primitive mantle, and, because it is moderately incompatible, concentrations of 5.5 ± 3.8 μg/g in mid-ocean-ridge basalt (MORB) (Marschall et al. 2017) and of ~ 18 μg/g in the bulk continental crust, which increases to 30.5 ± 3.6 μg/g in the upper continental crust (Sauzéat et al. 2015). In general, primary silicate minerals (i.e., silicates produced by igneous or metamorphic processes) contain orders of magnitude more lithium than carbonate minerals.

During water cycling across the Earth's surface, Li dissolved from continental rocks partitions between solution (rivers, soil pore waters, groundwaters) and secondary minerals such as clays, oxides, or zeolites (i.e., minerals often produced by the weathering process). Rivers have relatively low Li concentrations (the global riverine mean is 0.0015 μg/g, with a range of 2×10^{-7} to 0.1 μg/g) (Huh et al. 1998), but clays have high concentrations of Li (tens to hundreds of μg/g), meaning that a considerable proportion of Li dissolved from primary rocks ends up in secondary minerals. In contrast to rivers, the oceans (in which Li is a conservative element with a seawater residence time of just over a million years; Hathorne and James 2006) have a relatively high and uniform modern concentration of 0.18 μg/g (Tomascak et al. 2016).

Rivers comprise slightly over 50% of the Li input to the oceans (~55,000 t/y), with the rest (~41,000 t/y) derived from high-temperature hydrothermal fluids at mid-ocean ridges (Hathorne and James 2006). Submarine groundwater inputs have been estimated at ~35% of the riverine flux (Pogge von Strandmann et al. 2014) but these estimates are highly uncertain, being based on only a few measurements. Similar to its behaviour in rivers, lithium is removed from seawater by uptake into secondary clays. These are formed by alteration of the oceanic crust and through authigenic clay formation.

Lithium has two stable isotopes: ^{6}Li and ^{7}Li. The relative variations in abundance of these two isotopes in different materials are increasingly being used to trace Earth processes. The lithium isotope ratio δ^7Li is reported as ‰ (per mil) deviation of the ^{7}Li/^{6}Li ratio from the NIST-8454 LSVEC standard; modern analyses can reproduce δ^7Li with a precision of better than ~± 0.5‰. The δ^7Li value of the primitive mantle is 3.5 ± 1.0‰, while basalts of MORB composition have a similar range, from 3‰ to 5‰ (Marschall et al. 2017). However, the continental crust is distinctly different. This has δ^7Li values ranging between −10‰ and +10‰ (Tomascak et al. 2016), and with a statistical mean of +0.6‰ ± 0.6‰ (Sauzéat et al. 2015). The difference between the mantle and the continental crust is at the heart of the increasing use of Li isotopes to trace surface processes. Surface waters differ greatly in δ^7Li from primary rocks (riverine mean = 23‰, with a range of 2‰–43‰) (Huh et al. 1998; Dellinger et al. 2015; Murphy et al. 2019). This variability is largely due to secondary mineral formation during weathering and is discussed in more detail below.

In the oceans, the Li input from hydrothermal fluids has a δ^7Li of ~8‰, which is higher than their source basalts due to uptake of ^{6}Li by secondary minerals at high temperature (quasi analogous to continental weathering – see below). Lithium is removed from seawater by uptake into clay minerals with a cumulative fractionation factor (similar to that on the continents) of ~15‰ (Chan et al. 1992). This preferential uptake of isotopically light Li drives modern seawater to a relatively high δ^7Li value of 31‰.

Lithium also has some key advantages over other tracers of weathering, such as radiogenic Sr and Os isotopes, or stable Ca, Mg and Si isotopes. Lithium is one of the very few elements that is not biologically mediated: no isotope fractionation has been observed during the growth of plants (Clergue et al. 2015) or of phytoplankton (Pogge von Strandmann et al. 2016). Furthermore, because Li is so much more concentrated in silicate than carbonate minerals, Li isotopes effectively only trace silicate weathering (Dellinger et al. 2015; Gou et al. 2019). This is important, because it is the weathering of silicate minerals that exerts the primary influence on atmospheric CO_2 and, thereby, climate. Given the narrow range in the

δ^7Li values of primary silicate minerals, including their sedimentary or metamorphosed derivatives, this also means that dissolved Li isotope ratios are effectively independent of primary lithology – again giving Li an advantage over almost all other radiogenic isotope systems. In fact, Li isotopes are currently the only known proxy that can solely trace silicate weathering processes (Dellinger et al. 2015; Pogge von Strandmann et al. 2017b,c, 2019).

WHAT PROCESSES FRACTIONATE DISSOLVED LITHIUM ISOTOPES?

The dissolved lithium flux in rivers reflects a balance between Li input by primary mineral dissolution and Li output by secondary mineral formation. Thus, it follows that quantifying the extent of isotope fractionation that is associated with these processes is essential in understanding Li systematics in both modern-day and past weathering environments. This has been achieved through a combination of field studies (e.g., Wimpenny et al. 2010; Clergue et al. 2015; Dellinger et al. 2015) and experimental work (e.g., Pistiner and Henderson 2003; Vigier et al. 2008; Wimpenny et al. 2010; 2015), the latter of which has the advantage that key physical and chemical constraints—the reacting mineral, temperature, and pH—can be controlled.

The results of several leaching experiments show that no significant Li isotopic fractionation occurs during the dissolution of primary silicates (Pistiner and Henderson 2003; Wimpenny et al. 2010; Penniston-Dorland et al. 2017). Based on this, it follows that the isotopic heterogeneity measured in river waters and weathered sediments is primarily caused by secondary mineral formation. Researchers have quantified the extent of isotopic fractionation experimentally using a range of techniques, including direct mineral synthesis (Vigier et al. 2008; Hindshaw et al. 2019), alteration of primary silicate minerals (Millot et al. 2010; Wimpenny et al. 2010; Pogge von Strandmann et al. 2019) and acid leaching/sorption experiments involving natural sediments or pure mineral phases (Pistiner and Henderson 2003; Chan and Hein 2007; Wimpenny et al. 2010, 2015). In all cases, the bulk δ^7Li value of the solid phase is enriched in ^{6}Li compared to Li in the fluid phase, leading to a negative difference in δ^7Li between solid and solution ($\delta^7\text{Li}_{\text{solid}} - \delta^7\text{Li}_{\text{solution}} = \Delta^7\text{Li}_{\text{solid–solution}}$), in accordance with results from field studies. There is no clear relationship between $\Delta^7\text{Li}_{\text{solid–solution}}$ and the identity of the reacting mineral, nor with solution pH or solution composition (e.g., Hindshaw et al. 2019). However, $\Delta^7\text{Li}_{\text{solid–solution}}$ does decrease with increasing temperature (Vigier et al. 2008; Millot et al. 2010) as is expected from stable isotope fractionation theory. At temperatures relevant to continental weathering (≤25 °C), typical $\Delta^7\text{Li}_{\text{solid–solution}}$ values range between −14‰ and −23‰ (FIG. 1).

A complication in understanding Li isotope behaviour is that secondary silicates, including clays, contain two isotopically distinct reservoirs of Li: structurally bound Li, which strongly favours ^{6}Li (Δ^7Li = −14‰ to −24‰), and exchangeable Li, which is taken up with relatively less isotope fractionation (−0‰ to −12‰) (FIG. 1) (Chan and Hein 2007; Wimpenny et al. 2015; Hindshaw et al. 2019; Pogge von Strandmann et al. 2019). Once this second, exchangeable pool is accounted for, the $\Delta^7\mathrm{Li}_{\mathrm{solid-solution}}$ value associated with incorporation of structural Li is estimated to be >-21‰ (FIG. 1) (Hindshaw et al. 2019; Pogge von Strandmann et al. 2019).

We can therefore assume that dissolved Li isotope ratios are controlled simply by the ratio of primary silicate mineral dissolution to secondary mineral formation (FIG. 2). This ratio is known as the 'weathering congruency': if a rock congruently dissolves with no secondary mineral formation, then the dissolved load will have a low, rock-like, δ^7Li. Conversely, incongruent weathering, involving secondary mineral formation, results in fractionated (higher) dissolved δ^7Li values (Misra and Froelich 2012; Pogge von Strandmann et al. 2017b). Effectively, weathering congruency may also inform on CO_2 drawdown efficiency, because if cations such as Ca or Mg (critical for the sequestration of carbon via carbonate formation) or Fe or K (critical nutrients for organic carbon burial) are retained on the continents in clays or soils (as during incongruent weathering) rather than being delivered to the oceans (as during congruent weathering), less CO_2 will be sequestered per unit of silicate rock dissolved. In other words, the higher the dissolved δ^7Li value, the less efficient is CO_2 drawdown via silicate weathering (FIG. 2) (Pogge von Strandmann et al. 2017b).

Overall, the congruency control on fractionation allows Li isotopes to act as a tracer for silicate weathering intensity, which is the ratio of the weathering rate to the erosion rate [expressed as weathering rate/denudation rate (W/D), i.e., weathering rate/(weathering rate + erosion rate)] (Dellinger et al. 2015). The relationship between weathering rate and δ^7Li has been referred to as 'boomerang' in shape (FIG. 3A). Effectively, when the weathering intensity is low then the weathering regime is kinetically limited, the weathering is congruent, and the $\delta^7\mathrm{Li}_{\mathrm{water}}$ is low. The dissolved Li flux (amount of Li per unit time) and yield (flux per unit area) in this regime is high (FIG. 3B). Regimes such as this exist in regions with high physical erosion rates (Dellinger et al. 2015; Pogge von Strandmann et al. 2017b). Then, as the weathering intensity rises, $\delta^7\mathrm{Li}_{\mathrm{water}}$ and secondary mineral precipitation increases. Because, in this case, congruency decreases, Li is incorporated into secondary minerals, the Li yield starts to decrease and δ^7Li of the water rises (FIG. 3). Finally, at very high weathering intensity, the regime moves to a supply limited regime, and pre-formed clays begin to be leached or dissolved. These cause a decrease in $\delta^7\mathrm{Li}_{\mathrm{water}}$ again. However, the Li flux and Li yield in terrains with high W/D are low (and, therefore, do not affect seawater composition), and most observed river systems show a negative linear relationship between Li yield and weathering intensity (FIG. 3B). High W/D river systems are, therefore, irrelevant for reconstructing past seawater. Consequently, low δ^7Li values come from areas with high physical erosion (low W/D), such as mountainous and glaciated terrains. Clay and soil formation then occur on the flatter floodplains (intermediate W/D), resulting in increased δ^7Li.

Addition of more recent river data (Gou et al. 2019; Murphy et al. 2019) has increased the variation within the relationship plotted in FIGURE 3A. In particular, the Yellow River (China) has a wide range in W/D for constant δ^7Li values (Gou et al. 2019). This may be a function of the Yellow River data representing a time-series at a single location, rather than multiple sample locations as was done for other river data, but does imply that further investigation is required, and that caution must be used before Li isotopes are accepted as a universal tracer of silicate weathering intensity.

WHAT CAN LITHIUM TELL US ABOUT THE MODERN CARBON CYCLE?

A key question about the Li isotope composition of surface waters is how the behaviour of Li can be related to that of elements more important to the carbon cycle, such as Ca, Mg, or Fe. Calcium is especially important, given that marine calcium carbonate precipitation is a critical sink of atmospheric CO_2. It is useful to base this comparison in terms of the relative weathering mobilities of Ca, Mg, and Fe. An element is said to be mobile during weathering if it readily goes into solution (e.g., Na, K, Ca, Mg), but is said to be immobile if it prefers to go into secondary solids (e.g., Fe, Al, Ti).

The relative mobility of Li to Ca is calculated by the formula $(\mathrm{Li/Ca})_{\mathrm{water}}/(\mathrm{Li/Ca})_{\mathrm{rock}}$, meaning that it is only defined in cases where one knows the identities and proportions of the dissolving minerals that contribute cations to catchment waters. Available data allow us to evaluate the relative mobilities from basaltic terrains (e.g., Iceland and the Azores), andesitic terrains (e.g., Guadeloupe) and gneissic terrains (e.g., Greenland) (FIG. 4), as well as from hydrothermal springs from Iceland (Penniston-Dorland et al. 2017). In hydrothermal waters, the relative mobility between Li and Ca varies by almost four orders of magnitude (FIG. 4). The key is that this relative mobility co-varies with the δ^7Li of the waters. When δ^7Li is low (i.e., rock-like, as observed in soil pore waters and hydrothermal waters), weathering is congruent, little to no Li is taken up into secondary minerals, and Li is relatively mobile compared to Ca. The decrease in Ca mobility in waters where weathering in congruent is likely due to secondary calcite formation, common in these waters, which takes up Ca but not Li. In contrast, in all examined rivers, Li and Ca are within an order of magnitude of each other's mobility, and the same is true of relative mobilities of Li vs Mg or Si (Pogge von Strandmann et al. 2016, 2019). Here δ^7Li is high, and weathering is, therefore, incongruent and secondary mineral formation is relatively high. These secondary minerals remove Li from solution, making it less mobile than Ca (mobility <1). Based on this trend, the Li/Ca mobility ratio that corresponds to the average riverine δ^7Li value is ~0.26 ± 0.05. Thus, the global budget is dominated by catchments in which weathering is, on average, incongruent.

Whereas the trend in FIGURE 4 needs to be investigated in more river systems, laboratory weathering experiments have been able to reproduce it (Pogge von Strandmann et al. 2019). The illustrated trend implies that Li isotope ratios in waters may be used to quantitively link the behaviour of Li isotopes to that of the element Ca (or other elements important for the carbon cycle), which in turn allows one to determine the amount of sequestered atmospheric CO_2 though weathering. If the fraction of Li in solution is known by comparing $\delta^7Li_{solution}$ to δ^7Li_{rock} then, from the mobility relationship, the fraction of Ca in solution can be determined (Dellinger et al. 2015; Pogge von Strandmann et al. 2017c). If a Li flux is known (or modelled), then the Ca flux can also be determined (Pogge von Strandmann et al. 2017a). This in turn can be linked to a CO_2 sequestration flux, although we need more natural and experimental constraints before this logic can be universally applied.

THE PAST BEHAVIOUR OF LITHUM AND THE WEATHERING THERMOSTAT

The 'weathering thermostat' is a feedback control on global climatic temperature whereby warm climates promote faster silicate weathering, which then draws down atmospheric CO_2, cools the climate, and thereby slows weathering. This process is widely suggested as a mechanism that allows Earth's climate to recover from perturbations. However, it has been difficult to acquire evidence of how rapidly the thermostat operates. In principle, the ability of Li isotopes to trace silicate weathering changes, independent of variations in lithology or biology, makes it an ideal tracer to understand the weathering thermostat. Calcite appears to be a useful archive of fluid δ^7Li. Inorganic calcite and many forms of biogenic calcite (brachiopods, corals, foraminifera, echinoderms and bulk) all have a relatively small and constant Li isotope fractionation factor of 3‰–6‰ with respect to Li in seawater (Marriott et al. 2004; Dellinger et al. 2018), although some vital effects in benthic foraminifera have been proposed.

Given lithium's long ocean residence time, marine carbonates cannot be used to reconstruct global weathering variation on Cenozoic glacial–interglacial timescales of tens of thousands of years. However, local silicate weathering changes can be reconstructed using speleothems (cave carbonates) because there is no buffering effect by seawater on speleothem source waters. In theory, the isotope ratios of soil pore waters, which reflect silicate weathering occurring above caves, should be archived in the carbonates precipitating from those drip waters in the caves. Data obtained from several caves in Israel show that δ^7Li was significantly lower in warmer interglacial periods compared to colder glacial periods (FIG. 5A). This suggests a correlation between δ^7Li and palaeo-temperatures that, in turn, suggests that changes in silicate weathering congruency and intensity are climate-dependent (Pogge von Strandmann et al. 2017c). During warmer and wetter interglacials, the lower, more rock-like, δ^7Li implies greater weathering congruency and lower W/D (relatively more primary mineral dissolution), and, hence, more efficient CO_2 drawdown. In contrast, in the colder and drier glacials, silicate weathering is more incongruent and produces a more intermediate W/D (relatively higher secondary mineral formation). Lithium isotopes suggest that at higher temperatures the solubility of both primary and secondary minerals increases, meaning that primary rocks dissolve faster and that there is less secondary mineral precipitation (Pogge von Strandmann et al. 2017c). In other words, higher temperatures lead to a lowering in W/D due to an increase in congruency (as shown by modern rivers) (FIG. 3A), which is coupled to increase in erosion (and, hence, D) due to higher runoff rates. This leads to greater cation fluxes to the oceans and to the sequestering of more carbon per unit of dissolved silicate rock. In contrast, colder temperatures decrease solubility, meaning that less dissolved material actually makes it to the oceans, decreasing CO_2 drawdown efficiency.

In order to examine more distant periods of climate change, ones that were wholly driven by changes in greenhouse gas concentration, marine carbonates must be used. However, lithium systematics in seawater are complicated by the fact that only part of the total Li flux is derived from weathering. For climatic perturbations lasting less than a few million years, it can be assumed that the mid-ocean ridge spreading rates (and hence hydrothermal input flux) and the fractionation factor during Li removal from seawater remain constant. This then leaves two unknowns: the riverine Li flux, and the riverine Li isotope ratio. In theory, these two variables can be obtained by taking a single measurement of seawater δ^7Li, because the correlation between Li yields and Li isotope ratios of rivers (FIG. 3) imposes an additional constraint on the Li budget. Data from rapid warming events, such as the hyperthermal oceanic anoxic event during the Cretaceous, show negative Li isotope excursions in marine carbonates (FIG. 5B). Different oceanic anoxic events exhibit different excursion sizes, but in all cases the negative direction of shift in δ^7Li is the same (Pogge von Strandmann et al. 2013; Lechler et al. 2015). A global cooling event, the end-Ordovician

Hirnantian glaciation shows a positive δ^7Li excursion (Fig. 5C) (Pogge von Strandmann et al. 2017a).

The directions of these shifts in marine carbonate δ^7Li replicate those observed in the speleothem record of warming and cooling across glacial–interglacial periods. This is also precisely what would be expected if the weathering thermostat is operating as predicted: during warm periods, weathering rates increase, and weathering becomes more congruent and efficient. The Li mobility increases relative to Ca (approaching unity in modern rivers that drain catchments with basaltic rocks) (Fig. 4), removing more Ca and, hence, more atmospheric CO_2 and stabilising the climate back to pre-excursion conditions. Equally, during cooling, silicate weathering becomes less congruent, retaining Li and other metals in secondary minerals, and, thus, becomes less efficient at removing CO_2, which, combined with a decrease in weathering flux, allows atmospheric pCO_2 and climate to recover.

A complication with interpreting palaeo-Li isotope records is that, although there is no reported temperature effect on fractionation during Li incorporation into carbonate minerals (Marriott et al. 2004), there does appear to be a temperature effect during uptake of Li by clays of an ~0.15‰ to 0.18‰ decrease in the amplitude of the mineral–solution fractionation per 1 K increase in the range of 0–40 °C (Pogge von Strandmann et al. 2017a). Thus, for example, ~1.5‰–1.9‰ of the ~12‰ variability in the speleothems is simply due to changing temperature with no other effect from weathering.

The temperature-dependent fractionation will also occur during weathering and clay formation on the continents, and during the removal of Li from seawater, which is also driven by clay formation. Thus, if there were (for simplicity's sake) a 5 °C warming for the continents and in the shallow and deep oceans, then this would result in −1.1‰ to −1.4‰ change in the δ^7Li of marine carbonates simply from changing temperature without any concomitant change in weathering congruence. Thus, of the 20‰ change in δ^7Li observed at the Cenomanian–Turonian oceanic anoxic event (Fig. 5B), approximately 1‰ may have been due to temperature. A similar effect on the much smaller (~4‰) excursion observed at the Aptian oceanic anoxic event (Fig. 5B) would, however, mean that ~25% of that signal is solely due to a change in temperature. In terms of the largest geologically known hyperthermal, the Permo-Triassic boundary, between half to all of the observed δ^7Li decline (Sun et al. 2018) could be due to the extreme increase in temperature. Equally, ~10%–13% of the δ^7Li increase during the Hirnantian cooling was also likely due to temperature. This interpretation becomes slightly more challenging for the entirety of the Cenozoic, for which a 9‰ δ^7Li rise has been reported (Hathorne and James 2006; Misra and Froelich 2012).

However, it is likely that between ~20%–40% of that signal is due to the steadily decreasing temperatures during that time (Gou et al. 2019).

CONCLUSIONS

Lithium and its isotopes are proving to be a useful tracer of chemical weathering processes, which are themselves a key control on climate, largely because the Li isotope ratio is solely controlled by the ratio of primary silicate rock dissolution to secondary mineral formation. Known as the weathering congruency, this ratio can provide abundant information on CO_2 drawdown processes. Application of this to the geological past has shown that weathering processes clearly respond to changing climates, and these weathering processes act to mitigate climate change on the order of tens of thousands of years. Broadly, Li isotopes have provided some of the first unequivocal evidence from the geological record for the operation of the weathering thermostat.

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FIGURE CAPTIONS

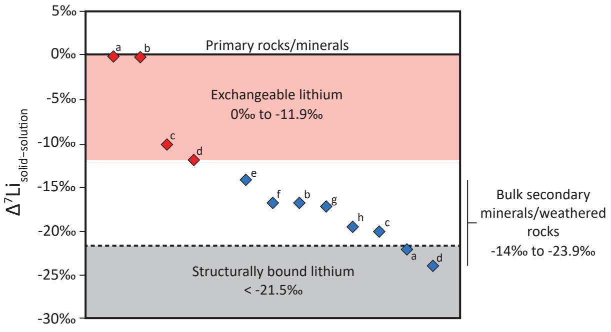

FIGURE 1 Compilation of published Li isotope systematics during the experimental formation of secondary silicates at temperatures <25 °C. Results show that exchangeable Li and structurally bound Li are isotopically distinct; exchangeable Li having a δ^7Li value relatively close to the fluid phase (red symbols), while structurally bound Li has a $\Delta^7\text{Li}_{\text{solid–solution}}$ value of < -21‰ (Hindshaw et al. 2019). Note that $\Delta^7\text{Li}_{\text{solid–solution}} = \delta^7\text{Li}_{\text{solid}} - \delta^7\text{Li}_{\text{solution}}$. Bulk secondary minerals contain a combination of exchangeable and structural Li, and so fall between these end-members. Reference letters on figure: a = Chan and Hein (2007); b = Hindshaw et al. (2019); c = Wimpenny et al. (2010a); d = Pogge von Strandmann et al. (2019); e = Pistiner and Henderson (2003); f = Vigier et al. (2008); g = Wimpenny et al. (2015); h = Millot et al. (2010).

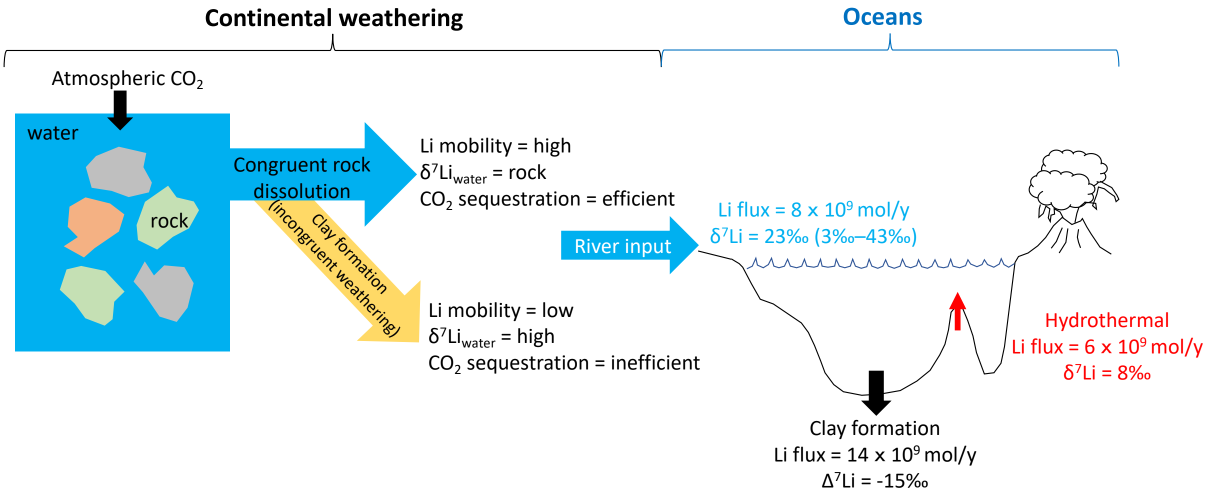

FIGURE 2 A cartoon showing the behaviour of Li isotopes during continental weathering, and its impact on the Li budget of the oceans, including the sources and sinks of Li. The δ^7Li is the deviation of the ^{7}Li/^{6}Li ratio from the NIST-8454 LSVEC standard (in parts per mil ‰); $\Delta^7\mathrm{Li}_{\mathrm{solid-solution}} = \delta^7\mathrm{Li}_{\mathrm{solid}} - \delta^7\mathrm{Li}_{\mathrm{solution}}$.

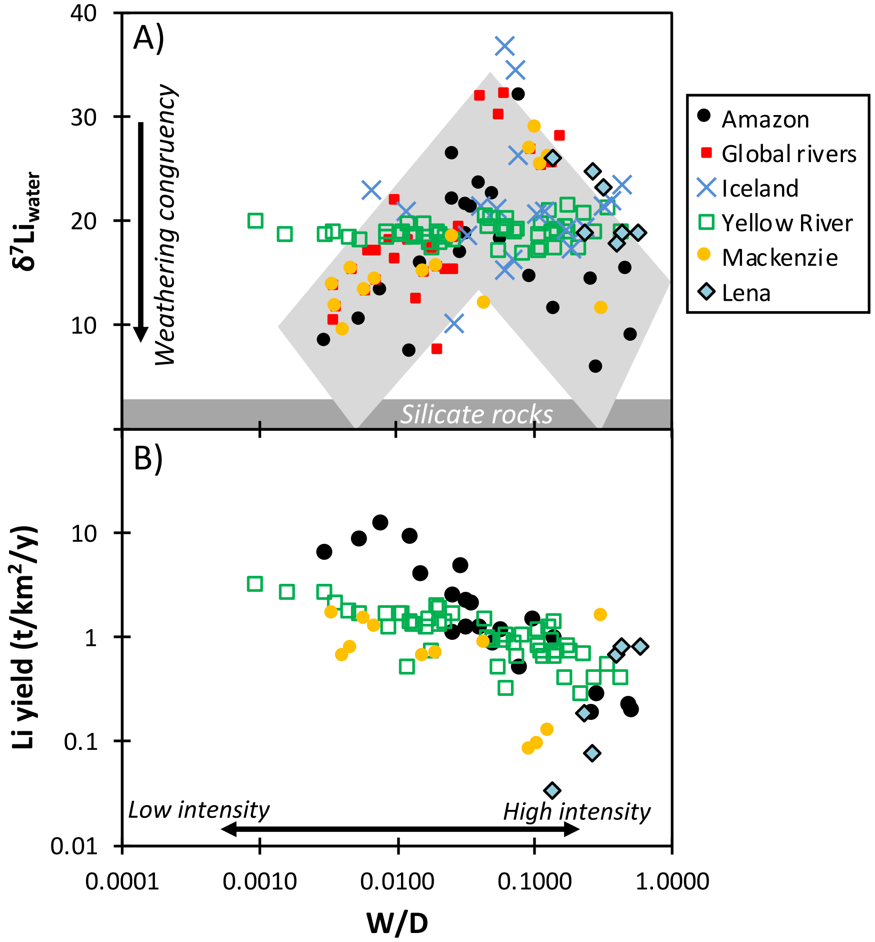

FIGURE 3 The behaviour of modern riverine δ^7Li as affected by different variables. Rivers are as follows: Amazon River (South America); global rivers together; Icelandic rivers; Yellow River (China); Mackenzie River (Canada); Lena River (Siberia, Russia). (**A**) Relationship between riverine δ^7Li and the weathering intensity (W/D = weathering rate/denudation rate). The grey field shows the original 'boomerang' shape proposed by Dellinger et al. (2015); this diagram also incorporates newer studies which make the relationship less clear. (**B**) Relationship between weathering intensity and Li yield, showing that most rivers exhibit a negative co-variation, meaning that terrains with a high weathering intensity (e.g., rain forests or stable tundra) have a negligible impact on the ocean mass balance. References: Huh et al., 1998; Pogge von Strandmann et al., 2006; Millot et al., 2010; Dellinger et al., 2015; Gou et al., 2019; Murphy et al., 2019.

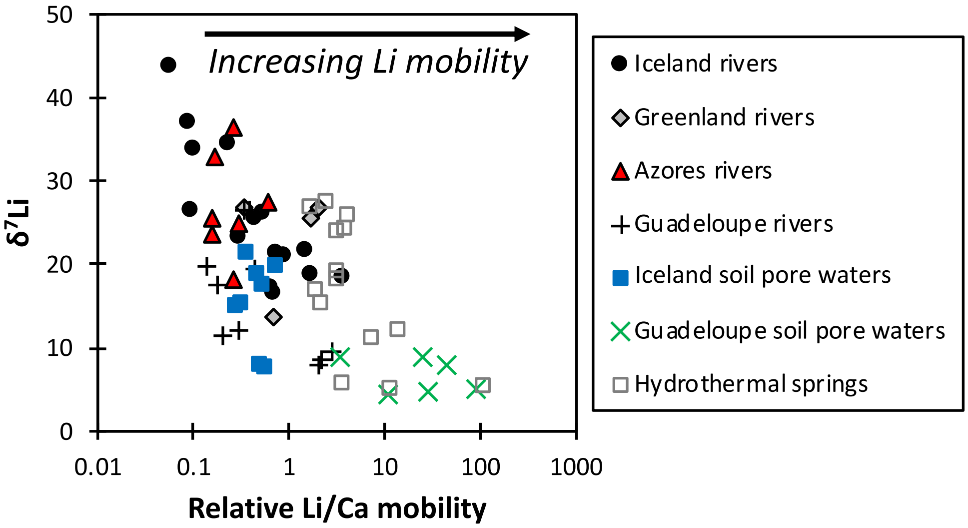

Figure 4 The relationship between the relative mobility of Li to Ca ($Li/Ca_{river}/Li/Ca_{rock}$) in rivers compared to their δ^7Li. The weathering mobility reflects the tendency of lithium to go either into solution (high mobility) or into secondary solids (low mobility) relative to calcium. The observed relationship suggests that δ^7Li can be used to recreate the behaviour of the calcium, which is critical to the carbon cycle, in the geological past.

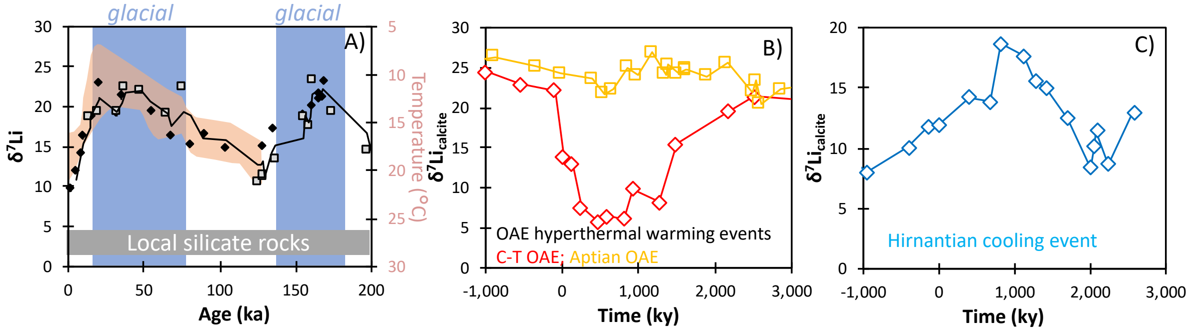

Figure 5 The behaviour of Li isotopes in calcitic archives of palaeo-fluids, and models of palaeo-fluid behaviour. (**A**) Lithium isotopes in Israeli speleothems, which act as local archives of silicate weathering and temperature proxies at glacial (dark bands) and interglacial (white bands) timescales. After Pogge von Strandmann et al. (2017c). (**B**) Lithium isotope data for two hyperthermal warming periods during the Cretaceous: the Cenomanian–Turonian oceanic anoxic event (OAE) (diamond symbols) and the Aptian oceanic anoxic event (square symbols). A negative δ^7Li excursion implies more weathering higher CO_2 drawdown. After Pogge von Strandmann et al. (2013) and Lechler et al. (2015).

(**C**) Lithium isotope data for a cooling period, here exemplified by the end-Ordovician Hirnantian glaciation. A positive δ^7Li excursion implies decreases weathering and CO_2 drawdown. AFTER POGGE VON STRANDMANN ET AL. (2017A). Combined, these data exhibit very strong evidence for the operation of the silicate weathering thermostat for controlling and mitigating climate.