Responses to Reviewers: Manuscript Number: cp-2018-113 Title: Lithium isotopes in dolostone as a palaeo-environmental proxy – An experimental approach Climate of the Past

We would like to thank the reviewer for all comments and recommendations. Please find below our detailed response (in blue font) to the reviewers' comments (in black, italicised font).

Reviewer #1

This manuscript presents new results from an experimental study of lithium isotope fractionation in dolostone along with leaching tests on dolomite and coral samples. The two main goals of the study were i) to quantify the Li isotope fractionation between inorganic dolomite and fluid from which it precipitates and ii) to determine the best leaching method to dissolve dolomite without contaminating with the detrital component of mixed dolomitesilicate samples. This work is important for reconstructing the past Li isotope composition of seawater using dolomites which are abundant in the deep time sedimentary record. They find that the Li isotope fractionation factor between the precipitated phase (a mixture of dolomite and magnesite) and the solution is a function of the temperature with a value of -

5‰ at 220°C and -9‰ at 150°C. Extrapolating to low temperature (25°C), this gives a fractionation factor value of -23‰ which is significantly lower than the fractionation factor between inorganic calcite (-3‰ or aragonite (-11‰ and solution. For the leaching method, the authors demonstrate that the best protocol to dissolve dolomite without leaching silicate is to leach with 0.05N HCl for 60 minutes.

Altogether, the manuscript is well-written and straightforward. The conclusions of the study are relevant and important for future paleo reconstruction of marine Li isotope composition using dolomite. I suggest that this manuscript be published in Climate of the Past with minor revisions. The few minor points that should be clarified in order to improve the manuscript are discussed below. The authors should expand further the critical discussion on the applicability of their experiment results to natural samples (section 4.1). For example, is it justified (and why) to extrapolate the relation obtained (fractionation factor – temperature) from the high-temperature of the experiment to low temperature? (e.g. in Vigier et al., 2008, the fractionation factor between smectite and solution doesn't linearly increase with the inverse of the temperature).

We agree that in order for our results to be applicable to natural samples, the relationship between Li isotope fractionation and temperature found at temperatures >150 °C needs to also be validated at lower temperatures. However, the precipitation of dolomite at low temperature is a well-known challenge (termed in the literature as 'the dolomite problem') due to the kinetic inhibition of inorganic dolomite formation at low temperatures.

Note that in Vigier et al. (2008), the difference in isotopic fractionation at high and low temperatures is explained by the complex crystal structure of smectite and the possible coordination for Li (structural Li in octahedron within the crystal or at its edges, and exchangeable Li between smectite layers). In the case of dolomite, the crystal structure and coordination of Li are much simpler, thus a change in isotopic fractionation similar to that in smectite is not expected (at least not for the reasons given for smectite).

In the revised manuscript (MS), we now indicate several arguments which could support the applicability of our results at high temperatures to low temperatures characteristic of natural environments:

- (i) The temperature dependant relationship of Li isotope fractionation in our high temperature experiments follow the usual isotope fractionation approach considering equilibrium fractionation (Hoefs, 2015) (lines 190-192), thus suggesting it may be valid at lower temperatures too.
- (ii) At both high and low temperatures, ⁶Li seems to be preferentially incorporated into the mineral phase over ⁷Li during mineral formation, which is consistent with the work of Marriott et al. (2004a,b) in calcium carbonate. This observation suggests that the same mechanisms are at play at high and low temperatures and supports that our results at high temperature may be applicable to natural environments.
- (iii) Previous work has shown that dolomites synthetized at high and low temperatures display similar characteristics and growth mechanisms (Kaczmarek and Sibley, 2007), possibly also supporting that Li isotope fractionation in dolomite follows the same mechanisms at high and low temperatures. Additionally, several previous studies have shown that dolomites precipitated during high-temperature, inorganic, precipitation experiments are characterized by the same growth and dissolution features as natural, lower temperature, dolomites (Bullen and Sibley, 1984). Notably, Bullen and Sibley (1984) showed that microscopic textures on a variety of fossils dolomitized at high temperatures in the laboratory were the same as the microscopic textures observed in naturally dolomitized specimens and Kaczmarek and Sibley (2007) much more recently showed that synthetic dolomite crystals formed under a wide range of conditions and growth rates to be characterized by the same growth and dissolution features as natural, diagenetic dolomites.

This discussion has been added to the revised MS (lines 190-201).

Regarding the form of the paper, I suggest improving the quality of the figures, especially adding units where they are missing. A table with leaching test trace elements data is missing in this version of the manuscript and should be included in the revised version. The quality of all figures has been improved and units in Figure 7 are included into the legend as there are two different units displayed in the x-axis. The trace elemental data has been included into Table 3 in the revised MS.

Additional more specific comments:

Line 85: you can cite here the paper of Bastian et al., (2018) in which more leaching tests have been done.

We appreciate the suggestion of the above reference, and it has been included into the revised MS.

Line 94: did you analyse the Li concentration and isotope composition of the speleothem aragonite used for the synthesis experiment?

The aragonite was just used as a Ca and DIC source and it completely dissolved during the experiments. Furthermore, the Li elemental and isotope distribution of the solution does not change significantly throughout the dissolution of the aragonite as the amount of Li liberated into the solution is insignificant compared to its high initial concentration of 1.7 ppm.

Our results are referring to the (Mg,Ca)CO₃ precipitating solution, thus, representing the elemental and isotopic exchange between the newly formed minerals and reactive solution (as valid for Equation 2 in the MS).

Line 107: replace "than" by "then".

This has been corrected in the revised MS.

Line 114: please specify the age of the formation here.

The age of the Nuccaleena Formation is approximately 635 Ma. This has been included into the revised MS (line 64).

Line 146 and 159: did you analyse any carbonate reference materials to validate the Li, Al, Ca and Mg measurements on solid carbonate samples?

We used a natural water standard NIST 1640a along with several in-house standards and further confirmed concentration measurements by analysing the synthesized carbonates from the study of Füger et al. (2019).

Line 202: which is similar to what is observed for calcite carbonates I think (see Marriott et al., 2004a, b).

Yes, the Li/Ca values of inorganic calcite in Marriott et al. (2004 a,b) show a decrease from 12.95 to 4.26 g/g 10^{-7} with increasing temperature from 5-30°C. These observations have been included and made clear in the revised MS (lines 129-130).

Line 206: remove the "± 0.6 ‰ (1s; n=3)" here.

Thank you for the suggestion, this has been removed from the revised MS.

Section 3.2. Please provide the units here, is it in mol/mol or g/g?

Units are mol/mol, thus the term "molar" has been added as a prefix when necessary in the MS, thank you for pointing that out.

Line 248: At what temperature?

The Li isotope composition of precipitated minerals (4.8 to 8.6 ‰) are the averages over all temperatures. This has been made clearer in the revised MS.

Note that this is the same HCl concentration (0.05N) and leaching time (1h) used for leaching modern biogenic carbonates in Dellinger et al., (2018).

Yes, this leaching procedure is similar to that of Dellinger et al., 2018 and this has now been noted in the revised MS.

Figure 2: change the x axis to have '0' at the origin '-5' and '100' in the end instead of '95'. Thank you for the suggestion, these corrections have been made to the revised MS.

Figure 4: Why are the error bars smaller in this figure than in the figure 2?

The error bars in Figure 4 are the 2 SE (standard error) of Li isotope compositions for solids synthesized at a given temperature. In Figure 2, the error bars are the 2 SD (standard deviation) considering all replicate aliquots together – irrespective of temperature (as indicated lines 120-123).

Figure 7: What is the unit of the acid concentration?

The units in this figure are included into the legend as there are two different units displayed on the x axis.

Reviewer #2

Dear authors,

I first would like to apologize for the delay in reaching a decision about your manuscript. Because one (several times) promised review is still missing, I decided to review your contribution, although I'm certainly not a specialist of isotope geochemistry.

Measuring the lithium isotopic signature of dolomites would allow to explore the behaviour of the global geochemical cycles in the deep time, for periods where sedimentary dolomites are more abundant than aragonite or calcite. The present contribution determines the isotopic fractionation between the dolomite minerals and the fluids from which it precipitates. A cleaning procedure is also tested to get rid of the siliciclastic component of dolomitic formation, to avoid contamination of the signal.

The paper is well written. I can hardly comment on the technical sections of the paper, being not a specialist. The two points I would like to raise are the following:

1. Regarding the extrapolation of the present results to the natural environment.

Experiments were conducted at a quite high temperature above 150°C. These high temperatures are justified by the extremely low precipitation rate of dolomite at ambient temperatures. The authors show that the isotopic fraction is a function of

temperature above 150°C. A quite large extrapolation must be done to reach temperatures typical of the surficial Earth environment. There is no guarantee that the extrapolation can be approximated by a linear relationship. I think more discussions, based on published literature, are needed here.

Thank you for this insightful review, we have revised the discussion to include a clearer explanation. This concern is already addressed in our response to Reviewer #1.

2. The abundance of dolomitic sediments in the distant past remains largely unexplained. Indeed, it has been shown that microbes can accelerate the dolomite precipitation rate. But it is highly probable that most of the dolomites have precipitated during diagenetic alteration of the sediments. This is mentioned on line 290 and following. This discussion should be a bit expanded. In the introduction, it is

stated that the use of dolomitic materials may allow to explore periods as old as the Precambrian. Is this realistic?

In the revised discussion we have expanded the explanation about the possible diagenetic affects and limitations (lines 202-210).

The "dolomite problem" (inability to precipitate well-ordered dolomite at ambient temperatures) is still hotly debated. Although marine dolomite may be of secondary origin as a result of diagenetic replacement of pre-existing calcium carbonates, primary marine deposition has been invoked for dolomite formation in many studies (even in Precambrian dolostones; Fairchild and Kennedy (2007), Rose and Maloof (2010), Kunzmann et al. (2013), Liu et al. (2014)). Thus, while we acknowledge limitations of the applicability of these results, we still contend that Li isotopes in dolomite have a potential use in understanding palaeo-environmental changes where it can be shown that dolomite is of primary origin (as shown even for Precambrian dolostones; see references above). This discussion has been included to the revised MS (lines 210-212).

Overall, I think this contribution deserves publication in Clim Past, given that these questions are addressed.

Thank you kindly, we hope that you are satisfied with the changes we have made following your useful advice and look forward to hearing your response.

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

Holly L. Taylor¹, Isaac J. Kell Duivestein², Juraj Farkas^{3,4}, Martin Dietzel², and Anthony Dosseto¹ ¹Wollongong Isotope Geochronology Laboratory. School of Earth, Atmospheric and Life Sciences. University of Wollongong. Wollongong, NSW, Australia ²Institute of Applied Geosciences. Graz University of Technology. Graz, Austria ³Department of Earth Sciences. University of Adelaide. Adelaide, SA, Australia ⁴Department of Environmental Geosciences, Czech University of Life Sciences, Prague, Czech Republic **Correspondence:** Holly Taylor (hlt434@uowmail.edu.au)

Abstract. Lithium (Li) isotopes in marine carbonates have considerable potential as a proxy to constrain past changes in 1 silicate weathering fluxes and improve our understanding of Earth's climate. To date the majority of Li isotope studies on 2 marine carbonates have focussed on calcium carbonates. Determination of the Li isotope fractionation between dolomite and 3 a dolomitizing fluid, would allow us to extend investigations to deep times (i.e., Precambrian) when dolostones were the 4 5 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-6 associated Li is measured. This study aims to serve two main goals: (1) determining the Li isotope fractionation between 7 Ca-Mg carbonates and solution and (2) to develop a method for leaching the carbonate-associated Li out of dolostone while 8 not affecting that contained within the detrital portion of the rock. We synthesized Ca-Mg carbonates at high temperature (150 9 10 to 220 °C) and measured the Li isotope composition ($\delta^7 Li$) of precipitated solids and their respective reactive solutions. The relationship of the Li isotope fractionation factor with temperature was obtained: 11

12
$$10^3 . ln\alpha_{prec-sol} = -((2.56 \pm 0.27) . 10^6)/T^2 + (5.8 \pm 1.3)$$
 (1)

Competitive nucleation and growth between dolomite and magnesite were observed during the experiments, however, with-13 out notable effect of their relative proportion on the apparent Li isotope fractionation. We found that Li isotope fractionation 14 between precipitated solid and solution is higher for Ca-Mg carbonates than for Ca carbonates. If the temperature of a precipi-15 tating solution is known or can be estimated independently, the above equation could be used in conjunction with the Li isotope 16 17 composition of dolostones to derive that of the solution and hence make inferrals about the past Li cycle. In addition, we also conducted leaching experiments on a Neoproterozoic dolostone and a Holocene coral. Results show that leaching with 0.05M 18 HCl or 0.5 % acetic acid at room temperature for 60 min releases Li from the carbonate fraction without significant contribution 19 20 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 21

22 evolution of Earth's surface environments.

24 1 Introduction

25 Lithium isotopes in marine carbonates have emerged as a powerful proxy to understand the evolution of the ocean chemistry, 26 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, 27 28 2012; Li et al., 2014; Wanner et al., 2014; Vigier and Goddéris, 2015; Hathorne and James, 2006), oceanic anoxic events 29 (Pogge von Strandmann et al., 2013; 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., 30 31 2000), the application of Li isotopes to marine dolostone could help to extend our understanding of the geochemical evolution of ancient dolomitizing solutions, particularly in early Earth geological history (i.e., Precambrian). 32

While data of Li isotopic fractionation during calcite precipitation has been relatively well constrained (Marriott et al., 2004a, b; 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., 2013; Bastian et al., 2018). 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 carbonateassociated Li fraction in dolostones exclusively.

46 2 Methods

47 2.1 Ca-Mg carbonate synthesis

48 Synthesis of Ca-Mg carbonates was conducted in Teflon-lined, stainless steel autoclaves at temperatures of 150, 180 and 49 220 °C ± 5 °C) through the reaction of ~300 mg of powdered inorganic aragonite (speleothem aragonite; in-house mineral 50 collection at Graz University of Technology) with an artificial brine solution containing 200 mM Mg, 0.245 mM Li and 50 51 mM NaHCO₃. The reactive fluid was prepared by dissolving analytical grade MgCl₂.6H₂O (Roth; ≥ 99 %, p.a, ACS), LiCl 52 (Merck; ≥ 99 %, ACS, Reag. Ph Eur) and NaHCO₃ (Roth; ≥ 99.5 %, p.a., ACS, ISO) in ultrapure water (Millipore Integral 3: 53 18.2 MΩ.cm-1). The stock solution was subsequently filtered through a 0.45 µm cellulose acetate membrane filter (Sartorius).

The reagent inorganic aragonite was milled to a grain size $< 20 \ \mu m$ using a vibratory mill (McCrone Micronizing Mill) for 54 10 minutes and collected by dry sieving prior to use in the experiments. Autoclayes were sealed immediately after mixing the 55 inorganic aragonite with the appropriate volume of stock solution and placed in preheated ovens. Samples were taken from the 56 autoclaves at each operating temperature after a given reaction time (Table 1), including repeat samples. Upon removal from 57 heat, the reactors were quenched and the samples were subsequently filtered through a 0.2 µm cellulose acetate membrane 58 59 (Sartorius) using a vacuum filtration unit. Samples were then thoroughly rinsed with ultrapure water (Millipore Integral 3: 18.2 M Ω ·cm-1) to remove any soluble salts from the matrix and subsequently dried in an oven at 40 °C overnight to be ready 60 61 for solid phase analysis. An aliquot of the reactive fluid was acidified to a $\sim 3 \%$ HNO₃ matrix for elemental and Li isotope analyses using Merck[®] Suprapur[™] HNO₃. 62

63 2.2 Leaching experiments

A Neoproterozoic dolostone from the Nuccaleena Formation (Flinders Ranges, South Australia, ~635 Ma) and a Holocene 64 Porites coral were used to evaluate the effect of different leaching protocols on the measured Li isotope composition. Sam-65 ples were ground to a powder using a TEMA chromium-ring grinding mill. An aliquot of powdered dolostone was used for 66 67 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 68 (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 69 70 and HCl solutions were prepared from trace grade glacial acetic acid (Merck® SuprapurTM) and ultra-trace grade 30 % HCl (Merck® UltrapurTM). In each case, the powder and solution reacted at room temperature for one hour, while continuous mix-71 72 ing was achieved 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 73 Li was subsequently sampled for cation exchange chromatography. 74

75 2.3 Mineralogy quantification

76 Quantitative phase contents of the synthesized solids were determined by powder X-ray diffraction (XRD) of finely ground 77 aliquots performed on a PANalytical X'Pert PRO diffractometer outfitted with a Co-target tube (operated at 40 kV and 40 mA), 78 a high-speed Scientific X'Celerator detector, 0.5 °antiscattering and divergence slits, spinner stage, primary and secondary 79 soller and automatic sample changer. Samples were finely ground by hand using a mortar and pestle prior to analysis and were 80 loaded in a random orientation using the top loading technique. The samples were analysed over the range $4 - 85^{\circ}2\theta$ with a 81 step size of $0.008^{\circ}2\theta$ and a count time of 40 seconds/step. Mineral quantification was obtained by Rietveld Refinement of the 82 XRD patterns using the PANalytical X'Pert HighScore Plus Software and its implemented pdf-2 database.

83 2.4 Elemental concentrations

Lithium concentrations of solutions were analysed in acidified (0.3 M HNO₃) 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 (2 σ , 3 replicates) of \pm 3% relative to the standard. For synthesized solids, an aliquot of each precipitate was dissolved in 0.9 M HNO₃ 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.

90 2.5 Lithium isotopes

Sample preparation for Li isotope measurement was undertaken in a Class 100 cleanroom at the Wollongong Isotope Geochronology Laboratory, University of Wollongong. For mineral precipitates, the samples were ground using a mortar and pestle before aliquots of <0.05 g were weighed. The sample aliquots were dissolved in dilute HNO₃ (UltrapurTM) and 0.2 mL of concentrated H₂O₂ (31 % UltrapurTM) was added to ensure the breakdown of organics.

The samples were then placed on a hotplate overnight at 50 $^{\circ}$ C to reflux and ensure complete digestion of the solids. After 95 complete digestion of the solids, Li concentrations were measured by Quadrupole ICP-MS. An aliquot of the digested samples 96 containing ~ 60 ng of Li was then dried down and taken up into 1.5 mL of UltrapurTM 1 M HCl. Samples were then treated with 97 a two-step cation exchange chromatography procedure, following the methods of Balter and Vigier (2014) to separate Li from 98 the sample matrix. For Li isotope measurements it is crucial that 100 % of Li is recovered from the cation exchange columns 99 as δ^7 Li compositions have been shown to vary by up to ~ 200 % during chromatography due to incomplete recovery (Pistiner 100 and Henderson, 2003). It is also crucial to remove elements such as Na and Ca as large amounts of Ca can coat the cones of the 101 102 mass spectrometer while Na can reduce Li ionisation in the plasma, and cause further Li isotopic fractionation during analysis 103 (James and Palmer, 2000). For chromatography, 30 mL Savillex micro columns (6.4 mm internal diameter, 9.6 cm outside diameter, 25 cm capillary length) were used together with Biorad AG50W-X8 resin as the cation exchange medium (volume = 104 105 3.06 cm^3). The columns were calibrated with seawater prior to treating the samples to verify that the procedure yielded 100 % of the Li (Table A1). The columns were cleaned with 30 mL of 6M HCl, rinsed with 2 mL of MilliQTM water and conditioned 106 107 using 8 mL of titrated, 1 M UltrapurTM HCl before sample loading. To ensure the complete removal of interfering elements from the Li, samples were passed through the columns twice; after the first elution, the samples were dried down, taken up 108 in 1 M HCl and reloaded into the columns. The Li elutions were dried down and subsequently re-dissolved in UltrapurTM 109 0.3M HNO₃ ready for isotopic analysis. Lithium isotope ratios were measured by multi collector inductively coupled plasma 110 mass spectrometry (MC ICP-MS) on a ThermoFisher Neptune Plus at the Wollongong Isotope Geochronology Laboratory, 111 112 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 113 between 5-30 mV. During analysis, standard bracketing, using IRMM-16 as the primary standard, was applied to correct the 114 measured ⁷Li/⁶Li values for mass bias (Flesch et al., 1973). Instrumental blanks were measured before each sample so that 115

116 background signal could be accounted for. The ⁷Li/⁶Li ratios were converted to δ^7 Li values using L-SVEC as reference to

117 (Carignan et al., 2007) (Eq.(2)).

118
$$\delta^7 Li = (({}^7 Li/{}^6 Li)_{sample}/({}^7 Li/{}^6 Li)_{L-SVEC}) - 1 \times 1000$$
 (2)

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^7 Li compositions (at 2 σ level) was evaluated by measurement of precipitated solids and solutions from repeat experiments at 150 °C (n = 3) and 180 °C (n = 2), amounting to 0.86 ‰ for precipitated solids and 1.2 ‰ for solutions.

124 3 Results

125 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 reactive solutions ranges from 1,666 to 3,695 μ g.L⁻¹ (Table A2) and shows no correlation with reaction temperature. On the contrary, the Li concentration of precipitated solids are consistent with (Marriott et al., 2004a, b) as it decreases with increasing temperature (from 25.9 to 8.20 ppm; Table A2).

131 The δ^7 Li of the initial reactive solution is 7.85 % (Table 2). After reaction the δ^7 Li value of the solution (δ^7 Li_{sol}) vary 132 between 7.87 and 9.48 %, while the δ^7 Li values in the precipitated solid (δ^7 Li_{prec}) range from -0.63 to 3.08 % (Table 2). 133 The precipitated solids are 4.79 to 8.6 % lighter than the solution, and this difference (termed $10^3.ln\alpha_{prec-sol}$) increases with 134 decreasing temperature (Table 2).

The Li isotope fractionation factor between the precipitated solid and the solution (calculated as $10^3 ln\alpha_{prec-sol} = 10^3 ln(1000 + \delta^7 Li_{sol})$ 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 $(D_{[Li]prec-sol} = [Li]_{prec}/[Li]_{sol})$, 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 $10^3 ln\alpha_{prec-sol}$ and the reaction temperature (Fig. 4).

141 3.2 Leaching experiments

142 For the dolostone, δ^7 Li values of the leaching solution decrease from 9.5 to 4.0 %, with increasing HCl concentration (Table

143 3; Fig. 5a). The molar 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 molar Li/Ca ratio from 6.3×10^{-6} to 25×10^{-6} with decreasing $\delta^7 \text{Li}$
- 145 (Fig. 6a). Furthermore, the molar Li/Mg ratio increases from 5 to 12×10^{-5} with increasing δ^7 Li (Fig. 6b). Very little carbonate

- 146 minerals other than dolomite (1.1 wt % calcite and 2.1 wt % ankerite) are present in the dolostone sample, and the silicate 147 minerals represents ~26 wt % of the sample (14 wt % quartz, 6.2 wt % muscovite and 5.1 wt % albite) (Table A3). Leaching 148 with acetic acid yields δ^7 Li compositions in the solution similar to values observed in very dilute HCl (Fig. 7). The δ^7 Li of the 149 2 % HAc leaching solution is lower than that of the 0.5 % HAc leaching solution.
- 150 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 $\delta^7 Li$ values decreasing from 20.1 to 16.9 % with increasing HCl concentra-
- 152 tion (Table 3; Fig. 8). Total dissolution of the coral yields a δ^7 Li value in the solution of 20.6 %, which is within error of the
- 153 values determined for HCl leaching experiments with acid concentrations <0.5 M (Table 3).

154 4 Discussion

155 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 $(CaMg(CO_3)_2)$ 156 and magnesite (MgCO₃) (Table 1). The δ^7 Li composition of the precipitated solid is systematically isotopically lighter than 157 that of the reactive solution (Table 2). These results are consistent with previous experimental work on Li isotope fractionation 158 159 during calcite precipitation (Marriott et al., 2004a, b), which showed that the Li isotope composition of calcite is isotopically 160 lighter than that of the corresponding fluid. Teng et al. (2008) have suggested that the incorporation of ⁶Li over ⁷Li in minerals compared to the growth solution reflects a change from four- to six-fold coordination of Li during mineral growth. In calcite 161 from foraminifera and aragonite from corals, $\delta^7 Li$ values are respectively about 3 and 11 % lower compared to their growth 162 solutions (Marriott et al., 2004a). Here, the precipitated minerals are 4.8 to 8.6 \pm 0.6 % (1 σ ; n=3) lighter than the solution 163 164 over all temperatures (150, 180 and 220 °C). This difference increases with decreasing temperature, as would be expected for stable isotope fractionation at equilibrium. As our experiments were conducted at high temperatures (150, 180 and 220 165 °C), the system can be reasonable considered to be approaching isotope equilibrium conditions as fractionation scales with 166 167 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 168 169 $\sim 80 \%$) than that observed (both in calcite and in Ca-Mg carbonate), thus requiring boundary layer processes or the presence 170 of a back-reaction, for which there is no evidence. (ii) Observed isotopic fractionation between calcite and growth solution, as 171 well as between Ca-Mg carbonate and growth solution, are consistent with ab initio calculations for equilibrium fractionation (Kazuyo Yamaji et al., 2001). (iii) Lithium isotope fractionation between calcite and growth solution is relatively constant 172 across a wide range of concentration of Li incorporated in calcite (this was not tested here). 173

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^7 Li composition of the precipitated solids or that of their respective reactive solutions and the magnesite:dolomite ratio of the precipitated 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 ($10^3 ln\alpha_{prec-sol}$; Fig. 2) or the Li distribution coefficient between solid and solution $(D_{[Li]prec-sol}; Fig. 3)$, despite a wide range of mineral abundances. For instance, most $10^3.ln\alpha_{prec-sol}$ 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

182 $(\sim 11\%)$ was much greater than in calcite $(\sim 3\%)$.

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

186
$$10^3 ln\alpha_{prec-sol} = -((2.56 \pm 0.27).10^6)/T^2 + (5.8 \pm 1.3)$$
 (3)

187 where T is the temperature of precipitation in K.

188 Using Eq. (3), the Li isotopic fractionation at 25 °C is estimated to be -23.0 \pm 5.7 % (1 σ) (Fig. 4). Although there is a large error on this estimate, our results suggest that Li isotopic fractionation during dolomite/magnesite precipitation is sig-189 nificantly larger than during calcium carbonate precipitation (Marriott et al., 2004a). This temperature dependant relationship 190 191 of Li isotope fractionation in our high temperature experiments follows the isotope fractionation approach considering equilibrium fractionation (Hoefs, 2015), Furthermore, we see that at high temperature ⁶Li is preferentially incorporated into the 192 mineral phase over 7 Li, similar to what has been observed at low temperature for calcium carbonate (Marriott et al., 2004a, 193 194 b). Finally, despite a wide range of formation conditions between high-temperature synthetic dolomites and low-temperature 195 natural dolomites, Kaczmarek and Sibley (2007) showed that natural and synthetic dolomite form by the same growth mechanisms. This was suggested through identification of identical growth features in etched natural and synthetic dolomite samples 196 as well as unetched synthetic dolomite. The growth fabrics of high-temperature synthetic dolomite and low-temperature nat-197 ural dolomite have also been compared by Bullen and Sibley (1984), these results suggest that high-temperature synthetic 198 199 dolomites produce fabrics similar to that of naturally grown dolomites. Altogether, these observations suggest that the rela-200 tionship between Li isotope fractionation and temperature derived from high temperature experiments may also be valid at low temperatures characteristic of natural environments. 201 202 If the temperature of the solution from which dolomite is precipitated is known or can be calculated (e.g., via clumped

 Δ_{47} proxy; Winkelstern et al. (2016)), the above relationship in combination with the $\delta^7 Li$ of dolostone could potentially 203 204 be used to determine an estimate for 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, while 205 it has been proposed that bacterial mediation could play a major role in the precipitation of dolomite from natural waters 206 at ambient conditions (Vasconcelos et al., 1995). Bacterial mediation was invoked to solve the "dolomite problem", i.e. the 207 inability to precipitate dolomite at ambient temperatures; the topic of the origin of dolomite formation still being hotly debated 208 (Liu et al., 2019; Ahm et al., 2019; Gregg et al., 2015). Other models invoke a primary or secondary (diagenetic) origin for 209 dolomite. Primary marine deposition has been invoked for dolomite formation in many studies, even in Precambrian dolostones 210

(Fairchild and Kennedy, 2007; Rose and Maloof, 2010; Kunzmann et al., 2013; Liu et al., 2014). Thus, where it can be shown

(212) (that dolomite is of primary origin, its Li isotopic composition could provide valuable information on palaeo-environments.

213 4.2 Extraction of carbonate-bound Li in dolostones

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

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

228 Leaching experiments were also conducted on a *Porites* coral of Holocene age to test the proposed protocol, since the $\delta^7 Li$ of modern coral is known (Marriott et al., 2004a; Rollion-Bard et al., 2009). Furthermore, because the aragonitic skeleton of 229 modern corals is generally free of detrital material, we can also test that the chosen leaching protocol yields the same Li isotopic 230 composition in the resulting solution, as with total dissolution of the coral. Total dissolution of the modern coral yields a $\delta^7 Li$ 231 232 value of 20.6 % (Fig. 8). Leaching solutions with HCl concentrations <0.5 M HCl exhibit δ^7 Li values within error of that obtained from total dissolution. These values are also consistent with $\delta^7 Li$ compositions between 18.4 and 19.6 % measured 233 in Porites, and 21 % in Acropora corals (Marriott et al., 2004a). Biomineralization has no major effect on the incorporation 234 of Li in coral or foraminifera as Li has no known biological function. The Li isotopic difference between coral and seawater is 235 -11 % (Marriott et al., 2004a). Therefore, $\delta^7 Li$ values obtained from the total dissolution and for leaching solutions with a HCl 236 237 concentration <0.5 M would yield a δ^7 Li composition for modern seawater of 31%, consistent with published values (Misra and Froelich, 2012). Consequently, these results, which are similar to that of Dellinger et al., (2018) suggest that leaching with 238 239 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^7 Li 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 HNO₃ 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^7 Li 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.</p>

Leaching of dolostone with acetic acid yields δ^7 Li compositions in the solution similar to that of solutions with a HCl concentration ≤ 0.1 M (Fig. 7). The δ^7 Li 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.

251 5 Summary and Conclusions

252 Precipitation experiments at high temperature (150, 180 and 220 °C) yielded dolomite and magnesite in variable proportions. 253 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 254 previous experiments on calcium carbonates (Marriott et al., 2004b, a). The isotope fractionation factor is mainly controlled 255 by temperature, which in turn allows us to calculate the Li isotopic composition of the solution using $\delta^7 Li$ value of the Ca-256 Mg carbonate, if the precipitation temperature can be estimated independently (e.g. oxygen or clumped isotope thermometry). 257 Thus, the temperature dependent relationship in Eq. (3) could be useful for reconstructing $\delta^7 Li$ of palaeo-dolomitizing fluids 258 (i.e., reactive solution) as an approximation based on the Li isotope composition of dolostones in geological records. 259

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 considerable potential to further constraints the evolution of the Li isotopic composition of ancient precipitation fluids, including seawater and basinal fluids, thus improve our understanding of changes in the Earth's palaeo-environments.

268 6 Appendix

Table A1. Column calibration using seawater samples

Column ID	$\delta^7 { m Li}$ (‰)
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^7 Li value being significantly different from the seawater value.

Sample ID	$[Li]_{sol} (\mu g. L^{-1})$	[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

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

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

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

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

Concentration (wt%)
97
1.0
0.4
1.6

- 269 Author contributions. HLT, AD, JF and MD designed the project; MD and IJKD conducted the precipitation experiments; HLT conducted
- 270 the leaching experiments and all other analytical work; HLT and AD wrote the manuscript; all authors edited the manuscript.
- 271 Competing interests. The authors have no competing interests to declare.

Acknowledgements. We would like to thank Jasmine Hunter and Helen McGregor (University of Wollongong) for providing the coral samples, Alexander Corrick (University of Adelaide) for help collecting the Nuccaleena dolomite samples and Andre Baldermann (Graz University of Technology) for performing the Li concentration analytics. The laboratory precipitation experiments and fieldwork related to this study was supported by the Base-Line Earth project (ITN MC Horizon 2020, grant agreement No. 643084), Czech Science Foundation (GACR grant No. 17-18120S), Australian Government Research Training Program and ARC Linkage Project LP160101353.

277 References

- Ahm, A.-S. C., Maloof, A. C., Macdonald, F. A., Hoffman, P. F., Bjerrum, C. J., Bold, U., Rose, C. V., Strauss, J. V., and Higgins,
 J. A.: An early diagenetic deglacial origin for basal Ediacaran "cap dolostones", Earth and Planetary Science Letters, 506, 292–307,
- 280 https://doi.org/10.1016/J.EPSL.2018.10.046, https://www.sciencedirect.com/science/article/pii/S0012821X18306484, 2019.
- Arvidson, R. S. and Mackenzie, F. T.: The dolomite problem; control of precipitation kinetics by temperature and saturation state, American
 Journal of Science, 299, 257–288, 1999.
- Balter, V. and Vigier, N.: Natural variations of lithium isotopes in a mammalian model, Metallomics, 6, 582–586,
 https://doi.org/10.1039/C3MT00295K, http://dx.doi.org/10.1039/C3MT00295K, 2014.
- 285 Bastian, L., Vigier, N., Reynaud, S., Kerros, M.-E., Revel, M., and Bayon, G.: Lithium Isotope Composition of Marine Biogenic Carbonates
- and Related Reference Materials, Geostandards and Geoanalytical Research, 42, 403–415, https://doi.org/10.1111/ggr.12218, http://doi.
 wiley.com/10.1111/ggr.12218, 2018.
- Bullen, S. B. and Sibley, D. F.: Dolomite selectivity and mimic replacement, Geology, 12, 655, https://doi.org/10.1130/0091-7613(1984)12<655:DSAMR>2.0.CO;2, https://pubs.geoscienceworld.org/geology/article/12/11/655-658/188317, 1984.
- Burns, S. J., Mckenzie, J. A., and Vasconcelos, C.: Dolomite formation and biogeochemical cycles in the Phanerozoic, Sedimentology, 47,
 49–61, 2000.
- Carignan, J., Vigier, N., and Millot, R.: Three secondary reference materials for lithium isotope measurements: Li7-N, Li6-N and LiCl-N
 solutions, Geostandards and Geoanalytical Research, 31, 7–12, 2007.
- Dellinger, M., West, A. J., Paris, G., Adkins, J. F., von Strandmann, P. A. P., Ullmann, C. V., Eagle, R. A., Freitas, P., Bagard, M.-L., and
 Ries, J. B.: The Li isotope composition of marine biogenic carbonates: Patterns and Mechanisms, Geochimica et Cosmochimica Acta,
 2018.
- Fairchild, I. J. and Kennedy, M. J.: Neoproterozoic glaciation in the Earth System, Journal of the Geological Society, 164, 895–921,
 https://doi.org/10.1144/0016-76492006-191, http://jgs.lyellcollection.org/lookup/doi/10.1144/0016-76492006-191, 2007.
- Flesch, G. D., Anderson, A. R., and Svec, H. J.: A secondary isotopic standard for 6Li/7Li determinations, International Journal of Mass
 Spectrometry and Ion Physics, 12, 265–272, 1973.
- Geske, A., Zorlu, J., Richter, D., Buhl, D., Niedermayr, A., and Immenhauser, A.: Impact of diagenesis and low grade metamorphosis on isotope (δ²⁶Mg, δ¹³C, δ¹⁸O and ⁸⁷Sr/⁸⁶Sr) and elemental (Ca, Mg, Mn, Fe and Sr) signatures of Triassic sabkha dolomites, Chemical Geology, 332, 45–64, 2012.
- Gregg, J. M., Bish, D. L., Kaczmarek, S. E., and Machel, H. G.: Mineralogy, nucleation and growth of dolomite in the laboratory and
 sedimentary environment: A review, Sedimentology, 62, 1749–1769, https://doi.org/10.1111/sed.12202, http://doi.wiley.com/10.1111/
 sed.12202, 2015.
- 307 Hathorne, E. C. and James, R. H.: Temporal record of lithium in seawater: A tracer for silicate weather308 ing?, Earth and Planetary Science Letters, 246, 393–406, http://www.scopus.com/inward/record.url?eid=2-s2.
- 309 0-33747107536&partnerID=40&md5=eaa584abda4cb4fe510137c52bc40355https://ac-els-cdn-com.ezproxy.uow.edu.au/
- 310 S0012821X06003086/1-s2.0-S0012821X06003086-main.pdf?_tid=2497a4da-cd95-11e7-9ebf-00000aacb35d&acdnat=1511142790_
- 311 96f8e94acb3fcc4519433bade7e2c481, 2006.
- 312 Hoefs, J.: Theoretical and Experimental Principles, in: Stable Isotope Geochemistry, pp. 1–46, Springer International Publishing, Cham,
- 313 https://doi.org/10.1007/978-3-319-19716-6_1, http://link.springer.com/10.1007/978-3-319-19716-6{_}1, 2015.

- James, R. H. and Palmer, M. R.: The lithium isotope composition of international rock standards, Chem. Geol., 166, 319–326, 2000.
- 315 Kaczmarek, S. E. and Sibley, D. F.: A Comparison of Nanometer-Scale Growth and Dissolution Features on Natural and Synthetic Dolomite
- 316 Crystals: Implications for the Origin of Dolomite, Journal of Sedimentary Research, 77, 424–432, https://doi.org/10.2110/jsr.2007.035,
- 317 https://pubs.geoscienceworld.org/jsedres/article/77/5/424-432/145154, 2007.
- 318 Kazuyo Yamaji, Yoji Makita, Hidekazu Watanabe, Akinari Sonoda, Hirofumi Kanoh, ., , Takahiro Hirotsu, and Ooi*, K.: Theoretical Esti-
- mation of Lithium Isotopic Reduced Partition Function Ratio for Lithium Ions in Aqueous Solution, https://doi.org/10.1021/JP001303I,
 https://pubs.acs.org/doi/abs/10.1021/jp001303i, 2001.
- Kunzmann, M., Halverson, G. P., Sossi, P. A., Raub, T. D., Payne, J. L., and Kirby, J.: Zn isotope evidence for immediate resumption of primary productivity after snowball Earth, Geology, 41, 27–30, https://doi.org/10.1130/g33422.1, http://geology.gsapubs.org/content/41/
 1/27.abstract. 2013.
- Land, L. S.: Failure to precipitate dolomite at 25 degrees C from dilute solution despite 1000-fold oversaturation after 32 years, Aquatic
 Geochemistry, 4, 361–368, https://doi.org/10.1023/A:1009688315854, 1998.
- Lechler, M., Pogge von Strandmann, P. A. E., Jenkyns, H. C., Prosser, G., and Parente, M.: Lithium-isotope evidence for
 enhanced silicate weathering during OAE 1a (Early Aptian Selli event), Earth and Planetary Science Letters, 432, 210–
 222, https://doi.org/http://dx.doi.org/10.1016/j.epsl.2015.09.052, http://www.sciencedirect.com/science/article/pii/S0012821X15006299,
 2015.
- Li, D. D., Jacobson, A. D., and McInerney, D. J.: A reactive-transport model for examining tectonic and climatic controls on chemical weathering and atmospheric CO2 consumption in granitic regolith, Chemical Geology, 365, 30–42, https://doi.org/http://dx.doi.org/10.1016/j.chemgeo.2013.11.028, http://www.sciencedirect.com/science/article/pii/S0009254113005664, 2014.
- Liu, C., Wang, Z., Raub, T. D., Macdonald, F. A., and Evans, D. A. D.: Neoproterozoic cap-dolostone deposition in stratified glacial meltwater
 plume, Earth and Planetary Science Letters, 404, 22–32, https://doi.org/10.1016/j.epsl.2014.06.039, 2014.
- Liu, D., Xu, Y., Papineau, D., Yu, N., Fan, Q., Qiu, X., and Wang, H.: Experimental evidence for abiotic formation of low-temperature
 proto-dolomite facilitated by clay minerals, Geochimica et Cosmochimica Acta, 247, 83–95, https://doi.org/10.1016/J.GCA.2018.12.036,
 https://www.sciencedirect.com/science/article/pii/S0016703718307257, 2019.
- Marriott, C. S., Henderson, G. M., Belshaw, N. S., and Tudhope, A. W.: Temperature dependence of δ^7 Li, δ^{44} Ca and Li/Ca during growth of calcium carbonate, Earth and Planetary Science Letters, 222, 615–624, 2004a.
- Marriott, C. S., Henderson, G. M., Crompton, R., Staubwasser, M., and Shaw, S.: Effect of mineralogy, salinity, and temperature on Li/Ca
 and Li isotope composition of calcium carbonate, Chemical Geology, 212, 5–15, 2004b.
- Misra, S. and Froelich, P. N.: Lithium isotope history of Cenozoic seawater: Changes in silicate weathering and reverse weathering, Science,
 335, 818–823, https://doi.org/DOI 10.1126/science.1214697, <GotoISI>://000300356400035, 2012.
- Pistiner, J. S. and Henderson, G. M.: Lithium-isotope fractionation during continental weathering processes, Earth and Planetary Science
 Letters, 214, 327–339, https://doi.org/10.1016/s0012-821x(03)00348-0, 2003.
- Pogge von Strandmann, P. A. E., Jenkyns, H. C., and Woodfine, R. G.: Lithium isotope evidence for enhanced weathering during Oceanic Anoxic Event 2, Nature Geosci, 6, 668–672, https://doi.org/10.1038/ngeo1875
 http://www.nature.com/ngeo/journal/v6/n8/abs/ngeo1875.html#supplementary-information, http://dx.doi.org/10.1038/ngeo1875, 2013.

- Pogge von Strandmann, P. A. E., Desrochers, A., Murphy, M. J., Finlay, A. J., Selby, D., and Lenton, T. M.: Global climate stabilisation by chemical weathering during the Hirnantian glaciation, Geochemical Perspectives Letters, pp. 230–237, https://doi.org/10.7185/geochemlet.1726, 2017.
- Rollion-Bard, C., Vigier, N., Meibom, A., Blamart, D., Reynaud, S., Rodolfo-Metalpa, R., Martin, S., and Gattuso, J.-P.: Effect of environ mental conditions and skeletal ultrastructure on the Li isotopic composition of scleractinian corals, Earth and Planetary Science Letters,
 286, 63–70, https://doi.org/10.1016/j.epsl.2009.06.015, 2009.
- Rose, C. V. and Maloof, A. C.: Testing models for post-glacial 'cap dolostone' deposition: Nuccaleena Formation, South Australia, Earth
 and Planetary Science Letters, 296, 165–180, https://doi.org/10.1016/i.epsl.2010.03.031, 2010.
- Teng, F. Z., Dauphas, N., and Helz, R. T.: Iron Isotope Fractionation During Magmatic Differentiation in Kilauea Iki Lava Lake, Science,
 320, 1620–1622, https://doi.org/10.1126/science.1157166, 2008.
- Vasconcelos, C., McKenzie, J. A., Bernasconi, S., Grujic, D., and Tiens, A. J.: Microbial mediation as a possible mechanism for natural dolomite formation at low temperatures, Nature, 377, 220, https://doi.org/10.1038/377220a0, http://dx.doi.org/10.1038/377220a0http:
 //www.nature.com/articles/377220a0, 1995.
- Vigier, N. and Goddéris, Y.: A new approach for modeling Cenozoic oceanic lithium isotope paleo-variations: the key role of climate, Climate
 of the Past, 11, 635–645, https://doi.org/10.5194/cp-11-635-2015, 2015.
- Wanner, C., Sonnenthal, E. L., and Liu, X.-M.: Seawater δ⁷Li: A direct proxy for global CO2 consumption by continental silicate weather ing?, Chemical Geology, https://doi.org/http://dx.doi.org/10.1016/j.chemgeo.2014.05.005, http://www.sciencedirect.com/science/article/
 pii/S0009254114002435, 2014.
- 368 Winkelstern, I. Z., Kaczmarek, S. E., Lohmann, K. C., and Humphrey, J. D.: Calibration of dolomite clumped isotope thermometry, Chemical
- Geology, 443, 32–38, https://doi.org/10.1016/j.chemgeo.2016.09.021, http://dx.doi.org/10.1016/j.chemgeo.2016.09.021, 2016.



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



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



Figure 3. The distribution coefficient of Li between solid and solution ($D_{[Li]prec-sol}$) 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. (3). Error is not shown for the isotope fractionation factor at 220 °C 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^7 Li 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 HNO₃ does not release isotopically light Li into solution, although no residue was observed during dissolution in dilute HNO₃.



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^7 Li 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.

371 Tables

Sample ID	Reaction time	T (°C)	magnesite	dolomite	dolomite:
	(days)	1 (0)	mugnesite	uoronnite	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

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

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.

Sample ID	Temperature	δ^7 Li	δ^7 Li	$10^{3} lm(\alpha - 1)$		
Sample ID	(°C)	solution (%)	solid (‰)	10 $ln(\alpha_{prec-sol})$	$\nu_{[Li]prec-sol}$	
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	

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

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

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

 HCl and HAc

HCl concentration (M)	$\delta^7 { m Li}_d$ (%)	$\delta^7 { m Li}_c~(\%)$	Al (ppb)	Li (ppb)	Mg (ppm)	Ca (ppm)
0.05	9.46	20.1	151.0	19.8	162.0	3151.1
0.10	8.00	20.2	241.5	28.6	353.3	3407.1
0.15	7.27	20.2	637.4	32.4	538.9	3206.8
0.20	7.13	19.5	712.3	38.4	811.8	3612.8
0.30	7.62	19.3	848.9	51.3	1257.6	3984.8
0.50	7.04	17.8	2024.1	81.0	2209.0	4867.5
0.80	6.78	7.04	13588.1	114.6	2864.1	5649.2
1.00	6.29	16.7	21984.3	110.4	3245.4	6714.2
6.00	4.00	16.9	32541.9	161.7	3317.0	6406.7
total dissolution	n/a	20.6				
HAc concentration (%)	$\delta^7 { m Li}_d$ (‰)	_				
0.5	10.9					
2	8.37					

 $\delta^7 \text{Li}_d$ (%) and $\delta^7 \text{Li}_c$ (%) are the Li isotope composition of solutions from dolostone and coral leaching experiments, respectively.