

Introduction

Chemical weathering of continental rocks is one of the fundamental Earth system processes that affects climate and ocean chemistry. The weathering of silicate rocks removes carbon from the atmosphere, transporting it as alkalinity together with associated cations (most importantly Ca and Mg) to the oceans (Walker et al., 1981; West et al., 2005). The delivery of alkalinity enhances ocean uptake of CO₂ over centennial timescales and drives burial of carbonate and resulting CO₂ sequestration on timescales of thousands of years. At the same time, weathering provides critical nutrients to the coastal oceans, where they promote primary productivity. Burial of the resulting organic carbon is enhanced via association with clay minerals (Kennedy and Wagner, 2011), which are also provided by chemical weathering. In summary, silicate weathering is one of the primary controllers of the Earth's climate on various timescales.

It is not a surprise, then, that a great deal of research seeking to understand the evolution of Earth's climate, as well as the nutrient fluxes that support life, has focused on evaluating the processes that control weathering. Such controls are generally thought to be either climate-related (temperature, runoff, vegetation) or erosion-related (supply of fresh rock to be weathered) (West et al., 2005). The former would allow a temperature-controlled feedback on weathering (i.e. weathering accelerates during warming, removing more CO₂ and cooling the climate, and vice versa), known as the “weathering thermostat” that keeps the long-term climate relatively stable (Walker et al., 1981). The latter would drive long-term cooling processes when mineral supply increases, for example during mountain-building events (Raymo et al., 1988).

For this reason, a lot of effort has gone into characterizing and quantifying weathering processes both in the present and in Earth's geological past. Lithium isotopes have great potential in this field. Lithium is moderately incompatible during igneous processes and highly fluid mobile during surface processes (Penniston-Dorland et al., 2017; Tomascak et al., 2016). It tends to be concentrated in the continental crust relative to the mantle, and even more concentrated in clays and other secondary products of weathering (Teng et al., 2010).

Lithium has two stable isotopes (⁶Li and ⁷Li), the ratio of which, as for other stable isotope systems, is reported in the delta notation, as parts per thousand deviation from the L-SVEC standard: δ⁷Li. The pioneering work of Lui-Heung Chan, starting in the late 80s, showed that Li isotopes strongly fractionate during low-temperature clay formation. Chan focused on alteration of the oceanic crust and reverse weathering in the oceans, showing that clays preferentially take up the light Li isotope (⁶Li), driving residual waters (including the oceans) isotopically heavy (Chan et al., 1992). This concept was taken forward

into examining river waters by Youngsook Huh in the late 1990s. Her work showed that clay formation in riverine weathering environments acts the same way as it does in the oceans, driving river waters isotopically heavy (Huh et al., 2001; Huh et al., 1998). This isotopic fractionation, combined with the silicate origin of Li, is the basis for the increasing use of Li isotopes as a tracer of silicate weathering processes.

This chapter will discuss the possibilities for using Li isotopes as a weathering tracer in the modern environment, as well as some of the limitations. It will then examine the potential archives of Li for reconstructing past weathering processes, before moving on to examples of the use of Li in tracing weathering through climatic perturbations in the geologic past, focusing on times prior to the Cenozoic.

Lithium Isotopes as a Tracer of Silicate Weathering Intensity

Dissolved Riverine Fluxes of Lithium and Their Isotopic Composition

Primary silicate rocks have a relatively narrow range in $\delta^7\text{Li}$ (MORB: 3–5‰, continental crust: –10 to +10‰, with a mean of $0.6 \pm 0.6\text{‰}$ (Tomascak et al., 2016)). River waters, on the other hand, have a wide range of 2–44‰ (Dellinger et al., 2015; Huh et al., 1998; Murphy et al., 2019), universally isotopically heavier than the rocks they drain (Fig. 2). It has been demonstrated that carbonate weathering insignificantly affects Li dissolved in rivers, even in carbonate-dominated catchments (Kisakürek et al., 2005). Evaporites can, on occasion, affect local riverine Li isotope signals (Gou et al., 2019). Overall, Li isotopes are, for the most part, a selective tracer of silicate weathering processes, in contrast to isotopic systems such as Sr and Os. Although some Li isotope fractionation has been reported in some plants (Li et al., 2020), other studies report no effect (Clergue et al., 2015; Lemarchand et al., 2010). In all cases the lithium content in vegetation is low, and hence its effect on Li cycles is expected to be relatively small. No effect from phytoplankton on Li isotope ratios has been observed (Pogge von Strandmann et al., 2016), which overall gives Li isotopes an advantage over other many stable isotope tracers including Si, B, Mg and Ca isotopes.

Dissolution of rocks drives the $\delta^7\text{Li}$ of the waters towards the value of the rock (low $\delta^7\text{Li}$, as shown by scenario (i) in Fig. 1). In contrast, secondary mineral formation during weathering (including clays, zeolites and oxyhydroxides) drives water $\delta^7\text{Li}$ to higher values (scenarios (ii), (iii) and (iv) in Fig. 1). This means that the $\delta^7\text{Li}$ value of river waters is determined by the ratio of primary mineral dissolution to secondary mineral formation – a process known

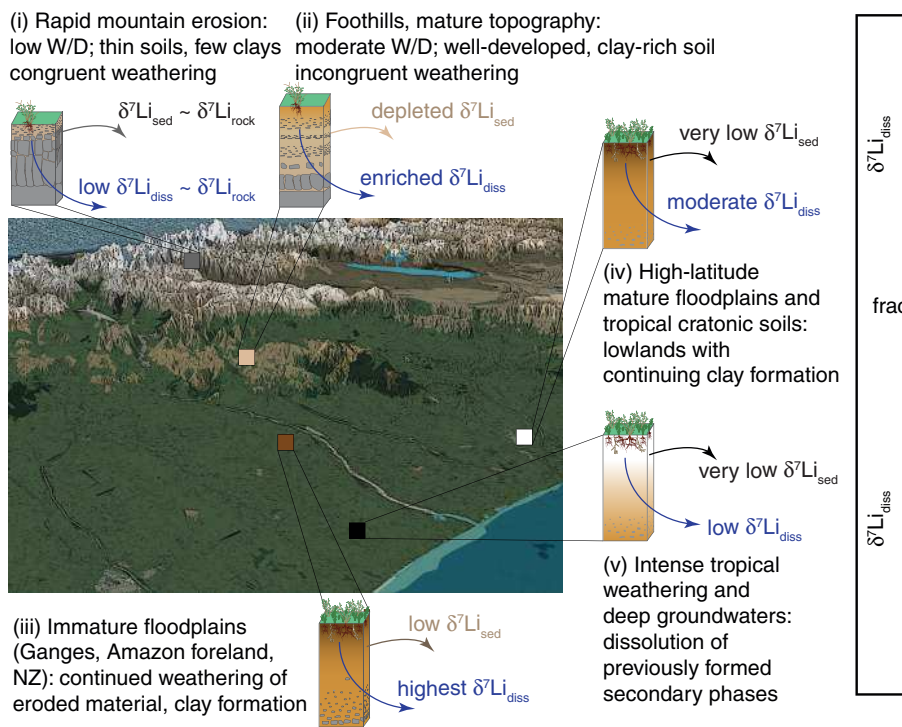


Figure 1 Cartoon showing the processes that fractionate dissolved and sediment $\delta^7\text{Li}$ during weathering in the text. The panels on the right show the positioning of the different scenarios on plots of dissolved vs. sediment $\delta^7\text{Li}$ (top), and as a function of the weathering intensity (W/D) (bottom). The x-axis represents the dissolved Li yield (e.g. in $\text{kg.km}^{-2}.\text{yr}^{-1}$) of the different scenarios.

as the weathering congruency (Misra and Froelich, 2012; Pogge von Strandmann and Henderson, 2015). When weathering is congruent, rocks dissolve with little secondary mineral formation, and water $\delta^7\text{Li}$ is low (close to the starting rock value). Conversely, when weathering is incongruent, secondary minerals form, and dissolved $\delta^7\text{Li}$ is high. A final scenario, where previously formed clays redissolve (v), drives $\delta^7\text{Li}$ low again.

Data from the Amazon River (Dellinger et al., 2015), Ganges River (Pogge von Strandmann et al., 2017b), High Himalayas (Bohlin and Bickle, 2019), New Zealand (Pogge von Strandmann and Henderson, 2015) and Yangtze (Ma et al., 2020) suggest that in areas where the exposure rate of fresh rock is rapid and water–rock contact time is relatively short (e.g. in mountains), riverine $\delta^7\text{Li}$ values are low and rocklike, as a result of relatively congruent weathering (Fig. 1). In contrast, on flatter floodplains, riverine $\delta^7\text{Li}$ increases, that is, weathering becomes more incongruent (Bagard et al., 2015; Dellinger et al., 2015; Pogge von Strandmann and Henderson, 2015), probably because there is longer water–sediment interaction time, leading to more clay mineral formation (Liu et al., 2015; Wanner et al., 2014).

These observations lead to the notion that riverine $\delta^7\text{Li}$ is related to the intensity of silicate weathering (Dellinger et al., 2015), that is, the ratio of the weathering rate (W) to the denudation rate (D). Denudation is the sum of chemical weathering and physical erosion – so weathering intensity effectively gives the ratio of chemical silicate weathering to physical erosion rates. Mountainous areas have high erosion rates, and hence a low W/D value (low weathering intensity) and a low riverine $\delta^7\text{Li}$ value, but also a high river Li yield (flux per unit area), because there are few clays to remove cations. Due to the lack of secondary mineral formation, river sediments have $\delta^7\text{Li}$ close to that of the original rock (Fig. 1i). As the downstream topography matures, such as in foothills with more developed soils, clays begin to form and water $\delta^7\text{Li}$ increases, while sediment $\delta^7\text{Li}$ begins to decrease (Fig. 1ii). Further downstream, immature floodplains have even higher weathering intensity, with relatively greater clay formation relative to rock dissolution, which drives riverine $\delta^7\text{Li}$ high, the sediment $\delta^7\text{Li}$ low and the dissolved Li yield lower (Fig. 1iii) (Dellinger et al., 2015; Pogge von Strandmann et al., 2020). High-intensity weathering regimes also exist. These tend to be supply-limited (i.e. little supply of primary rock to dissolve), such as in high-latitude and tropical lowlands (Fig. 1iv), and even more extremely in tropical rainforests (Fig. 1v). As weathering intensity increases, previously formed secondary clays start to be leached. The dissolved $\delta^7\text{Li}$ signal of these regimes is low again, but the Li yield is also extremely low, suggesting that these supply-limited regimes will have less direct influence on the mass balance of

seawater. River sediments have extremely low $\delta^7\text{Li}$ in these regimes. Combined, these different process regimes yield a “boomerang” shape when plotting dissolved $\delta^7\text{Li}$ against W/D. Importantly, the dissolved Li yield increases as W/D decreases (Fig. 1 insert; Fig 2a), and hence for the marine mass balance, scenarios (i), (ii) and (iii) are expected to be most relevant.

There is relatively little difference in the riverine $\delta^7\text{Li}$ ranges between tropical, temperate and polar rivers (Fig. 2) (Murphy et al., 2019), suggesting that the fractionating processes and fractionation factors remain broadly the same, regardless of climate. It is also noticeable that the general “boomerang” shape in the $\delta^7\text{Li}$ –W/D relationship is observed independently in rivers from different terrains, such as basaltic, polar and tropical rivers (Fig. 2), with higher $\delta^7\text{Li}$ in intermediate W/D regimes in all cases. Hence, the weathering regime appears to be the dominant control on the dissolved Li isotope ratio, and not lithology or climate.

Ocean Processes Affecting Lithium Isotopes

Lithium in modern oceans has a residence time of approximately 1 million years (Huh et al., 1998). Rivers make up ~60 per cent of the modern ocean inputs ($\sim 8 \times 10^9$ mol/yr) (Hathorne and James, 2006; Huh et al., 1998). The other major input is from high-temperature hydrothermal fluids at mid-ocean ridges (MORs), which, if modern oceans are at steady state, is $\sim 6 \times 10^9$ mol/yr. The Li sinks from seawater are uptake onto low-temperature clays that form during alteration of oceanic crust (AOC) and during the formation of marine authigenic aluminous clays (MAAC) (Chan et al., 1992; Hathorne and James, 2006; Misra and Froelich, 2012). The mean $\delta^7\text{Li}$ of the global riverine dissolved flux is ~23‰ (Huh et al., 1998), and the average hydrothermal input is ~8‰ (Penniston-Dorland et al., 2017). Combined, this would give seawater a $\delta^7\text{Li}$ value of ~17‰. However, the sink into clay minerals imparts a combined fractionation factor of 14–16‰, driving the modern seawater value to 31.2 ± 0.2 ‰ (Fig. 3a) (Jeffcoate et al., 2004).

It can be assumed that the hydrothermal $\delta^7\text{Li}$ value has remained constant through time, because it is effectively basalt weathering at high temperatures, which is characterized by low fractionation (Fig. 3b). If the hydrothermal flux through time can be extrapolated from MOR spreading rates, then rivers remain the primary unknown. In high-weathering-intensity regimes, the Li flux is low, and hence such a regime globally would mean that the hydrothermal input would dominate the seawater Li budget rather than the river $\delta^7\text{Li}$ directly (e.g. Seyedali et al., 2021). When weathering fluxes globally are

dominated by lower-intensity weathering, as is the case in the present day, river $\delta^7\text{Li}$ will have a direct influence on seawater $\delta^7\text{Li}$, and it appears that the river flux and isotope ratio are linked: when the isotope ratio is low (congruent weathering), the flux is high, while when there is more clay formation (incongruent weathering), the flux decreases and the isotope ratio increases (Fig. 1) (Dellinger et al., 2015). Hence, it may be possible to use this relationship to

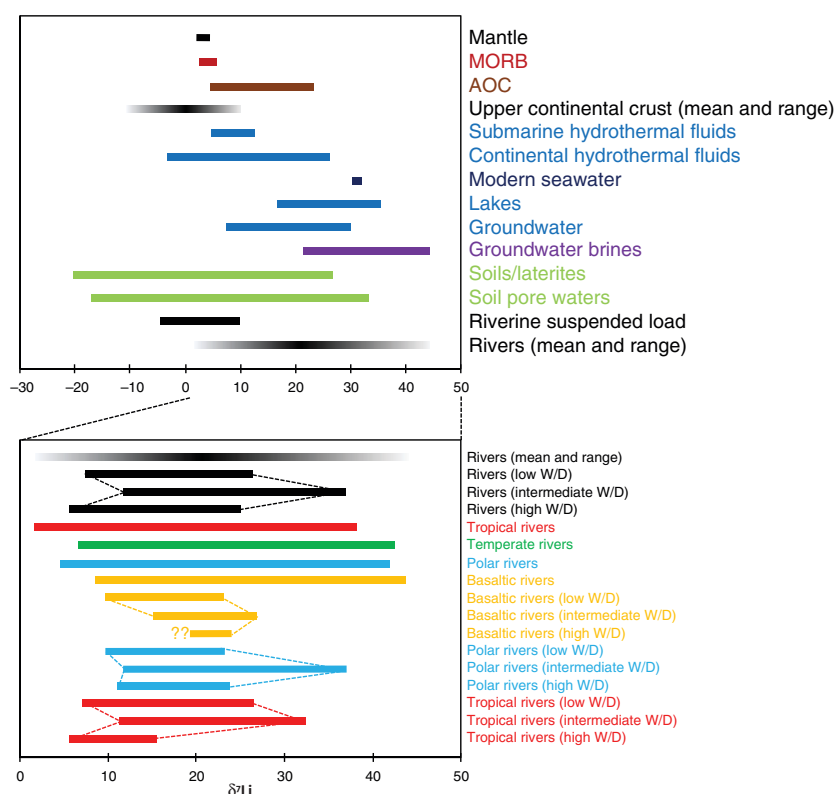


Figure 2 Ranges of $\delta^7\text{Li}$ of different solid and dissolved Li reservoirs (Penniston-Dorland et al., 2017). MORB = Mid-Ocean Ridge Basalt; AOC = Altered Oceanic Crust. The expanded plot shows the $\delta^7\text{Li}$ ranges for different river scenarios (Clergue et al., 2015; Dellinger et al., 2017; Dellinger et al., 2015; Gou et al., 2019; Huh et al., 2001; Huh et al., 1998; Kisakürek et al., 2005; Ma et al., 2020; Millot et al., 2010; Murphy et al., 2019; Pogge von Strandmann et al., 2016; Pogge von Strandmann et al., 2017b; Pogge von Strandmann and Henderson, 2015; Tomascak et al., 2016). It is noticeable that for each detailed regime (tropical, polar and basaltic rivers), intermediate W/D rivers range to higher $\delta^7\text{Li}$ values than low or high W/D rivers. We note that very few basaltic rivers exist with high W/D, and hence this is denoted with ‘??’.

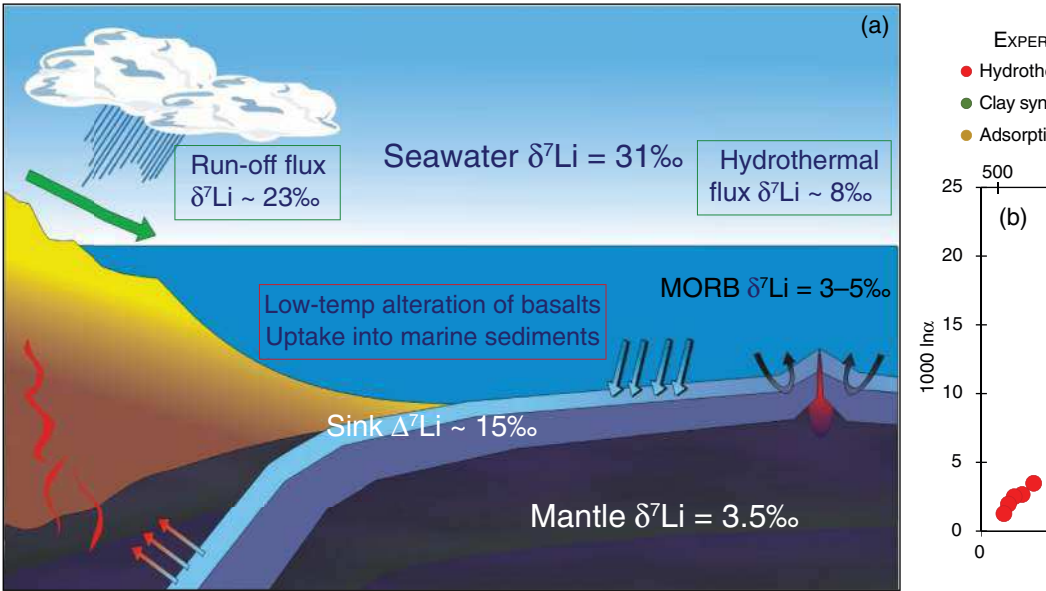


Figure 3 (a) The seawater mass balance of Li, showing the primary sources and sinks, and the dependence of Li isotope fractionation, based on experiments and field measurements (Hindshaw et al., 2020; Pistiner and Henderson, 2003; Pogge von Strandmann et al., 2019a; Wimpenny et al., 2015; data point is based on the global riverine mean (Huh et al., 1998)).

extrapolate past changes in weathering flux and processes from the seawater isotope composition.

Because of the temperature dependence of the fractionation factor (Li and West, 2014; Vigier et al., 2015), the fractionation factors associated with AOC and MAAC are different. Therefore ‘sink-shifts’ that change the proportion of AOC and MAAC (i.e. changes in global fluxes of reverse weathering in marine sediments or weathering of seafloor basalts) can also potentially alter the seawater isotope ratio (Coogan et al., 2017; Li and West, 2014).

Methods and Archive Materials

Sample Preparation and Mass Spectrometry

In early studies, Li isotope ratios were measured by thermal ionization mass spectrometry (TIMS) (Chan et al., 1992). However, high-precision TIMS analyses of a system with only two stable isotopes are challenging. Hence, for the past 25 years, Li isotope ratios have been analysed by multi-collector ICP-MS. The latest generation of mass spectrometers can analyse less than 0.5 ng of Li to a high precision (Bohlin et al., 2018; Jeffcoate et al., 2004; Pogge von Strandmann et al., 2019a), which allows analyses of almost all materials (e.g. carbonates, waters, silicates, plants). Some studies have used quadrupole ICP-MS because this requires less sample on the whole (0.2–2 ng Li), but precision is considerably worse ($\leq \pm 1.5\%$) (Liu and Li, 2019; Misra and Froelich, 2009), compared to $\leq \pm 0.5\%$ by multi-collector ICP-MS (see below). Purification chemistry involves cation exchange columns, where care must be taken to 1) remove all matrix from the purified solution, and 2) achieve as close to 100% column yields as possible. This is because Li isotopes fractionate on the columns, so low yields will cause unquantifiable isotope fractionation. Hence, yields must always be monitored for each sample, by collecting elute before and after the Li collection bracket and analysing for Li content. Yields lower than 100% will cause reproducibility to worsen, observationally by $\sim 1.7\%$ per 1% loss of yield (Wilson, pers. comm).

Isotopic analysis is conducted by sample-standard bracketing, either using the L-SVEC standard, or the newer, virtually identical, IRMM-016 standard (Jeffcoate et al., 2004; Pogge von Strandmann et al., 2019a). The long-term external error should always be quantified, by analysing the same natural standard (e.g. seawater, or international rock standards) every session. Long-term analysis (i.e. up to 50 or 100 separate sessions of purification chemistry and analysis) can yield 2sd errors of $< 0.5\%$ on modern mass spectrometers (reported down to $\pm 0.3\%$ on some machines over periods of > 5 years (Jeffcoate et al., 2004; Pogge von Strandmann et al., 2011)).

In terms of examining Li isotope behaviour in the geological record, two types of archive have been used. The main one is marine carbonates: bulk, foraminifera, brachiopods, belemnites, corals and bivalves. Inorganic carbonates (speleothems) also have been used. The second, less well-established archive is clays, either detrital or authigenic.

Carbonates

Different biogenic carbonates (e.g. foraminifera, brachiopods) have different partition coefficients for Li that are also different from those for inorganic carbonates (Dellinger et al., 2018). It has also been shown that the uptake of Li into inorganic carbonates is strongly temperature-dependent and also may be affected by the solute concentration, ionic strength and pH (Marriott et al., 2004a; Marriott et al., 2004b). For this reason, although studies typically report Li/Ca ratios, they are rarely used for interpretational purposes.

In contrast, some carbonates exhibit narrow ranges in Li isotope fractionation (Dellinger et al., 2018). Modern bulk aragonites have a fractionation factor of $\Delta^7\text{Li}_{\text{aragonite-seawater}} \sim 10\text{‰}$ (Gabitov et al., 2011; Marriott et al., 2004b; Pogge von Strandmann et al., 2019b), in agreement with inorganic aragonites (Marriott et al., 2004b; Pogge von Strandmann et al., 2019b). Similarly, biogenic aragonites such as corals (mean $\Delta^7\text{Li}_{\text{aragonite-seawater}} = -12 \pm 2\text{‰}$, 1σ , (Bastian et al., 2018; Marriott et al., 2004a; Marriott et al., 2004b; Rollion-Bard et al., 2009)) and aragonitic mollusks (mean $\Delta^7\text{Li}_{\text{aragonite-seawater}} = -13 \pm 3\text{‰}$, 1σ (Bastian et al., 2018; Dellinger et al., 2020)) have $\Delta^7\text{Li}$ similar to inorganic aragonite ($\sim 10\text{‰}$). Calcites tend to have lower fractionation factors than aragonite, with $\Delta^7\text{Li}_{\text{calcite-seawater}} \sim 6\text{‰}$ in modern core tops. High-Mg calcites have fractionation factors between the two (Dellinger et al., 2018).

Bulk carbonates, foraminifera and brachiopods (and potentially belemnites) appear to exhibit a fairly narrow range in fractionation factor (Dellinger et al., 2018; Ullmann et al., 2013), although there have been contrasting reports on foraminifera (Fig. 4). Planktic foraminifera have $\delta^7\text{Li}$ closer to seawater (i.e. less negative $\Delta^7\text{Li}_{\text{calcite-seawater}}$) compared to benthic foraminifera (Dellinger et al., 2018; Roberts et al., 2018), and there appear to be species-specific vital effects (Hathorne and James, 2006), although this is disputed (Misra and Froelich, 2012). There have also been reports of pH effects (Roberts et al., 2018), although again this is disputed (Vigier et al., 2015). The conflicting interpretations suggest that there may be complications associated with using foraminifera as a Li isotope archive – although Cenozoic $\delta^7\text{Li}$ records from foraminifera have been independently replicated in brachiopods (Misra and Froelich, 2012; Washington et al., 2020), and in-depth studies similar to those

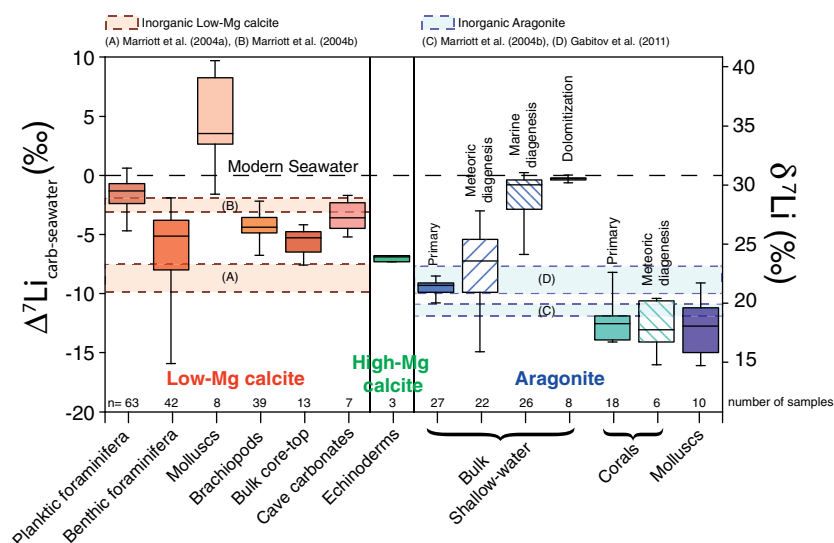


Figure 4 Plot of $\delta^7\text{Li}$ and $(\Delta^7\text{Li})_{\text{carb-seawater}} = \delta^7\text{Li}_{\text{carbonate}} - \delta^7\text{Li}_{\text{seawater}}$ ranges in modern carbonates, including the effect of diagenetic recrystallization of aragonite to low-Mg calcite and dolomite (see text for references). The boxes reflect the interquartile range with the median shown as the line and the extreme data points as the whiskers. The number of samples is indicated at the bottom of the figure. For biogenic carbonates, the number of samples corresponds to the number of different specimens analysed.

on foraminifera will need to be conducted on other types of biogenic carbonates. Bulk carbonates appear to be fairly robust archives of seawater $\delta^7\text{Li}$ (Dellinger et al., 2020; Pogge von Strandmann et al., 2019b), and within such carbonates the proportion of foraminifera to coccoliths does not affect the overall $\delta^7\text{Li}$ value, suggesting that both have similar overall fractionation factors (Pogge von Strandmann et al., 2019b). Finally, it appears that there are no temperature effects on the Li isotope fractionation factor in either inorganic or biogenic calcites (Dellinger et al., 2018). In contrast, molluscs appear to exhibit highly variable fractionation (on occasion, even in different layers from the same shells) and may not be so useful as a Li isotope archive (Dellinger et al., 2018).

Carbonate diagenesis can preserve or change the primary $\delta^7\text{Li}$ of carbonate depending upon the composition of the original carbonate (aragonite or calcite) and of the diagenetic fluid (marine or meteoric), and also depending on diagenesis style (fluid or sediment buffered) (Dellinger et al., 2020). Early marine diagenetic recrystallization of aragonite to calcite under fluid-buffered conditions (typical of platform top margins), as well as dolomitization, result in