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Temperature dependence of δ^7Li, δ^{44}Ca and Li/Ca during growth of calcium carbonate

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Abstract

Lithium and calcium isotope ratios, together with the Li/Ca element ratio, have been measured in calcites precipitated inorganically at temperatures ranging from 5 to 30 °C, and on seasonal growth bands from a coral. These measurements indicate the potential uses of these three environmental proxies. Carbonate Li isotopes are lighter than the solution from which they grow, probably due to equilibrium fractionation. This fractionation is not significantly influenced by temperature and, because Li is not involved in any known biological process, this suggests that carbonates will provide a recorder for the past Li-isotope composition of natural waters and hence for past weathering conditions. As has been observed previously for inorganic aragonite, the Ca-isotopes in inorganic calcite are lighter than the growth solution, and are only weakly dependent on temperature. This confirms that the temperature dependence observed in some species of foraminifera [Geochem. Geophys. Geosyst. 1 (2001)] reflects additional isotope fractionation due to biological processes during mineralization. Ca isotopes may therefore provide a powerful tool with which to investigate the processes of biomineralization. Finally, Li/Ca ratios in inorganic and biogenic carbonates increase as temperatures decrease with a sensitivity of ≈ 4% per °C. This temperature dependence of Li/Ca may prove useful to assess past temperatures in cold environments such as the deep ocean.

Keywords: lithium isotopes; calcium isotopes; calcium carbonate

1. Introduction

The trace element and isotope chemistry of calcium carbonates are generally fractionated from the media in which they precipitate. The degree of such fractionation is commonly influenced by aspects of the precipitation environment. This enables the use of measurements of trace element and isotope ratios as proxies to reconstruct the past environment. In this study, we assess the role of temperature, a key

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environmental variable, in controlling the fractionation of three such potential proxies in calcium carbonates—Ca isotopes, Li isotopes, and Li/Ca ratios.

Previous work has demonstrated temperature-dependent fractionation of Ca isotopes during calcite precipitation by both cultured [1] and natural [2] planktonic foraminifera. Such work has suggested the potential of Ca isotopes as a paleothermometer. The importance of Ca for foraminiferal biology, however, suggests that this fractionation may be biologically mediated and hence may also contain information about the mechanisms of calcification in foraminifera (and other biological carbonates). The importance of biological processes has been highlighted by recent work [3] which demonstrated that another species of planktonic foraminifera (*Orbulina universa*) contrasted with that originally analysed (*Globigernoides sacculifer*) in showing little or no temperature dependence in its Ca-isotope composition. Inorganic aragonite has also recently been shown to exhibit minimal fractionation [3]. In addition to changes in *T* and biological processes, variation in ancient foraminiferal δ^{44}Ca may reflect changes in oceanic δ^{44}Ca values and observed changes have been attributed to changes in the marine calcium cycle caused by differences in past weathering inputs [4].

Research on lithium isotopes has focused mainly on their potential uses as tracers for magmatic differentiation [5,6]; crust–mantle recycling [7]; and continental weathering [8,9]. There are presently very few measurements of Li isotopes in carbonates [10–12] and no previous work has systematically examined the controls on Li-isotope fractionation during incorporation into calcium carbonate. Sizeable Li isotope fractionation of 25‰ has, however, been measured in foraminifera and other natural calcium carbonate samples [10–12]. Li, unlike Ca, has no known biological function and is therefore much less likely to be influenced by biological processes during mineralization. The Li isotope composition of marine carbonates is therefore likely to be controlled directly by environmental conditions, or to reflect the composition of the seawater in which it formed.

Previous studies of the Li/Ca ratio in marine carbonates have demonstrated a temperature dependence in brachiopods [13] but no obvious dependence in foraminifera [14]. No previous study has investigated such a dependence in either inorganic carbonates, or coralline aragonite.

Recent advances in both thermal ionisation mass spectrometry (TIMS) and multi collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) have led to new interest in Ca and Li isotope research. New MC-ICP-MS instruments are able to precisely and accurately measure variations in these light isotope systems much more rapidly than by previous methods. This advance may allow the routine use of Ca and Li isotope measurements in marine carbonates to better understand the past environment. Such use, however, requires full understanding of the controls on isotope fractionation. This study attempts to constrain the role of temperature in such control.

2. Method

2.1. Inorganic growth experiments

To constrain the temperature dependence of isotope fractionation during inorganic growth, calcite samples were precipitated over a temperature range of 5–30 °C. To isolate the effect of temperature, all other variables (pH, solution composition, growth rate, etc) were monitored and kept constant between each precipitation. This precipitation was performed using an experimental setup adapted from Tesoriero and Pankow [15]—a well-established technique which has been widely used to assess trace-element incorporation during carbonate formation (e.g. Refs. [16–18]).

In this study, 425 ml of an initial reaction solution of 0.24 M $CaCl_2$ and 0.176 mM LiCl (L-SVEC standard) and 0.1 g seed calcite (Baker analysed reagent grade calcite) was kept agitated at constant temperature in a water bath. A dual syringe pump with two 50 ml syringes was used to add 0.5 M $NaHCO_3$ and 0.47 M $CaCl_2$ (+0.21 mM LiCl) to this solution at a constant input rate of 200 μl/min in all precipitation experiments. Addition of Ca and Li during the growth period, to compensate for the solid precipitated, ensured that the Ca and Li concentration of the growth solution remained respectively within 2% and 12% of the starting concentration in all growth experiments. Air was bubbled through the reaction vessel during the experiment to maintain a constant pCO_2 at atmospheric levels and to ensure constant pH (measured at 6.9–7.1 at frequent intervals during each precipitation experiment). Precipitation was performed over a period of 5 h at all temperatures, in which time approximately 1 g of calcite was precipitated. No relationship between growth temperature and mass of calcite precipitated was observed. The resulting calcite was then washed, filtered, oven dried and a portion used for XRD analysis to confirm the calcite mineralogy. All reagents used for this growth were analysed and found to contain insignificant levels of Li.

Growth rate is known to be an important factor in determining trace element partitioning into inorganic [19] and biogenic [20] calcite, even at very low growth rates. For this reason, growth rates were kept constant in each precipitation experiment by using an identical input rate and rapid sample mixing. This approach contrasts with a previous study of Ca isotope incorporation into aragonite [3] in which the growth rate was allowed to vary by a factor of 10 between low and high temperature growth experiments.

There are several differences between the inorganic growth experiments of this study and the environment of biogenic carbonate formation in the oceans. Inorganic growth rates are faster than typical biogenic carbonates, and the growth solutions used here have lower salinity and pH. This should be considered when comparing results with those of marine biogenic carbonates. The inorganic carbonates of this study do, however, more closely mirror conditions of precipitation of other natural carbonates, such as freshwater tufas, and were chosen as a simple starting point for investigation of Li and Ca incorporation without the complexity of competing ions and organic complexation.

2.2. Coral samples

To complement existing foraminiferal measurements, coral samples were also analysed. Fourteen subsamples were taken from a tropical pacific coral that has experienced significant inter-annual temperature variability. Analysis of these samples allowed isotope and element ratio variability during natural temperature changes to be observed.

An underwater hydraulic drill was used to collect a 75 mm diameter core from a living, 4 m diameter, massive *Porites* coral at Jarvis Island (0°22.3′ S, 159°59.0′ W) in September 1999. The coral lived in an unrestricted setting, well flushed with open-ocean water, and the top of the coral was at a depth of 4 m. For this study, 5 mm growth increments of ~ 200 mg weight were cut from the coral skeleton using a micro-saw. Annual cycles in $\delta^{13}C$ indicate that the coral grew at approximately 20 mm/year. These samples therefore represent ~seasonal temporal resolution. In addition, a high-resolution oxygen isotope profile was prepared by sampling 2 mm growth increments from the core slab immediately adjacent to where the 5 mm growth increments were cut. These subsamples, of 0.5–1.0 mg weight, were analysed on an isotope ratio mass spectrometer with automatic carbonate preparation system at Edinburgh. Long-term analytical precision of the analyses, as determined by analysis of internal consistency standards, is ± 0.16 ‰ (2σ). The 200 mg aragonite blocks were prepared for δ^7Li measurement by coarse crushing, washing in an ultrasonic cleaning bath (2×18 MΩ H_2O, $1 \times H_2O_2$, 1×18 MΩ H_2O), and ion-exchange separation of the Li. ICP-MS analysis of possible contaminant phases (e.g. Fe, Mn, Al) showed this cleaning to be sufficient for these samples. In addition to these *Porites* samples, a single sample from an *Acropora* coral was analysed to assess inter-species differences.

2.3. Chemistry

A complete separation of Li from Na and Ca is required before measurements of δ^7Li by MC-ICP-MS because the large amount of Ca present would otherwise coat the cones, and because the Na would cause a change in the mass bias during analysis. This separation must produce a 100% yield of Li because there is significant isotope fractionation during the column chemistry. The separation was achieved using a 20 ml column of BioRad AG50W × 8 (200–400 mesh) cation exchange resin and a mixed 1 M HCl, 80% methanol eluting solution (similar to that of Pistiner and Henderson [9], and based on that of Strelow [21]). The 100% recovery and lack of isotope fractionation during the separation was verified by measuring L-SVEC and seawater passed through chemistry.

For natural samples, chemical separation of Ca from other elements is necessary, particularly from Sr for which doubly charged ions interfere in the Ca-isotope spectrum [22]. In this study, inorganically precipitated samples were grown in a solution without Sr, so do not contain Sr, negating the need for such chemistry.

2.4. Mass spectrometry

Lithium and calcium isotopes were measured on a Nu Instruments MC-ICP-MS. The 12 Faraday cups and wide flight tube of the Nu Instruments machine allows simultaneous collection of ^{7}Li and ^{6}Li or ^{44}Ca, ^{43}Ca and ^{42}Ca isotopes.

Ca isotope ratios were measured as ^{44}Ca/^{42}Ca rather than ^{44}Ca/^{40}Ca because the large ^{40}Ar beam prevents measurement of ^{40}Ca by MC-ICP-MS. An existing MC-ICP-MS technique for calcium isotopes was followed [23] in which ^{44}Ca, ^{43}Ca and ^{42}Ca isotopes are collected in Faraday cups. Mass 43.5 and background signals (in mass positions 41.5, 42.5, 42.75, 43.25, 43.75, 44.5, and 45) are also monitored in Faraday cups to correct for any doubly-charged Sr and scattering from the large ^{40}Ca and ^{40}Ar beams. This correction was small for all the analyses of this study. Ten 10-s measurements were collected per sample. Samples were bracketed with standard measurements using the NIST Ca standard, SRM915a. A three-isotope plot of ^{44}Ca/^{42}Ca vs. ^{43}Ca/^{42}Ca verifies the validity of this measurement protocol: a range of Ca standard solutions fall on a line with a gradient of ≈ 0.5 [22] as predicted by mass-dependent fraction. We report results as δ^{44}Ca defined by: $[\{(^{44}\text{Ca}/^{42}\text{Ca})_{\text{sample}} - (^{44}\text{Ca}/^{42}\text{Ca})_{\text{standard}}\}/(^{44}\text{Ca}/^{42}\text{Ca})_{\text{standard}}] \times 10^3$ relative to Ca isotope standard SRM 915a. This differs from previous studies [1–4], which have used ^{40}Ca as the normalizing isotope and a variety of different normalizing standards. A reasonable conversion from δ^{44}Ca (vs. ^{42}Ca) to δ^{44}Ca (vs. ^{40}Ca) can be made by simply multiplying the former by 2. We have chosen not to do that in this study, because we believe that ^{42}Ca is a more suitable

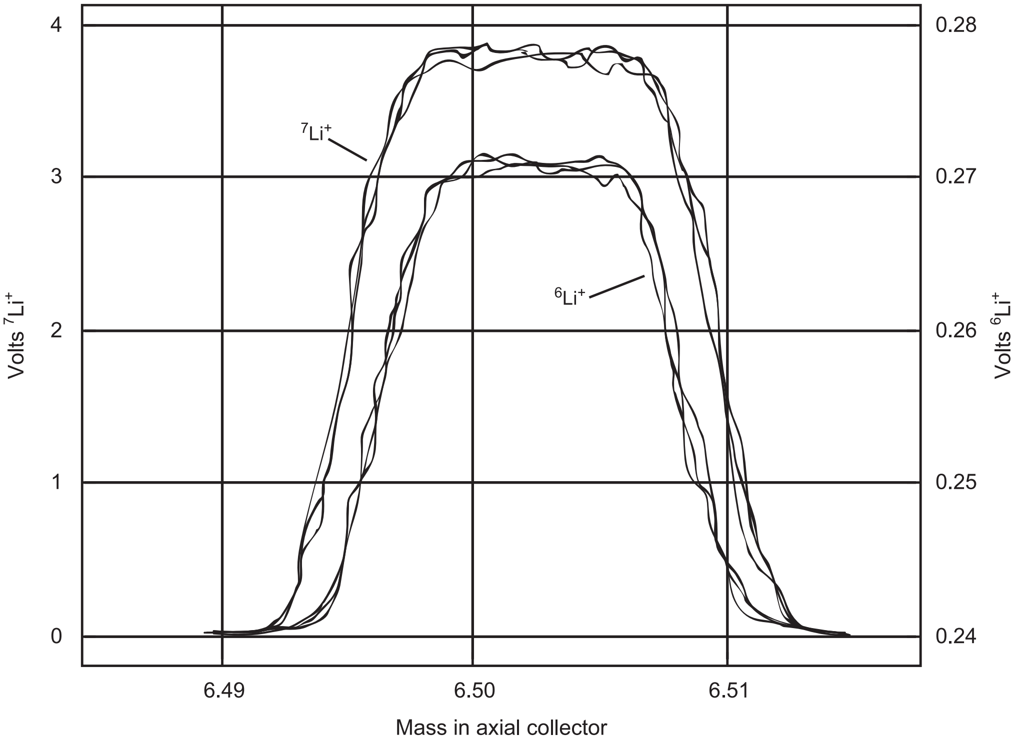

Fig. 1. Three repeat mass scans demonstrating the flat-topped peaks, magnet stability, and accurate alignment of ^{7}Li and ^{6}Li in two Faraday cups on the Nu Instruments MC-ICP-MS. Beams are centred at either end of the mass array using the "zoom" optics of the mass spectrometer.

isotope than ^{40}Ca for normalisation because of the presence of variable amounts of radiogenic ^{40}Ca in nature from decay of ^{40}K [24]. All data discussed in this paper have therefore been converted to δ^{44}Ca (vs. ^{42}Ca). External repeatability of δ^{44}Ca is ± 0.2 ‰ (2σ) based on repeated measurement of standards.

Lithium isotopes were also analysed on the Nu Instrument with ^{7}Li and ^{6}Li isotopes collected in Faraday cups at the far ends of the collector array. MC-ICP-MS offers significant advantages over the TIMS technique more commonly used for Li isotope analysis because the stability of fractionation during MC-ICP-MS enables higher precision and dramatically faster throughput [25]. In the Nu Instrument, a combined quadratic and linear field is applied to the "zoom" lens in order to centre the ^{7}Li and ^{6}Li beams into the two Faraday collectors (Fig. 1). The alignment and centring of the beams was checked frequently during each analysis session.

Standards and purified Li samples were introduced to the plasma by self-aspiration with a Cetac Aridus nebuliser with an uptake rate of approximately 80 μl/min. The instrument setup, including voltages to lenses and electrostatic analyser, gas flow rates and torch position, were optimized at the beginning of the session. Standards and samples were analysed as a 100 ppb Li solution in 2% nitric acid. This yielded 2.5×10^{8} counts per second of ^{7}Li^{+}—equivalent to an ion yield of 0.02 ‰. Total sample size per analysis was 30 ng of Li per sample. After an initial uptake of the sample for 60 s, ten 10-s ratio measurements were collected per sample. Background signals on the two Faraday cups were measured for 20 s before the start of the ratio measurement. After each analysis Li was washed from the system with 2% and 10% nitric acid for a total of 270 s.

A slight drift in instrumental mass fractionation occurring during each day of analysis was corrected using a standard-sample-standard bracketing technique with L-SVEC standard. The complete cycle from commencing one standard to commencing the next takes approximately 15 min and is sufficiently fast to remove this long-term drift. Memory effects were minimized by carefully matching sample and standard concentrations, and were monitored by analysis of 2% HNO_3 approximately every 2 h during an analysis run. Typical memories were reasonably constant during a day of analysis at 4 mV for ^{7}Li and are small compared to beam sizes of 4 V. Although this small memory is isotopically light (~ − 330 ‰), its isotope ratio does not change significantly with time so the matching of standard and sample concentra-

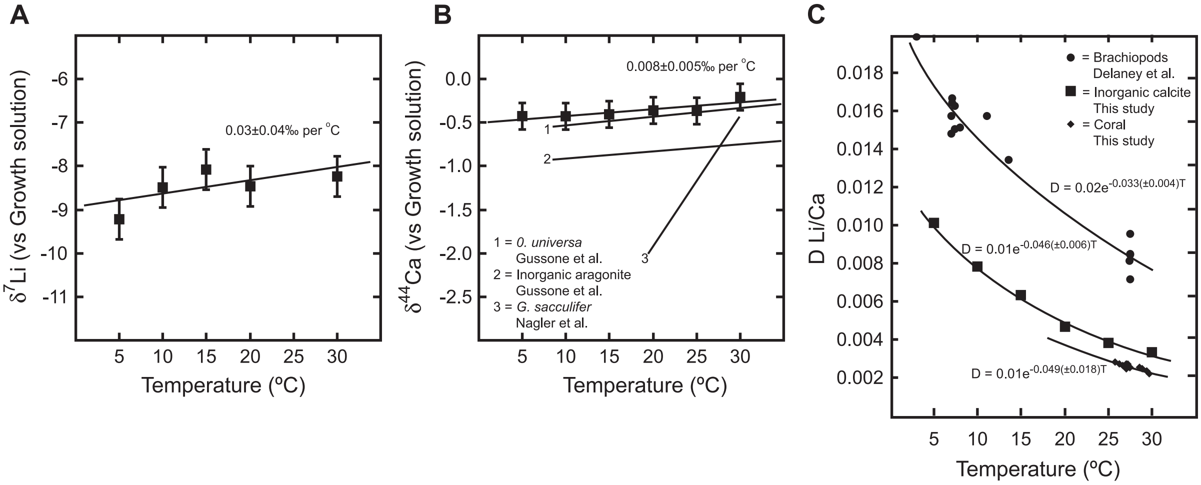

Fig. 2. (A) Lithium isotope ratios, (B) calcium isotope ratios and (C) Li/Ca distribution coefficients of inorganic calcite samples precipitated over a range of temperatures. $D_{(\mathrm{Li/Ca})}$ for the coral samples (Fig. 3) are also shown in panel C against an average SST for the sampling interval. These D values can be converted to Li/Ca mass ratios by multiplication by the seawater Li/Ca mass ratio of 0.000433. Errors on data and fits are 95% confidence. Note the small decrease of isotope fractionation and large decrease of Li/Ca with increasing temperature. Ca-isotope data are compared to previous data from Gussone et al. [3] and Nagler [1] recalculated according to the definition of δ^{44}Ca used in this study ($\delta^{44}\mathrm{Ca}=[\{(^{44}\mathrm{Ca}/^{42}\mathrm{Ca})_{\mathrm{sam.}} - (^{44}\mathrm{Ca}/^{42}\mathrm{Ca})_{\mathrm{std.}}\}/(^{44}\mathrm{Ca}/^{42}\mathrm{Ca})_{\mathrm{std.}}] \times 10^{3}$.

tions and standard bracketing also ensure that it does not bias measured isotope ratios.

Measurement of an in-house lithium standard (L-SVEC doped with ^{6}Li so as to be ≈ 10‰ lighter than L-SVEC) during a session of analysis allows the calculation of an external repeatability for each day of analysis (which is usually in the range ± 0.35–0.7‰, 2σ) and is also used as a monitor for the performance of the machine. We report results as $\delta^7\text{Li}=[\{(^7\text{Li}/^6\text{Li})_{\text{sample}} - (^7\text{Li}/^6\text{Li})_{\text{standard}}\}/(^7\text{Li}/^6\text{Li})_{\text{standard}}] \times 10^3$ relative to the L-SVEC Li-isotope standard.

Li concentrations in the samples were routinely measured by beam size comparison with a standard of known concentration to provide a concentration precision of ± 10%. Li/Ca ratios were also measured by quadrupole ICP-MS to a precision of ± 2%.

3. Results

Calcium isotope composition for the inorganically precipitated calcites show little dependence on temperature. A best fit to the δ^{44}Ca data suggests a temperature dependence of only 0.008 ± 0.005‰ per °C (Fig. 2B). The calcite is isotopically light with δ^{44}Ca 0.3–0.4‰ lower than the growth solution (which has δ^{44}Ca= + 0.31‰).

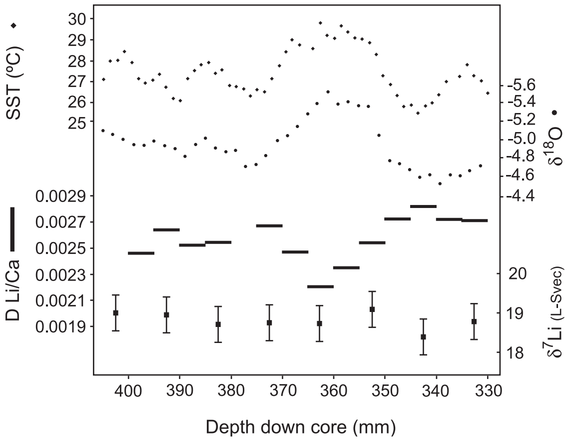

Fig. 3. Lithium isotope ratios and Li/Ca distribution coefficients of subsamples from the Jarvis Island coral with corresponding oxygen isotope and SST data. Li/Ca bars represent sampling interval. Note the lack of relationship between δ^7Li and temperature, but the clear inverse relationship between Li/Ca and temperature.

Table 1
Li and Ca data for inorganic calcite and coralline aragonite samples

Sample	Temperature (°C)	δ^{44}Ca (SRM-915a)	δ^7Li (L-SVEC)	Li/Ca (g/g 10^{-7})	D Li/Ca (10^{-3})
Inorganic calcite					
CM019	30		− 7.6 ± 0.6	4.26	3.33
			− 8.9 ± 0.6		
CM020	25			4.89	3.82
CM021	20		− 8.4 ± 0.6	5.98	4.67
			− 8.5 ± 0.6		
CM022	15		− 8.3 ± 0.6	8.11	6.33
			− 7.9 ± 0.6		
CM023	10		− 8.6 ± 0.6		
			− 8.1 ± 0.6		
CM025	10		− 8.8 ± 0.6	10.02	7.83
			− 8.6 ± 0.6		
CM024	5		− 8.6 ± 0.6	12.95	10.12
			− 10.1 ± 0.6		
CM040	30	0.09 ± 0.2			
CM039	25	− 0.07 ± 0.2			
CM038	20	− 0.06 ± 0.2			
CM041	15	− 0.11 ± 0.2			
CM042	10	− 0.13 ± 0.2			
CM043	5	− 0.13 ± 0.2			
Growth solution		0.31 ± 0.2			
Coral Samples					
jar99-2-4-lith9			18.8 ± 0.4	11.73	2.71
jar99-2-4-lith10				11.77	2.72
jar99-2-4-lith11			18.4 ± 0.4	12.19	2.82
jar99-2-4-lith12				11.78	2.72
jar99-2-4-lith13			19.1 ± 0.4	11.00	2.54
jar99-2-4-lith14				10.17	2.35
jar99-2-4-lith15			18.7 ± 0.4	9.54	2.20
jar99-2-4-lith16				10.69	2.47
jar99-2-4-lith17			18.8 ± 0.4	11.56	2.67
jar99-2-4-lith19			19.0 ± 0.4	11.01	2.54
jar99-2-4-lith20				10.91	2.52
jar99-2-4-lith21			18.9 ± 0.4	11.42	2.64
jar99-2-4-lith22				10.65	2.46
jar99-2-4-lith23			19.0 ± 0.4		
Acropora			21.0 ± 0.4		

Replicate analyses have same sample name, replicate precipitations have different sample names. Isotope errors are 2σ based on external repeatability measurements during the day of analysis. Li/Ca ratios are expressed as g/g and have errors of 2%. $\delta^7\text{Li}=[\{(^7\text{Li}/^6\text{Li})_{\text{sam.}} - (^7\text{Li}/^6\text{Li})_{\text{std.}}\}/(^7\text{Li}/^6\text{Li})_{\text{std.}}]$, $\delta^{44}\text{Ca}=[\{(^{44}\text{Ca}/^{42}\text{Ca})_{\text{sam.}} - (^{44}\text{Ca}/^{42}\text{Ca})_{\text{std.}}\}/(^{44}\text{Ca}/^{42}\text{Ca})_{\text{std.}}]$.

The δ^7Li of the calcite grown across the same range of temperature varies by only 1.5‰ and shows no significant temperature dependence (slope = 0.03 ± 0.04‰ per °C; Fig. 2A). Calcite δ^7Li is ≈ 8.5‰ lighter than the solution from which it was precipitated (L-SVEC).

The concentration of Li incorporated into the calcite decreases dramatically as temperature increases (Fig.

2C). Measured Li/Ca values have been converted into distribution coefficients (D) according to the equation, $D_{(Li/Ca)}$=[(Li/Ca)$_{carbonate}$/(Li/Ca)$_{solution}$]. Li/Ca in the carbonate was corrected for the mass of Ca present in the seed calcite prior to calculating $D_{(Li/Ca)}$. $D_{(Li/Ca)}$ values for the inorganic calcite decrease by a factor of 3 from 0.0092 at 5 °C to 0.0030 at 30 °C—a variation in $D_{(Li/Ca)}$ of 4.6(± 0.6)% per °C. There is therefore a strong discrimination against Li incorporation into the calcite at all temperatures, and this discrimination increases with increasing temperature.

For the 14 subsamples from the *Porites* coral, δ^7Li shows little variability, while the Li/Ca ratio varies in line with δ^{18}O changes (Fig. 3). δ^7Li varies by only 1.2‰, from 18.4 to 19.6 and are offset by − 11‰ from the seawater from which the coral grew. δ^7Li for the one *Acropora* sample is offset by − 8.5‰ relative to seawater (Fig. 3). A temperature change of approximately 5 °C (from 25 to 30 °C) is indicated by the δ^{18}O data and from instrumentally derived estimates of sea surface temperature at the coral site. Coralline Li/Ca varies from 0.95 to 1.22 mg/g (equivalent to a range of D from 0.0025 to 0.0030) over this range (Table 1), a change of 4.9(± 1.8)% per °C with the same inverse relationship to temperature as observed in inorganic calcite, despite the different mineralogy of the coral (Fig. 2c).

4. Discussion

4.1. δ^7Li

The δ^7Li offset from the growth solution indicates a preference for ^{6}Li incorporation during inorganic calcite precipitation (Fig. 2a) but, at the level of precision achieved here, this preferential incorporation is not temperature-dependent. Li is thought to incorporate into the interstitial sites within the calcite structure [26] rather than by direct substitution for Ca as seen for Mg and Sr [27].

The preferential incorporation of ^{6}Li into the calcite may be explained as either a kinetic or equilibrium fractionation. If it is kinetic, the maximum fractionation possible (≈ 80‰ assuming equal kinetic energy of Li atoms and the relative mass difference of ^{6}Li and ^{7}Li) is much larger than that observed (≈ 9‰). The small size of the observed fractionation could be explained by one or more of three processes: incorporation of Li as a heavy molecule rather than Li$^+$; impoverishment of Li from a boundary layer surrounding the mineral during growth; or the presence of a significant back reaction during growth so that equilibrium is approached before Li is irreversibly incorporated in the carbonate structure. Li is not generally associated with other elements in aqueous solution, but does have a first hydration sphere of 4 water molecules [28]. Li is unlikely to be incorporated into the carbonate in this hydrated state, however, because the maximum possible kinetic fractionation for a species of this mass is smaller (≈ 6‰) than that observed here (≈ 9‰). Boundary layer processes or the presence of a back-reaction would therefore have to be invoked if the Li fractionation is kinetically induced.

It is striking that the Li isotope fractionation appears constant, even over a three fold change in the concentration of Li incorporated into the calcite. This observation argues against a kinetic fractionation which would be expected to vary with the quantity of Li incorporated. Many minerals incorporate Li which is isotopically lighter than the growth medium from which they form. Teng et al. [29] have suggested that this might be explained by a change from four- to sixfold coordination of the Li during mineral growth, and a corresponding decrease in the strength of bonding. On the basis of ab initio calculations [30], this change in coordination is expected to result in isotopically light Li in the resulting mineral. Isotopically light Li in the grown calcites is therefore likely to be due to an equilibrium fractionation process.

The δ^7Li results for the coralline aragonite (Fig. 3) indicate a lack of temperature dependant fractionation of Li isotopes during incorporation into natural carbonates. This observation makes it likely that variations observed in ancient carbonates are likely to reflect changes in the composition of natural waters with time, without a variable offset caused by environmental changes.

4.2. δ^{44}Ca

As with Li, Ca isotopes in inorganic calcite are lighter than those in the growth medium and show little change with increasing temperature (Fig. 2b). As with Li, the size of the fractionation (≈ 0.5 ‰) is significantly smaller than the maximum fractionation possible due to kinetic effects (≈ 20 ‰). The role of a hydration sphere in controlling Ca isotope fractionation during carbonate growth has been suggested [3] but is unlikely to fully explain the small size of the observed fractionation because this would require a mass of ≈ 1000 (or about 50 water molecules) about twice the maximum hydrated mass of Ca [31,32]. The presence of boundary layer effects or of a significant back-reaction are therefore necessary to explain the small size of the fractionation if it is due to kinetic processes. The fractionation is better explained as due to equilibrium processes. As for Li, the change from bonding to water molecules in solution, to bonding within the carbonate structure, may involve a decrease in bond strength and a subsequent tendency for the carbonate to be enriched in the light isotope.

Such an equilibrium fractionation mechanism is supported by the close agreement between the fractionation and temperature dependence of Ca-isotope incorporation into inorganic calcite with that previously observed in the planktonic foraminifera, *Orbulina universa* [3] (Fig. 2b). Both have δ^{44}Ca offset from the growth medium by -0.5 ‰, and both show the same slight decrease in fractionation with increasing temperature. Given the different growth rates and mechanisms of the inorganic and biogenic calcite, this close agreement is very difficult to explain as a kinetic fractionation and suggests that equilibrium fractionation occurs both in the inorganic growth experiments conducted here, and during growth of *O. universa*. This conclusion is also consistent with the slight decrease in fractionation observed with increasing temperature.

The similarity of Ca isotope fractionation between inorganic calcite and that of *O. universa* suggests that this species of foraminifera precipitates its calcite directly from seawater by a simple inorganic process. This is in marked contrast to *G. sacculifer* which shows a generally greater degree of fractionation, and a stronger temperature dependence [1]. This behaviour indicates a strong additional biological fractionation of Ca isotopes during the calcification process of *G. sacculifer*. The difference in Ca isotope fractionation between *O. universa* and *G. sacculifer* may be explained by the different mineralization processes for these two species. Isotope doping experiments have indicated the presence of a biologically mediated internal Ca pool for *G. sacculifer* [33] but not for *O. universa* [34]—a conclusion supported by modelling work [35]. Many biological processes induce significant kinetic isotope fractionation, often because biological transport is unidirectional. The larger Ca isotope fractionation for *G. sacculifer* can be explained by the presence of active biological pumping of Ca into the internal pool, a process not present during inorganic growth or biomineralization by *O. universa*.

The small temperature dependence of Ca isotope fractionation during inorganic calcite fractionation, and the large biological overprint seen for species actively pumping Ca, suggests that Ca isotopes in natural carbonates samples will be difficult to use as a reliable paleothermometer. Ca isotopes do, however, show significant promise for the provision of information about biomineralization processes.

4.3. Li/Ca

An inverse correlation between Li/Ca and temperature is seen in both the inorganic calcite and the coralline aragonite. A similar relationship has also been seen for brachiopods [13] with a sensitivity of $-3.3 \pm 0.4\%$ per °C (Fig. 2c). These results indicate that Li is generally more readily incorporated into carbonates at low temperatures. Existing data on Li/Ca incorporation in cultured foraminifera suggest no such T dependence [14], but such foraminifera data is sufficiently limited that this observation may not be robust. It is therefore possible that many marine carbonates demonstrate an inverse relationship between Li/Ca and temperature.

$D_{(\mathrm{Li/Ca})}$ for inorganic calcite in this study differs by only 30% from that of coral aragonite, but this level of agreement may be coincidental. $D_{(\mathrm{Li/Ca})}$ for other carbonates differ more with, for instance, brachiopods having $D_{(\mathrm{Li/Ca})}$ more than twice as high as either the inorganic calcites or corals. Similarly, foraminifera show a range of $D_{(\mathrm{Li/Ca})}$ from 0.0045 to 0.0100 at 30 °C [14]. The difference in $D_{(\mathrm{Li/Ca})}$ between these various forms of calcium carbonate suggests that temperature is not the only influence on Li incorporation, although it obviously does play an important role in controlling $D_{(\mathrm{Li/Ca})}$.

The decrease in Li/Ca with increasing temperature might be explained by a solubility effect (in a similar way to decreases in Sr/Ca) if the solubility of Li_2CO_3 increases relative to $CaCO_3$ at higher temperatures [36]. However, the solubility of Li_2CO_3 actually decreases with temperature [37], indicating that solubility is not the primary control on carbonate Li/Ca. Indeed, the assumption of equilibrium and the use of thermodynamic solubility products in calculating distribution coefficients [38] is not likely to be valid for Li which does not form a solid solution with Ca and instead is probably incorporated into interstitial sites [26]. A better explanation is that Li incorporation into the calcite structure is exothermic and is therefore less favoured at higher temperatures. The energetics of trace-element incorporation into calcite differs depending on the crystal face of growth and on the available surface adsorption site [38,39]. Li is preferentially incorporated into the 0001 face in calcite [40]. This face is exothermic compared to other faces and is therefore likely to be favoured at lower temperatures [41]. This suggests that changes in the rate of growth of various crystal faces may play a role in the fractionation of trace elements such as Li into calcite.

The strong temperature dependence of $D_{(\mathrm{Li/Ca})}$ observed for inorganic and biogenic calcium carbonates could lend itself to possible applications as a paleothermometer with particular sensitivity at low temperatures such as those found in the deep ocean.

5. Conclusions

In summary, Li and Ca isotopes and Li/Ca ratios in carbonates show potential as environmental proxies in three areas. The lack of temperature dependence of lithium-isotope fractionation suggests that carbonates could be used as a direct record of the δ^7Li of natural waters to provide information about past weathering. Calcium isotopes encode more than a simple temperature signal and may provide insight into biomineralization processes. The inverse temperature dependence of Li/Ca is particularly sensitive at low T and may provide a tool to investigate past temperature changes in the deep-ocean.

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