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Lithium isotopes in dolostone as a palaeo-environmental proxy – An experimental approach

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Abstract

Lithium (Li) isotopes in marine carbonates have considerable potential as a proxy to constrain past changes in silicate weathering fluxes and improve our understanding of Earth's climate. To date the majority of Li isotope studies on marine carbonates have focussed on calcium carbonates. Determination of the Li isotope fractionation between dolomite and a dolomitizing fluid, would allow us to extend investigations to deep times (i.e., Precambrian) when dolostones were the most abundant marine carbonate archives. Dolostones often contain a significant proportion of detrital silicate material, which dominates the Li budget, thus pre-treatment needs to be designed so that only the isotope composition of the carbonate-associated Li is measured. This study aims to serve two main goals: (1) determining the Li isotope fractionation between Ca-Mg carbonates and solution and (2) to develop a method for leaching the carbonate-associated Li out of dolostone while not affecting that contained within the detrital portion of the rock.

We synthesized Ca-Mg carbonates at high temperature (150 to 220 °C) and measured the Li isotope composition (δ^7Li) of precipitated solids and their respective reactive solutions. The relationship of the Li isotope fractionation factor with temperature was obtained: $10^3 ln\alpha_{prec-sol} = -\frac{(2.56 \pm 0.27)\times 10^6}{T^2} + (5.8 \pm 1.3)$

Competitive nucleation and growth between dolomite and magnesite were observed during the experiments, however, without notable effect of their relative proportion on the apparent Li isotope fractionation. We found that Li isotope fractionation between precipitated solid and solution is much greater for Ca-Mg carbonates than for Ca carbonates. If the seawater temperature can be estimated independently, the above equation could be used in conjunction with the Li isotope composition of dolostones to derive those of the precipitating solutions and hence make inferrals about the past oceanic Li cycle.

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In addition, we also conducted leaching experiments on a Neoproterozoic dolostone and a Holocene coral. Results show that leaching with 0.05M HCl or 0.5% acetic acid at room temperature for 60 min releases Li from the carbonate fraction without significant contribution of Li from the siliciclastic detrital component.

These experimental and analytical developments provide a basis for the use of Li isotopes in dolostones as a palaeo-environmental proxy, which will contribute to further advance our understanding of the evolution of Earth's surface environments.

1. Introduction

Lithium isotopes in marine carbonates have emerged as a powerful proxy to understand the evolution of the ocean chemistry, past silicate weathering fluxes and their links to global climate. Application to calcium carbonates (e.g. foraminifera, limestone) has shed some light on hotly debated topics such as, the evolution of Earth's climate during the Cenozoic (Misra and Froelich, 2012;Li and West, 2014;Wanner et al., 2014;Vigier and Goddéris, 2015;Hathorne and James, 2006), oceanic anoxic events (Pogge von Strandmann et al., 2013b;Lechler et al., 2015) and Palaeozoic glaciation (Pogge von Strandmann et al., 2017). Although post-depositional alteration can play an important role in the formation of dolomite (Geske et al., 2012;Burns et al., 2000), the application of Li isotopes to marine dolostone could help to extend our understanding of the geochemical evolution of ancient seawater, particularly in early Earth geological history (i.e., Precambrian).

While data of Li isotopic fractionation during calcite precipitation has been relatively well constrained (Marriott et al., 2004a;Marriott et al., 2004b;Dellinger et al., 2018), there is currently no data available pertaining to Li isotope fractionation during dolomite formation. Therefore in this study, precipitation experiments were carried out at various temperatures

(150 – 220 °C), where the Li isotopic composition of the precipitated solids and their respective reactive solutions were subsequently measured in order to determine the fractionation factor between the fluid and solid phases. The experiments were conducted at elevated temperatures due to the impossibility of synthesizing well-ordered dolomite at ambient temperatures on a laboratory time scale (Land, 1998;Arvidson and Mackenzie, 1999;Gregg et al., 2015).

One major difficulty with interpreting Li isotopes in dolostone is that they often contain a significant proportion of siliciclastic material (e.g. detrital micas and/or authigenic clay minerals). The abundance of Li in silicate minerals is higher than in carbonates (typically more than two orders of magnitudes), thus sample pre-treatment must be undertaken to extract Li from only the carbonate fraction (Pogge von Strandmann et al., 2013b). Therefore, in this study we have tested various pre-treatment methods in order to refine a procedure that faithfully yields the isotopic composition of the carbonate-associated Li fraction in dolostones exclusively.

2. Methods

2.1. Ca-Mg carbonate synthesis

Synthesis of Ca-Mg carbonates was conducted in Teflon-lined, stainless steel autoclaves at temperatures of 150, 180 and 220°C (± 5°C) through the reaction of ~300 mg of powdered inorganic aragonite (speleothem aragonite; in-house mineral collection at Graz University of Technology) with an artificial brine solution containing 200 mM Mg, 0.245 mM Li and 50 mM $NaHCO_3$. The reactive fluid was prepared by dissolving analytical grade $MgCl_2 \cdot 6H_2O$ (Roth; ≥99 %, p.a, ACS), LiCl (Merck; ≥99 %, ACS, Reag. Ph Eur) and $NaHCO_3$ (Roth; ≥99.5 %, p.a., ACS, ISO) in ultrapure water (Millipore Integral 3: 18.2 $M\Omega \cdot cm^{-1}$). The stock solution was subsequently filtered through a 0.45 µm cellulose acetate membrane filter

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(Sartorius). The reagent inorganic aragonite was milled to a grain size < 20 µm using a vibratory mill (McCrone Micronizing Mill) for 10 minutes and collected by dry sieving prior to use in the experiments. Autoclaves were sealed immediately after mixing the inorganic aragonite with the appropriate volume of stock solution and placed in preheated ovens.

Samples were taken from the autoclaves at each operating temperature after a given reaction time (Table 1), including repeat samples. Upon removal from heat, the reactors were quenched and the samples were subsequently filtered through a 0.2 µm cellulose acetate membrane (Sartorius) using a vacuum filtration unit. Samples were than thoroughly rinsed with ultrapure water (Millipore Integral 3: 18.2 $M\Omega \cdot cm^{-1}$) to remove any soluble salts from the matrix and subsequently dried in an oven at 40°C overnight to be ready for solid phase analysis. An aliquot of the reactive fluid was acidified to a ~3 % HNO_3 matrix for elemental and Li isotope analyses using Merck® Suprapur™ HNO_3.

2.2. Leaching experiments

A Neoproterozoic dolostone from the Nuccaleena Formation (Flinders Ranges, South Australia) and a Holocene *Porites* coral were used to evaluate the effect of different leaching protocols on the measured Li isotope composition. Samples were ground to a powder using a TEMA chromium-ring grinding mill. An aliquot of powdered dolostone was used for mineralogy quantification performed using X-ray diffraction. Another aliquot of one gram was placed in a clean polypropylene centrifuge tube and 20 mL of solution was added. Leaching was tested with hydrochloric acid (HCl) of varying concentrations (0.05M, 0.1M, 0.15M, 0.2M, 0.3M, 0.5, 0.8M, 1M, 6M) and acetic acid (HAc) at concentrations of 0.5 and 2 %. Acetic acid and HCl solutions were prepared from trace grade glacial acetic acid (Merck® Suprapur™) and ultra-trace grade 30% HCl (Merck® Ultrapur™). In each case, the powder and solution reacted at room temperature for one hour, while continuous mixing was achieved

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with an orbital shaker. The supernatant fluid was separated by centrifugation at 4000 rpm for 15 minutes. After separation, the supernatant fluid was extracted using acid-washed disposable pipettes. An aliquot containing ~60 ng of Li was subsequently sampled for cation exchange chromatography.

2.3. Mineralogy quantification

Quantitative phase contents of the synthesized solids were determined by powder X-ray diffraction (XRD) of finely ground aliquots performed on a PANalytical X'Pert PRO diffractometer outfitted with a Co-target tube (operated at 40 kV and 40 mA), a high-speed Scientific X´Celerator detector, 0.5° antiscattering and divergence slits, spinner stage, primary and secondary soller and automatic sample changer. Samples were finely ground by hand using a mortar and pestle prior to analysis and were loaded in a random orientation using the top loading technique. The samples were analysed over the range 4 – 85° 2θ with a step size of 0.008° 2θ and a count time of 40 seconds/step. Mineral quantification was obtained by Rietveld Refinement of the XRD patterns using the PANalytical X'Pert HighScore Plus Software and its implemented pdf-2 database.

2.4. Elemental concentrations

Lithium concentrations of solutions were analysed in acidified (0.3 M HNO_3) aliquots by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a PerkinElmer Optima 8300. A range of in-house and NIST 1640a standards were measured at the beginning and end of a sample series, with an estimated analytical error (2σ, 3 replicates) of ±3% relative to the standard. For synthesized solids, an aliquot of each precipitate was dissolved in 0.9 M HNO_3 at 70°C for 12 hours in an ultrasonic bath to ensure complete digestion. Subsequently Li concentrations were analysed by ICP-OES following the same method as for the aqueous solutions.

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151 *2.5. Lithium isotopes*

152 Sample preparation for Li isotope measurement was undertaken in a Class 100
153 cleanroom at the Wollongong Isotope Geochronology Laboratory, University of Wollongong.
154 For mineral precipitates, the samples were ground using a mortar and pestle before aliquots of
155 <0.05 g were weighed. The sample aliquots were dissolved in dilute HNO_3 (Ultrapur™) and
156 0.2 mL of concentrated H_2O_2 (31% Ultrapur™) was added to ensure the breakdown of organics.
157 The samples were then placed on a hotplate overnight at 50°C to reflux and ensure complete
158 digestion of the solids. After complete digestion of the solids, Li concentrations were measured
159 by Quadrupole ICP-MS. An aliquot of the digested samples containing ~60 ng of Li was then
160 dried down and taken up into 1.5 mL of Ultrapur™ 1 M HCl. Samples were then treated with
161 a two-step cation exchange chromatography procedure, following the methods of Balter and
162 Vigier (2014) to separate Li from the sample matrix. For Li isotope measurements it is crucial
163 that 100% of Li is recovered from the cation exchange columns as δ^7Li compositions have been
164 shown to vary by up to ~200 ‰ during chromatography due to incomplete recovery (Pistiner
165 and Henderson, 2003). It is also crucial to remove elements such as Na and Ca as large amounts
166 of Ca can coat the cones of the mass spectrometer while Na can reduce Li ionisation in the
167 plasma, and cause further Li isotopic fractionation during analysis (James and Palmer, 2000).
168 For chromatography, 30 mL Savillex micro columns (6.4 mm internal diameter, 9.6 cm outside
169 diameter, 25 cm capillary length) were used together with Biorad AG50W-X8 resin as the
170 cation exchange medium (volume = 3.06 cm^3). The columns were calibrated with seawater
171 prior to treating the samples to verify that the procedure yielded 100% of the Li (Table A1).
172 The columns were cleaned with 30 mL of 6M HCl, rinsed with ~2 mL of MilliQ™ water and
173 conditioned using 8 mL of titrated, 1 M Ultrapur™ HCl before sample loading. To ensure the
174 complete removal of interfering elements from the Li, samples were passed through the
175 columns twice; after the first elution, the samples were dried down, taken up in 1 M HCl and

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reloaded into the columns. The Li elutions were dried down and subsequently re-dissolved in Ultrapur™ 0.3M HNO_3 ready for isotopic analysis. Lithium isotope ratios were measured by multi collector inductively coupled plasma mass spectrometry (MC ICP-MS) on a ThermoFisher Neptune Plus at the Wollongong Isotope Geochronology Laboratory, University of Wollongong. A 30 ppb solution of IRMM-16 Li isotopic standard was used at the start of each measurement session to tune the instrument. An intensity of ~1 V was routinely obtained for ^7Li, while the background ^7Li intensity was between 5-30 mV. During analysis, standard bracketing, using IRMM-16 as the primary standard, was applied to correct the measured $^7Li/^6Li$ values for mass bias (Flesch et al., 1973). Instrumental blanks were measured before each sample so that background signal could be accounted for. The $^7Li/^6Li$ ratios were converted to δ^7Li values using L-SVEC as reference to (Carignan et al., 2007) (Eq.(1)).

$$\delta^7Li = \left\{ \frac{\left(^7Li/^6Li\right)_{sample}}{\left(^7Li/^6Li\right)_{L-SVEC}} - 1 \right\}. 1000 \quad (1)$$

The accuracy of analysis was assessed using synthetic solutions Li6-N and Li7-N (Carignan et al., 2007) as secondary standards every 6 samples. The accuracy of chromatography and analysis was assessed using a seawater standard (Table A1). External uncertainty on δ^7Li compositions (at 2σ level) was evaluated by measurement of precipitated solids and solutions from repeat experiments at 150 ºC (n = 3) and 180 ºC (n = 2), amounting to 0.86 ‰ for precipitated solids and 1.2 ‰ for solutions.

3. Results

3.1. Precipitation experiments

Synthesized minerals are comprised of dolomite and magnesite (Table 1); their relative amount shows a relationship with temperature, with higher reaction temperatures yielding more magnesite and less dolomite compared to lower temperatures (Fig. 1). The Li concentration of

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reactive solutions ranges from 1,666 to 3,695 µg.L^{-1} (Table A2) and shows no correlation with reaction temperature. On the contrary, the Li concentration of precipitated solids decreases with increasing temperature (from 25.9 to 8.20 ppm; Table A2).

The δ^7Li of the initial reactive solution is 7.85 ‰ (Table 2). After reaction the δ^7Li value of the solution (δ^7Li_{sol}) vary between 7.87 and 9.48 ‰, while the δ^7Li values in the precipitated solid (δ^7Li_{prec}) range from -0.63 to 3.08 ‰ (Table 2). The precipitated solids are 4.79 to 8.6 ± 0.6 ‰ (1σ; n=3) lighter than the solution, and this difference (termed $10^3.ln\alpha_{prec\text{-}sol}$) increases with decreasing temperature (Table 2).

The Li isotope fractionation factor between the precipitated solid and the solution (calculated as $10^3.ln\alpha_{prec\text{-}sol} = 10^3.ln(1000+\delta^7Li_{prec}/1000+\delta^7Li_{sol})$) displays values within error of each other, despite a wide range of concentrations of dolomite or magnesite precipitated (Fig. 2). Similarly, there is no relationship between the Li distribution coefficient between precipitated solid and solution ($D_{[Li]prec\text{-}sol} = [Li]_{prec}/[Li]_{sol}$), where $[Li]_{prec}$ and $[Li]_{sol}$ are the Li concentrations in the precipitated solid and the solution, respectively), and mineral abundances (Fig. 3). Conversely, there is a positive relationship between $10^3.ln\alpha_{prec\text{-}sol}$ and the reaction temperature (Fig. 4).

3.2. Leaching experiments

For the dolostone, δ^7Li values of the leaching solution decrease from 9.5 to 4.0 ‰, with increasing HCl concentration (Table 3; Fig. 5a). The Al/Mg ratio in the leaching solutions increases at HCl concentrations >0.8 M from ~0.0009 to 0.01 (Fig. 5b). The leaching solutions show an increase in Li/Ca ratio from $6.3x10^{-6}$ to $25x10^{-6}$ with decreasing δ^7Li (Fig. 6a). Furthermore, the Li/Mg ratio increases from 5 to $12x10^{-5}$ with increasing δ^7Li (Fig. 6b). Very little carbonate minerals other than dolomite (1.1 wt % calcite and 2.1 wt % ankerite) are present in the dolostone sample, and the silicate minerals represents ~26 wt % of the sample

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(14 wt % quartz, 6.2 wt % muscovite and 5.1 wt% albite) (Table A3). Leaching with acetic acid yields δ^7Li compositions in the solution similar to values observed in very dilute HCl (Fig. 7). The δ^7Li of the 2% HAc leaching solution is lower than that of the 0.5 % HAc leaching solution.

For the Holocene coral, the sample is dominated by aragonite (Table A4) and the leaching solution shows a similar trend to that from the dolostone leaching experiment, with δ^7Li values decreasing from 20.1 to 16.9 ‰ with increasing HCl concentration (Table 3; Fig. 8). Total dissolution of the coral yields a δ^7Li value in the solution of 20.6‰, which is within error of the values determined for HCl leaching experiments with acid concentrations <0.5 M (Table 3).

4. Discussion

4.1. Lithium isotope fractionation during inorganic precipitation of Ca-Mg carbonate

The precipitated solids of the synthesis experiments consist of Mg-Ca carbonates with variable amounts of dolomite ($CaMg(CO_3)_2$) and magnesite ($MgCO_3$) (Table 1). The δ^7Li composition of the precipitated solid is systematically isotopically lighter than that of the reactive solution (Table 2). These results are consistent with previous experimental work on Li isotope fractionation during calcite precipitation (Marriott et al., 2004a;Marriott et al., 2004b), which showed that the Li isotope composition of calcite is isotopically lighter than that of the corresponding fluid. Teng et al. (2008) have suggested that the incorporation of ^{6}Li over ^{7}Li in minerals compared to the growth solution reflects a change from four- to six-fold coordination of Li during mineral growth. In calcite from foraminifera and aragonite from corals, δ^7Li values are respectively about 3 and 11 ‰ lower compared to their growth solutions (Marriott et al., 2004a). Here, the precipitated minerals are 4.8 to 8.6 ± 0.6 ‰ (1σ; n=3) lighter than the solution. This difference increases with decreasing temperature, as would be expected for

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stable isotope fractionation at equilibrium. As our experiments were conducted at high temperatures, the system can be reasonable considered to be approaching isotope equilibrium conditions as fractionation scales with the inverse of reaction temperature (see Fig. 3). Marriott et al. (2004a) suggested that Li isotope fractionation probably occurs at equilibrium even at lower temperatures for several reasons: (i) kinetic fractionation would probably be much greater (up to ~80 ‰) than that observed (both in calcite and in Ca-Mg carbonate), thus requiring boundary layer processes or the presence of a back-reaction, for which there is no evidence. (ii) Observed isotopic fractionation between calcite and growth solution, as well as between Ca-Mg carbonate and growth solution, are consistent with ab initio calculations for equilibrium fractionation (Yamaji et al., 2001). (iii) Lithium isotope fractionation between calcite and growth solution is relatively constant across a wide range of concentration of Li incorporated in calcite (this was not tested here).

Although Li isotope fractionation and the magnesite:dolomite ratio of the precipitated solid both co-vary with temperature, there is no relationship between the δ^7Li composition of the precipitate solids or that of their respective reactive solutions and the magnesite:dolomite ratio of the precipitate solid (not shown). This suggests that the nature of the Ca-Mg carbonate precipitated does not have a significant influence on Li isotope fractionation. This hypothesis is supported by the absence of significant variation in the Li isotope fractionation factor ($10^3\ln\alpha_{prec\text{-}sol}$; Fig. 2) or the Li distribution coefficient between solid and solution ($D_{[Li]prec\text{-}sol}$; Fig. 3), despite a wide range of mineral abundances. For instance, most $10^3\ln\alpha_{prec\text{-}sol}$ values are within error of each other while dolomite concentration varies from 17 to 82 wt % (Fig. 2a). This differs from what Marriott et al. (2004b) observed for calcium carbonates at ambient temperature, where the isotopic fractionation is aragonite (~11 ‰) was much greater than in calcite (~3 ‰).

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The relationship between $10^3\ln\alpha_{prec\text{-}sol}$ and temperature can be used to estimate the temperature dependency for Li isotope fractionation between Ca-Mg carbonate and solution. Using average $10^3\ln\alpha_{prec\text{-}sol}$ values for each reaction temperature, we obtain the following temperature-dependent relationship:

$$10^3 ln\alpha_{prec-sol} = -\frac{(2.56 \pm 0.27)\times 10^6}{T^2} + (5.8 \pm 1.3) \quad (2)$$

where T is the temperature of precipitation in K.

Using Eq. (2), the Li isotopic fractionation at 25 ºC is estimated to be -23.0 ± 5.7 ‰ (1σ) (Fig. 4). Although there is a large error on this estimate, our results suggest that Li isotopic fractionation during dolomite/magnesite precipitation is significant larger than during calcium carbonate precipitation (Marriott et al., 2004a).

If the temperature of the solution from which dolomite is precipitated can be known or calculated (e.g., via clumped Δ_{47} proxy, Winkelstern et al. 2016), the above relationship in combination with the δ^7Li of marine dolostone could be used to determine the Li isotopic composition of the precipitating palaeo-solution , e.g. brine or seawater. It is important to note that the applicability to natural systems may be limited to dolomite precipitated inorganically, as it has been proposed that bacterial mediation could play a major role in the precipitation of dolomite from natural waters at ambient conditions (Vasconcelos et al., 1995). In addition, marine dolomite is often of secondary origin, as a result of diagenetic replacement of calcium carbonate, thus a syn-depositional origin for dolomite must be ascertained before its δ^7Li composition can be use to estimate that of seawater.

4.2. Extraction of carbonate-bound Li in dolostones

Leaching of dolostone with solutions of variable HCl concentrations yields δ^7Li compositions of the leaching solution that decrease with increasing HCl concentrations, suggesting an increasing contribution of isotopically light Li from detrital silicates, such as clay

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299 minerals (Fig. 5a). This hypothesis is supported by a negative relationship between δ^7Li values
300 and Li/Ca ratios of the leaching solutions (Fig. 6), similarly to results from leaching
301 experiments on the Plenus Marl Limestone (Pogge von Strandmann et al., 2013a). The Li/Ca
302 ratio is used instead of Li/Mg because Mg is also present in silicate minerals. Indeed, δ^7Li and
303 Li/Mg ratios show a positive relationship (Fig. 8b), surprisingly suggesting that dolomite and
304 the detrital component are characterised by high and low Li/Mg ratios, respectively.

305 The increasing contribution of silicate minerals with the increasing HCl concentration
306 of the leaching solution is further illustrated by increasing Al/Mg ratios in the leaching solution
307 (Fig. 5b). The contribution from silicates becomes significant for HCl concentrations >0.5 M.
308 For HCl concentrations <0.8 M, the relationship between Al/Mg and HCl concentration breaks
309 down (Fig. 5b), indicating that silicates have a negligible role on the composition of the
310 solution. Nevertheless, δ^7Li values decrease for HCl concentrations as low as 0.1 M. Thus, we
311 propose that treatment of dolostone with a solution of 0.05 M HCl at room temperature for 60
312 mins, is the best compromise between minimising the contribution of silicates and obtaining
313 enough Li for isotopic analysis.

314 Leaching experiments were also conducted on a *Porites* coral of Holocene age to test the
315 proposed protocol, since the δ^7Li of modern coral is known (Marriott et al., 2004a;Rollion-
316 Bard et al., 2009). Furthermore, because the aragonitic skeleton of modern corals is generally
317 free of detrital material, we can also test that the chosen leaching protocol yields the same Li
318 isotopic composition in the resulting solution, as with total dissolution of the coral. Total
319 dissolution of the modern coral yields a δ^7Li value of 20.6 ‰ (Fig. 8). Leaching solutions with
320 HCl concentrations <0.5 M HCl exhibit δ^7Li values within error of that obtained from total
321 dissolution. These values are also consistent with δ^7Li compositions between 18.4 and 19.6 ‰
322 measured in *Porites*, and 21 ‰ in *Acropora* corals (Marriott et al., 2004a). Biomineralization
323 has no major effect on the incorporation of Li in coral or foraminifera as Li has no known

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biological function. The Li isotopic difference between coral and seawater is ~-11 ‰ (Marriott et al., 2004a). Therefore, δ^7Li values obtained from the total dissolution and for leaching solutions with a HCl concentration <0.5 M would yield a δ^7Li composition for modern seawater of 31‰, consistent with published values (Misra and Froelich, 2012). Consequently, these results suggest that leaching with a 0.05 M HCl solution is appropriate to derive the Li associated to the carbonate fraction only.

Interestingly both coral and dolostone leaching solutions show a decrease in δ^7Li values with increasing HCl concentration. This is surprising since the coral is at 97 % aragonite (2 % magnesite and 1% calcite) so the release of isotopically light Li from silicates is not expected. These results imply that total dissolution in dilute HNO_3 does not release isotopically light Li into solution, which could be contained in organic colloids, since no residue was observed. The lack of relationship between δ^7Li values and Li/Ca ratios (Fig. A1) suggests that this isotopically light Li is not bound to silicates (which would have a very different Li/Ca from aragonite). In the coral, this pool of Li remains unidentified. However, as shown above, leaching with solutions with <0.5 M HCl yield Li isotope compositions expected for a coral in equilibrium with the modern seawater.

Leaching of dolostone with acetic acid yields δ^7Li compositions in the solution similar to that of solutions with a HCl concentration ≤0.1 M (Fig. 7). The δ^7Li composition of the 2% HAc solution is lower (8.37 ‰) than that of the 0.5% HAc solution, which could maybe suggest a contribution from silicate-bound Li. Thus, treatment of dolostone with a solution of 0.5% HAc at room temperature for 60 mins could be an alternative method to derive carbonate-bound Li.

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5. Summary and Conclusions

Precipitation experiments at high temperature yielded dolomite and magnesite in variable proportions. However, varying mineralogy does not seem to measurably impact Li isotopic fractionation between the carbonate and the solution. The Li isotopic composition of the precipitated solid is isotopically lighter than the reactive solution, similarly to previous experiments on calcium carbonates (Marriott et al., 2004b;Marriott et al., 2004a). The isotope fractionation factor is mainly controlled by temperature, which in turn allows us to calculate the Li isotopic composition of the solution using δ^7Li value of the Ca-Mg carbonate, if the precipitation temperature can be estimated independently (e.g. oxygen or clumped isotope thermometry). Thus, the temperature dependenmt relationship in Eq. (2) could be useful for reconstructing δ^7Li of palaeo-seawater and/or dolomitizing fluids (i.e., reactive solution) as an approximation based on the Li isotope composition of dolostones in geological records.

Leaching experiments show that it is possible to selectively dissolve the carbonate-bound Li in dolostones by using 0.05 M HCl or 0.5% acetic acid at room temperature for 60 min. Leaching of coral with 0.05M HCl shows that this protocol yields a Li isotope composition for the solution representative of that of the carbonate minerals. Thus, the described protocol allows us to derive the Li isotope composition of the carbonate fraction of dolostones while leaving the Li from any co-present silicates intact.

Combined results from leaching and precipitation experiments show that future studies of Li isotopes in dolostones have high potential to further constraints the evolution of the Li isotopic composition of ancient precipitation fluids, like ocean and brines, thus improve our understanding of changes in the Earth's palaeo-environments.

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Appendix A

Table A1. Column calibration using seawater samples

Column ID	δ^7Li (‰)
Column A	31.1 ± 0.08
Column C	20.9 ± 0.08
Column D	31.6 ± 0.1
Column E	29.9 ± 0.08
Column F	31.7 ± 0.1
Column G	29.5 ± 0.07
Column H	30.7 ± 0.1
Column I	30.9 ± 0.1
Column J	30.9 ± 0.09
Column K	30.8 ± 0.09
Column L	32.0 ± 0.1
Column M	31.3 ± 0.1
Column N	30.7 ± 0.1
Column O	30.1 ± 0.1
Column P	30.8 ± 0.06
Column Q	30.6 ± 0.07
Column R	28.8 ± 0.08
Column S	31.1 ± 0.09
Column Z	29.3 ± 0.08

Errors are internal analytical uncertainties reported at the 2σ level. Column C was not used due to the δ^7Li value being significantly different from the seawater value.

Table A2. Concentrations of lithium in reactive fluids and precipitated solids

Sample ID	$[Li]_{sol}$ (µg. L^{-1})	$[Li]_{prec}$ (ppm)
LiDol – 150 – 4.1	3,695	25.9
LiDol – 150 – 4.2	3,415	20.5
LiDol – 150 – 4.3	3,036	21.8
LiDol – 180 – 4.1	3,434	16.0
LiDol – 180 – 4.2	3,238	15.7
LiDol – 220 – 3	1,666	8.20

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389 Table A3. Mineral concentration of Nuccaleena dolostone (EC26) used in the leaching
390 experiment
391

Mineral	Concentration (wt %)
Quartz	14
Albite	5.1
Calcite	1.1
Dolomite	70
Ankerite	2.1
Siderite	0.2
Kaolinite	1.0
Chlorite	0.2
Muscovite	6.2

392

393

394 Table A4. Mineral concentrations of coral used in the leaching experiment
395

Mineral	Concentration (wt %)
Aragonite	97
Calcite	1.0
Dolomite	0.4
Magnesite	1.6

396

397

398 **Author contribution**

399 HLT, AD, JF and MD designed the project; MD and IJKD conducted the precipitation
400 experiments; HLT conducted the leaching experiments and all other analytical work; HLT and
401 AD wrote the manuscript; all authors edited the manuscript.

402

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Figure captions

Figure 1. a) Dolomite and b) magnesite concentrations in the precipitated solid (in wt %) as function of reaction temperature (in ˚C). The data displayed are average values for each reaction temperature. Error is not shown for mineral concentrations at 220 ºC because no repeat analysis was performed. The error on the magnesite content at 150 ºC is within the symbol size.

Figure 2. Lithium isotope fractionation factor between the precipated solid and the solution ($10^3.\ln\alpha_{prec\text{-}sol}$) as a function of a) dolomite and b) magnesite contents (in wt %).

Figure 3. The distribution coefficent of Li between solid and solution ($D_{[Li]prec\text{-}sol}$) as a function of a) dolomite and b) magnesite contents (in wt %).

Figure 4. Lithium isotope fractionation factor as a function of the reaction temperature, T (in K). Average values for each temperature are shown. The dotted line shows the linear regression through these values according to Eq. (2). Error is not shown for the isotope fractionation factor at 220 ºC because no repeat analysis was performed.

Figure 5. a) Lithium isotope compositions and b) Al/Mg ratios of solutions from dolostone leaching, as a function of their HCl concentration. Decreasing δ^7Li values with increasing HCl concentration suggest a release of isotopically light Li from clay minerals, which is supported by the increase in Al/Mg ratios. Error bars are within the symbol size, if not shown.

Figure 6. Lithium isotopic compositions of solutions from dolostone leaching, as a function of their (a) Li/Ca and b) Li/Mg ratios. Error bars are within the symbol size, if not shown.

Figure 7. Lithium isotope composition of leaching solutions for experiments with HCl and acetic acid.

Figure 8. Lithium isotope composition of leaching solutions as a function of their HCl concentrations. Triangles and circles show the composition of solutions used to leach a Neoproterozoic dolostone and a modern coral, respectively. The square shows the composition of the coral total dissolution. Both coral and dolostone solutions show similar trends, suggesting release of silicate-bound Li at higher HCl concentrations. This is surprising since the coral is almost exclusively aragonite, so the release of isotopically light Li is not expected. This also implies that total dissolution in dilute HNO_3 does not release isotopically light Li into solution, although no residue was observed during dissolution in dilute HNO_3.

Figure A1. Lithium isotope composition of solutions from coral leaching, as a function of their Li/Ca ratio. Unlike for the dolostone, there is no relationship between δ^7Li and Li/Ca. This could indicate that the isotopically-light Li is bound to a fraction with a Li/Ca similar to that of aragonite. Error bars are within the symbol size, if not shown.

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Tables

Table 1. Reaction temperatures and mineral content from the precipitation experiments

Sample ID	Reaction time (days)	T (°C)	magnesite	dolomite	dolomite: magnesite
LiDol – 150 – 4.1	150	150	18.0	82.0	4.56
LiDol – 150 – 4.2	150	150	34.0	66.0	1.94
LiDol – 150 – 4.3	150	150	30.0	61.0	2.03
LiDol – 180 – 4.1	150	180	31.0	69.0	2.23
LiDol – 180 – 4.2	150	180	64.0	36.0	0.56
LiDol – 220 – 3	100	220	83.0	17.0	0.20

Mineral content in wt %. Note a maximum reaction time of 100 days was only possible at 220 °C, since no reacting solution was left after this time.

Table 2. Li isotope compositions solutions and precipitated solids for the precipitation experiments

Sample ID	Temperature (ºC)	δ^7Li solution (‰)	δ^7Li solid (‰)	$10^3\ln(\alpha_{prec\text{-}sol})$	$D_{[Li]\ prec\text{-}sol}$
LiCl reactive solution	-	7.85	-	-	-
LiDol - 150 - 4.1	150	7.87	0.03	-7.81	7.01
LiDol - 150 - 4.2	150	8.34	-0.63	-8.93	6.00
LiDol - 150 - 4.3	150	8.79	-0.10	-8.86	7.19
LiDol - 180 - 4.1	180	9.48	2.88	-6.56	4.66
LiDol - 180 - 4.2	180	7.88	1.71	-6.14	4.85
LiDol - 220 - 3	220	7.87	3.08	-4.77	4.92

External uncertainty (at the 2σ level) is 0.86 and 1.2 ‰ on the δ^7Li values of precipitated solids and solutions, respectively.

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Table 3. Lithium isotope compositions of solutions from the dolostone and coral leaching experiments with HCl and HAc

HCl concentration (M)	δ^7Li_d (‰)	δ^7Li_c (‰)
0.05	9.46	20.1
0.10	8.00	20.2
0.15	7.27	20.2
0.20	7.13	19.5
0.30	7.62	19.3
0.50	7.04	17.8
0.80	6.78	7.04
1.00	6.29	16.7
6.00	4.00	16.9
total dissolution	n/a	20.6
HAc concentration (%)	δ^7Li_d (‰)	
0.5	10.9	
2	8.37	

δ^7Li_d and δ^7Li_c are the Li isotope composition of solutions from dolostone and coral leaching experiments, respectively.

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Figures

Figure 1

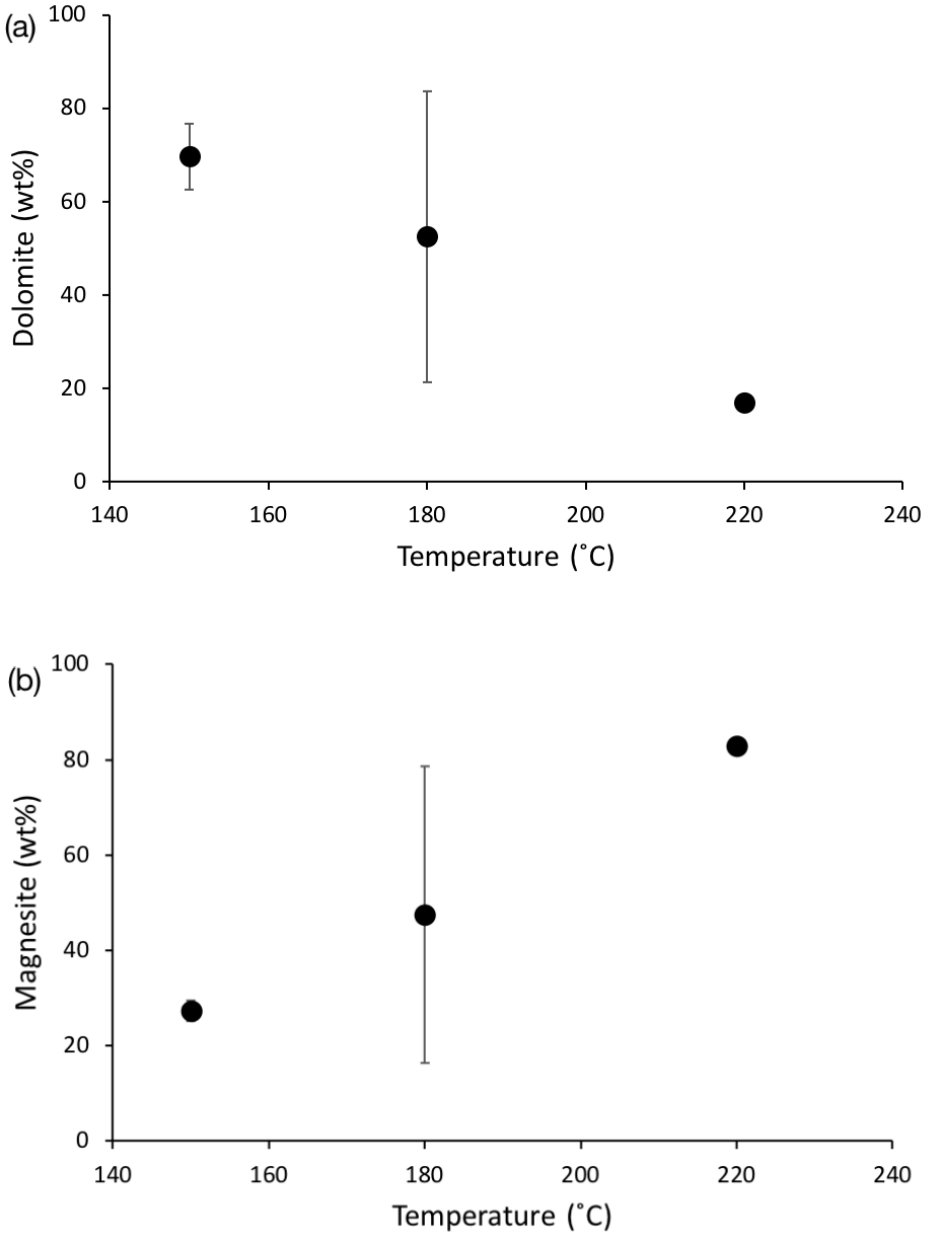

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Figure 2

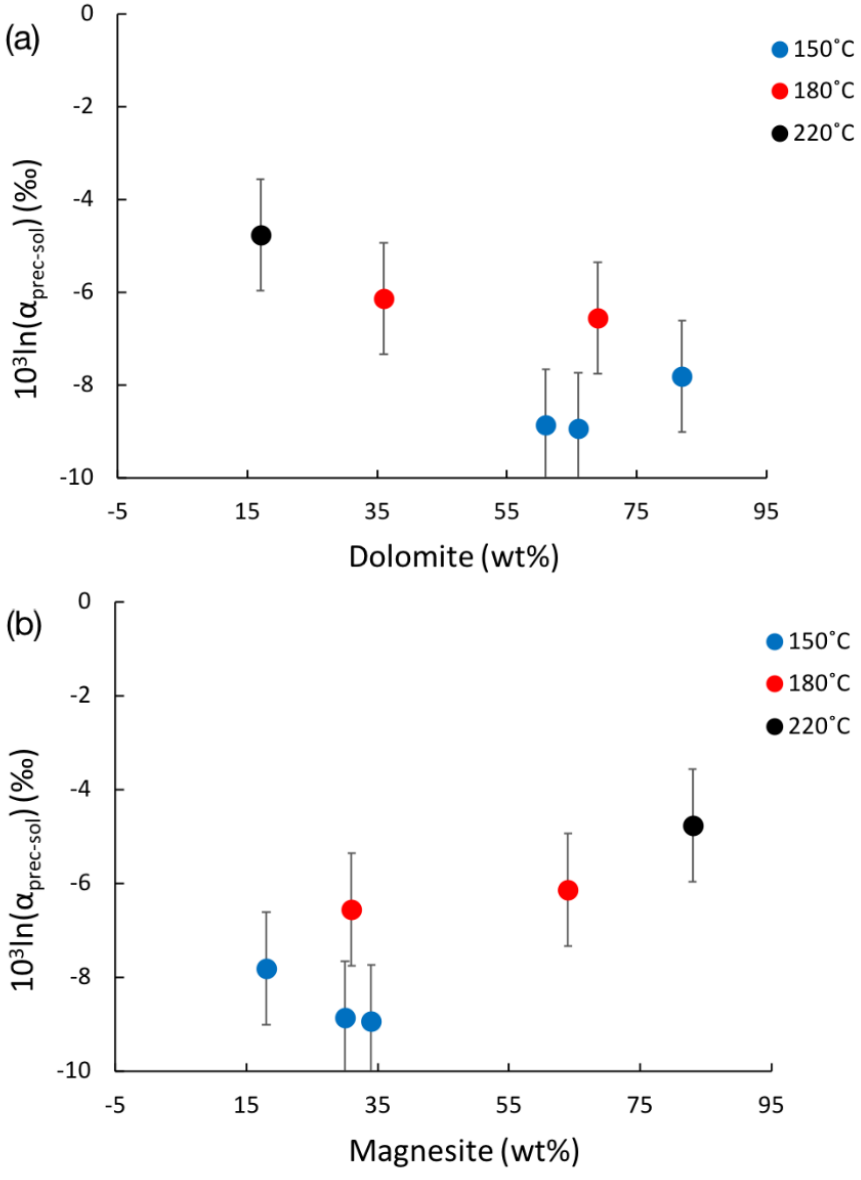

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Figure 3

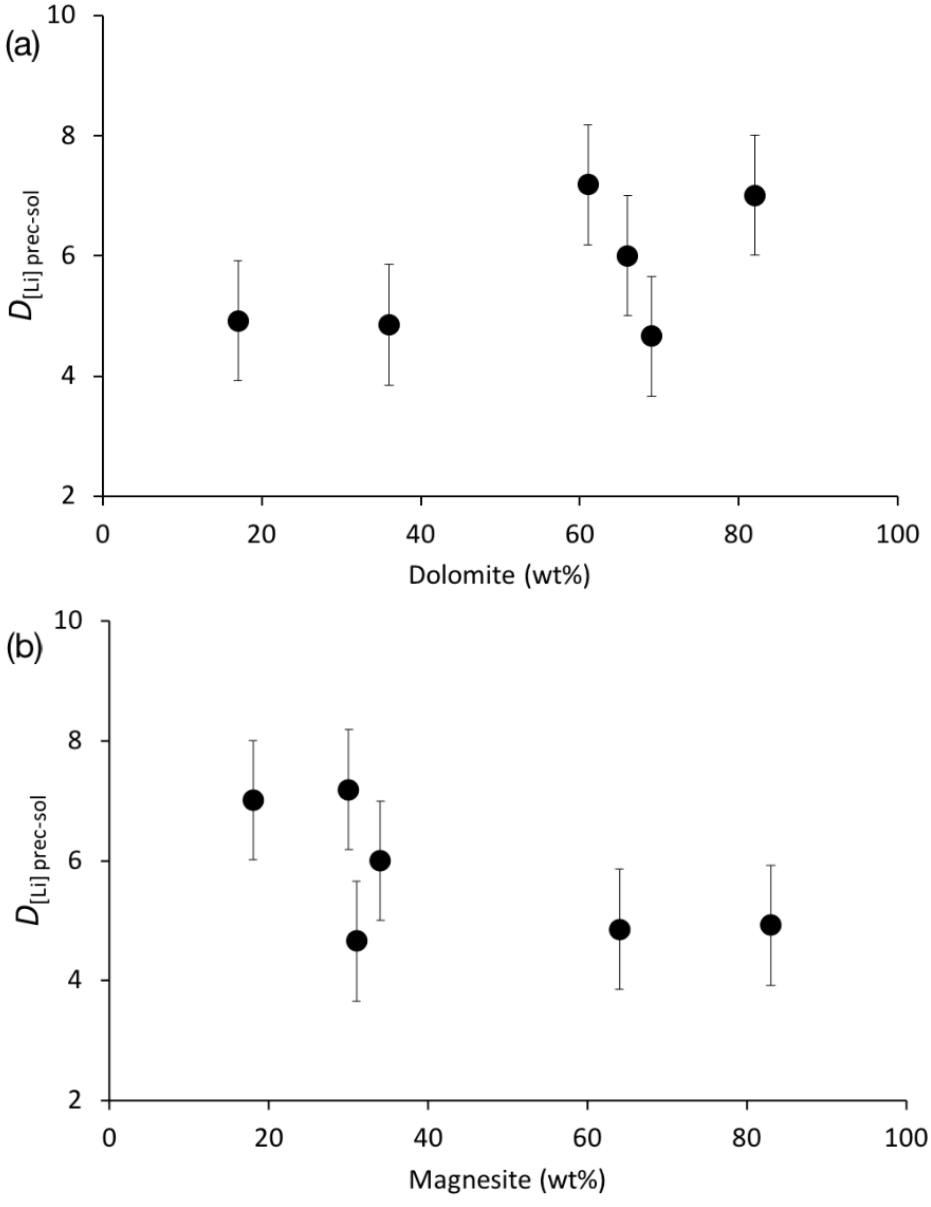

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Figure 4

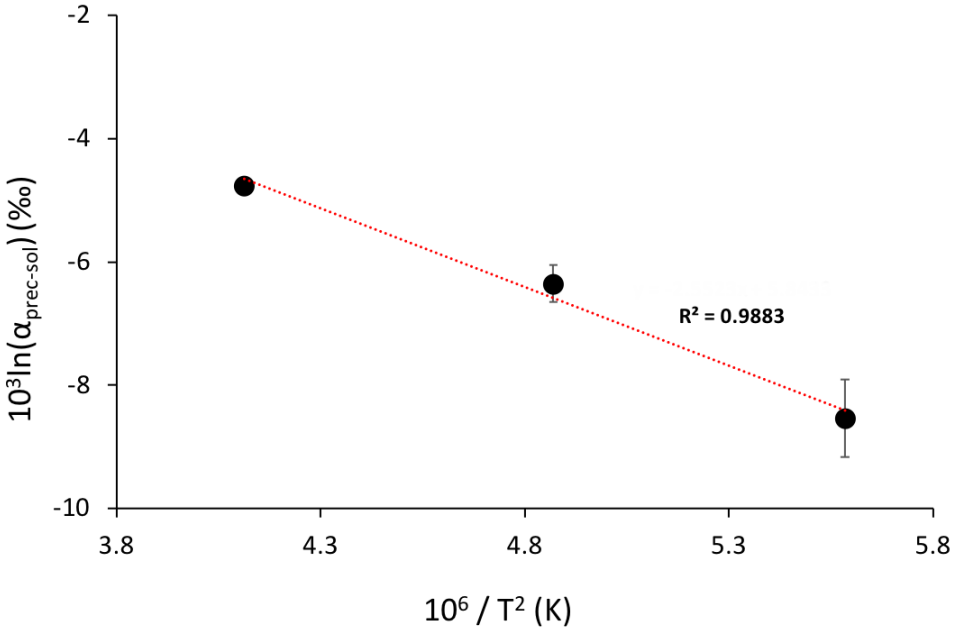

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Figure 5

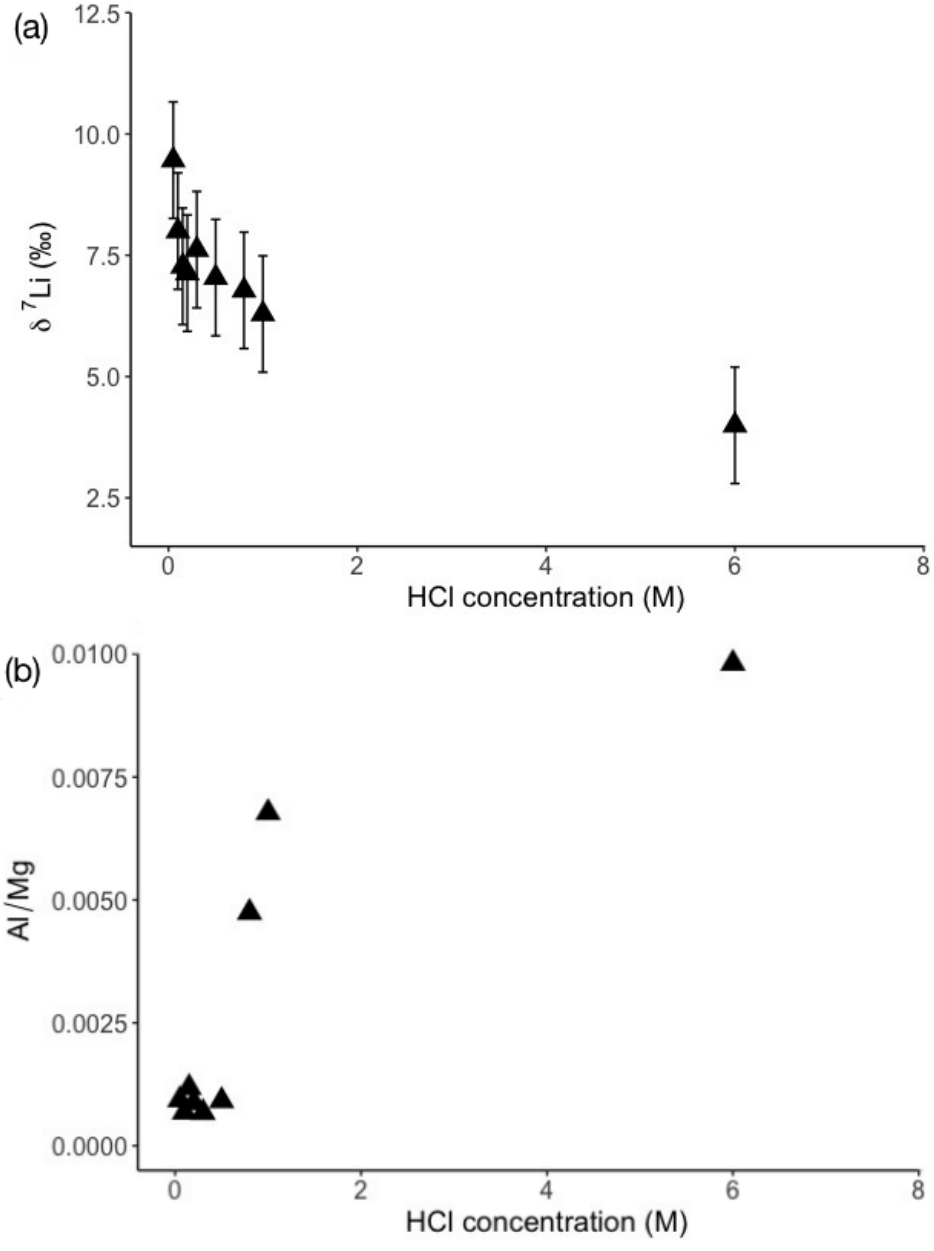

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Figure 6

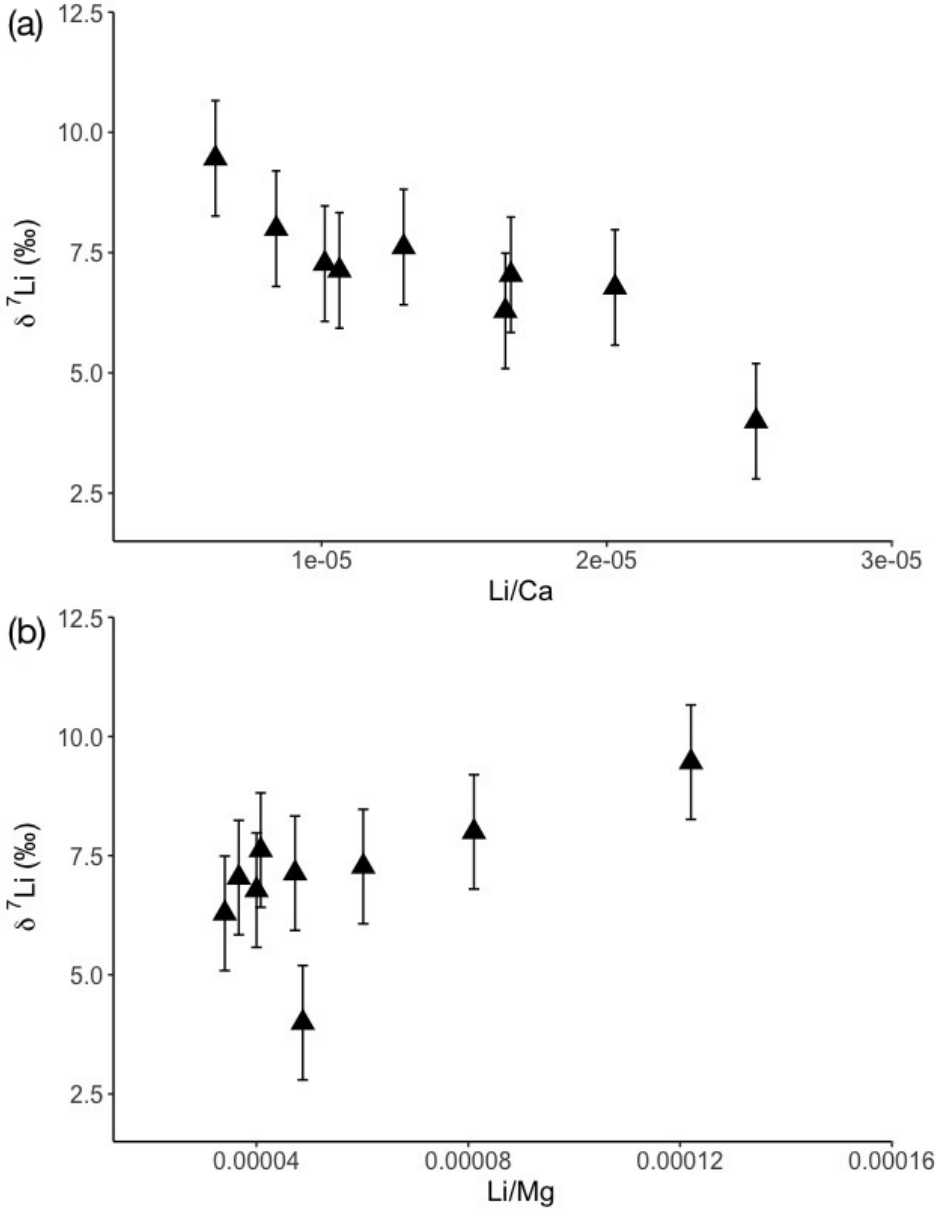

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Figure 7

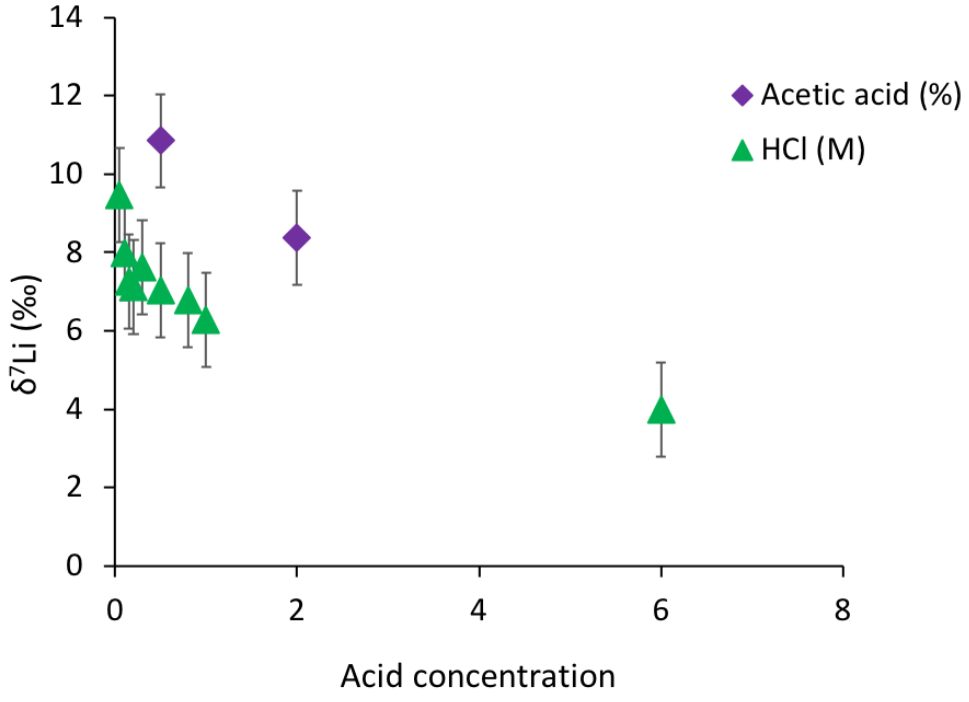

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Figure 8

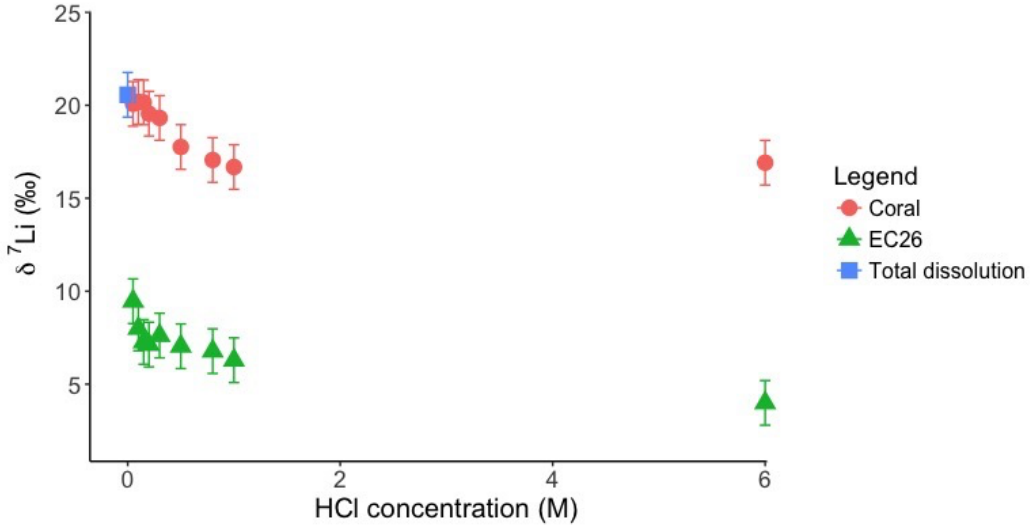

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Figure A1