

Effect of mineralogy, salinity, and temperature on Li/Ca and Li isotope composition of calcium carbonate

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Abstract

Li/Ca and Li isotope ratios in marine and freshwater calcium carbonates are potential tracers of past environmental variables such as weathering intensity and temperature. To make use of their potential requires full understanding of the fractionation of Li/Ca and ⁷Li/⁶Li during growth of calcium carbonate. This study improves such understanding with two sets of new measurements: on inorganic calcites and aragonites precipitated over a range of salinity and on the test of benthic foraminifera formed at a range of temperatures.

Li/Ca in inorganic calcite increases by a factor of four as salinity increases from 10‰ to 50‰. Inorganic aragonite demonstrates no significant change in Li/Ca over the same salinity range. The difference in behaviour is probably due to the incorporation mechanism of Li. Substitution of Li⁺ in the Ca²⁺ site in aragonite makes growth-solution Li/Ca the key variable, while interstitial incorporation of Li⁺ in calcite means that the growth-solution Li concentration is more important. Compared to the growth solution, ⁷Li/⁶Li is ≈ 3‰ lower in calcite and ≈ 11‰ lower in aragonite, with no relationship to salinity for either mineral. Similar isotope fractionation to these inorganic experiments are observed for biogenically produced calcite (foraminifera) and aragonite (corals). This suggests little biological control during Li incorporation into biogenic calcium carbonates. The difference in fractionation between calcite and aragonite is consistent with an equilibrium isotope fractionation reflecting different incorporation mechanisms for Li into the two minerals.

Four samples of the benthic foraminifera *Uvigerina*, precipitated over a temperature range of 14 °C, have Li/Ca ranging from 18.5 to 13.1 μmol/mol. The ratio is inversely related to temperature with a sensitivity of 2.5 ± 0.8% per °C. This sensitivity is similar to that observed in a previous study of foraminiferal Li/Ca, but about half that observed during inorganic calcite growth. The large variability in both Li/Ca and temperature sensitivity exhibited between various foraminifera species suggests an additional control on calcite Li/Ca apart from those of salinity and temperature observed in this study.

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1. Introduction

Natural calcium carbonate may provide an archive of the past Li/Ca and $^7\text{Li}/^6\text{Li}$, of natural waters which in turn may provide information about the past environment such as the intensity of global hydrothermal circulation or weathering. Alternatively, the offset of carbonate Li/Ca and $^7\text{Li}/^6\text{Li}$ from that in the waters may be dependant on environmental variables such as temperature or salinity, thus providing new proxies for past change. With these goals in mind, several previous studies have investigated Li incorporation into natural carbonates.

The first investigation of Li/Ca used cultured foraminifera to demonstrate that the Li/Ca of foraminiferal calcite was directly related to the Li/Ca ratio of the seawater from which it grew (Delaney et al. 1985). In a subsequent study, Delaney and Boyle (1986) used the Li/Ca concentration of mixed planktonic foraminifera samples to constrain seawater lithium concentration and to suggest that hydrothermal input to the ocean has not changed by more than 30–40% over the last 116 Ma. The first measurements of Li isotopes in four Pleistocene samples of the foraminifera *Pulleniatina obliquiloculata* (You and Chan, 1996) reported $\delta^7\text{Li}$ values of 19 and 23 for two glacial samples and 27 and 42 for two interglacial samples (where $\delta^7\text{Li} = \left\{ \frac{(^7\text{Li}/^6\text{Li})_{\text{sample}}}{(^7\text{Li}/^6\text{Li})_{\text{L-SVEC standard}}} - 1 \right\} \times 10^3$). More recently, Kosler et al. (2001) measured $\delta^7\text{Li}$ in modern foraminifera by quadrupole ICP-MS and reported values for Holocene *P. obliquiloculata* samples of 27 to 31 (close to the seawater value of ≈ 31), but values up to 51 for *Globorotalia tumida* from the same core tops. A study by Hoefs and Sywall (1997) reported a wider range of $\delta^7\text{Li}$ for Holocene samples (7 to 20) which may have been due to use of non-species-specific samples or to inadequate sample cleaning.

To develop these pioneering studies into a fuller understanding of the controls on Li/Ca and $\delta^7\text{Li}$, Marriott et al. (2004) investigated a series of laboratory-grown carbonates and natural coral samples. The Li isotope composition of inorganic calcite was shown to be independent of temperature, but the Li/Ca ratio showed a strong negative

relationship with temperature. Coral aragonite also showed no temperature dependence for $\delta^7\text{Li}$ and an identical inverse relationship between Li/Ca and temperature. These results therefore suggested that $\delta^7\text{Li}$ in natural calcium carbonates would act as a recorder of the isotope composition of the waters in which they grew, without a variable offset due to other environmental changes. This makes such carbonates potentially useful. There is an increasing body of evidence indicating that Li isotopes are fractionated during continental weathering processes so that the $\delta^7\text{Li}$ of natural waters, and particularly of seawater, might provide information about the past style of such weathering (Huh et al., 2001; Pistiner and Henderson, 2003). These early results also indicate that the Li/Ca of natural carbonates records information about both the water composition and the temperature of growth. The temperature effect is of particular interest because, due to its inverse nature, it may be a useful paleothermometer at low temperatures.

The potential of Li/Ca and $\delta^7\text{Li}$ as tracers of past weathering and temperature justify further investigation. In this study, we therefore address three specific questions not answered in earlier studies. First, what is the significance of mineralogy on Li/Ca and $\delta^7\text{Li}$ fractionation in calcium carbonates? Second, what is the role of ionic strength of the growth solution (i.e., its salinity)? And third, what is the temperature dependence of Li/Ca and $\delta^7\text{Li}$ in the naturally occurring calcite of marine foraminifera? The last question had not been addressed since the work of Delaney et al. (1985) and Delaney and Boyle (1986) until a comprehensive recent study by Hall and Chan (2004) who reported a temperature dependence for Li/Ca somewhat smaller than that found in inorganic precipitates, and suggested other controls on the Li/Ca ratio in addition to temperature. New results in this study are compared with the results of Hall and Chan (2004) below.

The goals of this study are to improve understanding of the incorporation of Li into calcium carbonates generally, be they inorganic (e.g., tufas, speleothems, etc.) or biogenic (e.g., corals, foraminifera, etc). We therefore make measurements on both inorganically precipitated laboratory samples and on foraminifera.

2. Sample preparation

2.1. Inorganic samples

Inorganic calcite and aragonite samples were precipitated over a salinity range of 10‰ to 50‰ using an experimental setup adapted from Tesoriero and Pankow (1996) and identical to that of Marriott et al. (2004). A large volume of artificial seawater (Kester et al., 1967) with a salinity of 50‰ was mixed, and aliquots diluted to the required salinity for each experiment. This artificial seawater contained Na^+ , Ca^{2+} , Sr^{2+} , Cl^- , Br^- , and F^- at ratios identical to those found in natural seawater. Trace metals (Li^+ , U^{4+} , Cd^{2+} , Ba^{2+} , and Zn^{2+}) were added at 10 times their seawater concentration to ensure sufficient mass for analysis in the grown carbonates. Lithium of known isotopic composition (L-SVEC) was added as Li_2CO_3 to give an initial Li concentration in the artificial seawater of ≈ 2 ppm (at 35‰ salinity) and a Li/Ca of ≈ 0.024 mol/mol. In order to prevent premature precipitation of calcium carbonate, no other CO_3^{2-} ion was added to the initial seawater solution. Mg^{2+} and SO_4^{2-} were at natural seawater concentrations (salinity normalized) for the aragonite growth experiments, but were reduced to one-tenth of the seawater concentration and zero respectively for the calcite growth experiments. The SO_4^{2-} concentration was found to control the mineral formed with calcite always forming in the absence of SO_4^{2-} regardless of the Mg^{2+} concentration.

For each experiment, 500 ml of growth solution was made from the 50‰ artificial-seawater solution by dilution with pure water. This solution was agitated by stirring and bubbling of air and kept at a constant temperature of 25 °C in a water bath. After 30 min, 0.10 g of Baker Analysed reagent-grade calcite powder was added as seed crystals (to both calcite and aragonite experiments) and stirring continued for a further 30 min. NaHCO_3 and CaCl_2 solutions were then added via a dual syringe pump at a rate of 1.5×10^{-5} moles/min for 5.5 h. The bubbled air ensured a constant $p\text{CO}_2$ and near constant pH. The latter was measured every 30 min during growth and always increased from 7.7 at the beginning of the experiment, to 8.3 after 2 h, before dropping to 8.1 by the end of the experiment.

The reaction vessel was left for 30 min with continued stirring after completion of reagent addi-

tion. Grown carbonates were then filtered from the solution with Whatman glass microfibre filters and rinsed three times with distilled water. Approximately 0.5 g of calcite and 0.31 g of aragonite was grown in each experiment, with no systematic relationship observed between mass grown and salinity. This compared to an expected growth mass of 0.5 g. The incomplete reaction for the aragonite experiments reflects the difficulty of precipitating calcium carbonate in the presence of Mg^{2+} and SO_4^{2-} . XRD analysis was performed on a small portion of each grown carbonate to confirm mineralogy.

It is important that the Li/Ca of the solution is well constrained and, preferably, constant during the carbonate growth. Two effects may cause a change in the solution chemistry. First, the precipitation of carbonate may deplete the solution in Li as it is incorporated into the mineral. Given the large volume of initial solution, and low Li content in the precipitated carbonate, this effect causes significantly less than 1% change to the solution Li/Ca ratio. The second effect is due to initial undersaturation of the reaction solution with respect to CaCO_3 . If the solution is significantly undersaturated, initial addition of CaCl_2 will simply increase the Ca content of the solution with a corresponding decrease in the Li/Ca ratio. In an attempt to minimize this problem, initial solutions were rich in Ca, but with low CO_3^{2-} concentrations. This ensured that addition of CO_3^{2-} was largely responsible for the precipitation of CaCO_3 , rather than addition of Ca^{2+} . The added Ca^{2+} served mostly to replenish that removed into the growing mineral. Given a solubility product for calcite in seawater of $4.6 \times 10^{-7} \text{ mol}^2 \text{ l}^{-2}$ (Ingle, 1975) and a starting Ca concentration of ≈ 0.01 M means that all solutions were expected to reach saturation within a few minutes of addition of reactants. During this time, only a small amount ($\approx 0.1\%$) of additional Ca is added to that initially present in the reaction vessel.

The success of this approach was assessed by measuring the Li/Ca in the reaction solution after completion of the growth experiment. During calcite growth, Li/Ca ratio was lowered by up to 16%, indicating an initial enrichment in the Ca content of the solution in some experiments. Li/Ca increased still further during some of the aragonite growth experiments (by a maximum of 44%) reflecting super-

saturation of the solution before aragonite growth in the presence of Mg^{2+} and SO_4^{2-} . These measured final Li/Ca ratios are used to assess the distribution coefficients of Li into the calcium carbonate phases on the assumption that the Li/Ca ratio of the growth solution was established early within the calcium-carbonate growth.

2.2. Benthic foraminifera

To assess the temperature dependence of Li/Ca and δ^7Li in foraminifera, the benthic genus *Uvigerina* was picked from the $>150 \mu m$ fraction of core tops from five Arabian Sea box cores taken in 1993 during cruise SONNE 90 from the Pakistan Margin (Staubwasser and Sirocko, 2001; von Rad et al., 1995) (Table 1). These cores span a depth range of 96–1796 m, corresponding to a temperature range of 23–3 °C (Fig. 1).

Before selection of final samples for analysis, a variety of cleaning methods were tested on a series of 0.5 mg *Uvigerina* samples picked from core 12 KG. A total of seven cleaning approaches were tested consisting of (C1) no cleaning; (C2) ultrasonic rinsing in water; (C3) gently crushed then ultrasonic rinsing in water; (C4) gently crushed, ultrasonic rinsing in water and then methanol; (C5) gently crushed, ultrasonic rinsing in water, methanol and then 30% H_2O_2 ; (C6) gently crushed, ultrasonic rinsing in water and methanol, heating with $NaOH/H_2O_2$, and leaching with 0.001 M HNO_3 ; (C7) gently crushed, ultrasonic rinsing in water and methanol, heating in hydrazine/ammonium citrate and $NaOH/H_2O_2$, leaching with 0.001 M HNO_3 . Cleaning routine C6 is similar to that used by Elderfield and Ganssen (2000) for the preparation of foraminifera samples for Mg/Ca analysis while cleaning C7 is similar to that developed by, e.g., Boyle and Keigwin (1985/1986) for analysis of Cd/Ca in foraminifera, and now used routinely in other labs measuring trace metal ratios in foraminifera (e.g., Martin and Lea, 2002).

Results of this sequential cleaning demonstrate a marked decrease in both Mg/Ca and Li/Ca due to the first rinse (Fig. 2), presumably due to removal of clays from the calcite surfaces. Cleaning C3 to C5 decrease both Mg/Ca and Li/Ca, while making little difference to Mn/Ca. Cleaning C6 and C7 make little change to Mg/Ca and Li/Ca, but cause a significant reduction of

Table 1
Core details and geochemical results for benthic foram samples

Core	Depth (m)	Latitude (N)	Longitude (E)	Temperature (°C)	Salinity (%)	Foram genus	Cleaning C6			Cleaning C7			δ^7Li	
							Li/Ca ($\mu mol/mol$)	Mg/Ca (mmol/mol)	Mn/Ca ($\mu mol/mol$)	Li/Ca ($\mu mol/mol$)	Mg/Ca (mmol/mol)	Mn/Ca ($\mu mol/mol$)		$D_{(Li,Ca)}$
120KG	96	23° 27.99	66° 53.54	22.5	36.2	<i>Uvigerina</i>	15.5	2.65	180.8	13.1	2.25	100.2	0.0054	25.0
42KG	316	24° 36.52	65° 59.03	16.0	36.0	<i>Uvigerina</i>	16.9	2.72	36.7	16.0	2.28	16.1	0.0066	26.3
12KG	789	24° 51.63	64° 18.20	10.3	35.5	<i>Uvigerina</i>	17.9	2.18	21.9	18.1	1.77	14.9	0.0075	26.2
107KG	992	23° 03.64	66° 30.32	8.9	35.4	<i>Uvigerina</i>	16.1	1.73	83.2	18.5	1.66	38.5	0.0076	24.8
115KG	1796	22° 43.80	66° 11.17	3.6	34.9	<i>Euvigerina</i>	13.8	1.17	186.9	14.4	1.09	25.0	0.0059	21.1

Cores are box cores and were recovered on cruise SONNE 90 in 1993 (Staubwasser and Sirocko, 2001; von Rad et al., 1995). Details of the two cleaning procedures are given in Section 2.2. Precision on the trace element ratios are $\pm 2\%$, and on δ^7Li are $\pm 0.8\%$ (2σ).

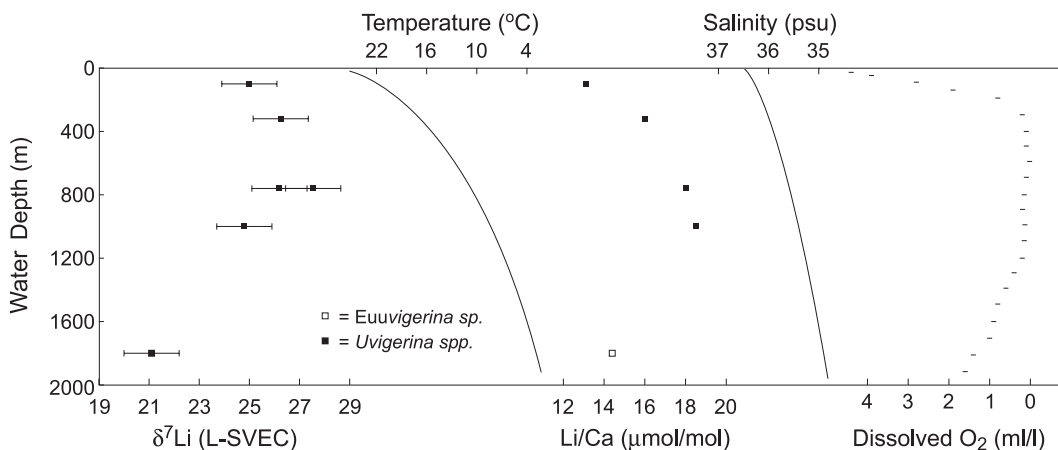


Fig. 1. $\delta^7\text{Li}$ and Li/Ca for benthic foraminifera picked from the core-tops of five Arabian Sea cores spanning a depth range of 96–1796 m (Staubwasser and Sirocko, 2001; von Rad et al., 1995). Errors are 2σ and are within symbol size for the Li/Ca measurements. Also shown are typical Temperature, Salinity, and O_2 profiles for the area from which these cores were recovered (LDEO Levitus 94).

Mn/Ca due to the removal of Mn oxides. On the basis of this single sample, cleaning C4 would seem appropriate for Li/Ca measurements. The similar pattern observed between Li/Ca and Mg/Ca suggest, however, that Li and Mg are hosted in similar phases within the samples. On the basis of an extensive literature on Mg/Ca cleaning (Elderfield and Ganssen, 2000; Boyle and Keigwin, 1985/1986; Lea and Boyle, 1993; Rosenthal et al., 1997) we have therefore used the full C7 cleaning on samples in this study. This reductive cleaning removes Mn from the foraminifera,

and, although it leaves Mg/Ca and Li/Ca virtually unaltered in our one test sample, it is known to improve Mg/Ca data in other samples (Martin and Lea, 2002).

Approximately 20 mg of foraminifera tests were then picked from each core top and subjected to the full C7 cleaning. *Uvigerina* spp. were picked from the upper four cores but this genus was almost entirely absent from the deepest core so *Euuvigerina* spp. was picked in its place. These cleaned samples were then dissolved ready for Li isotope analysis.

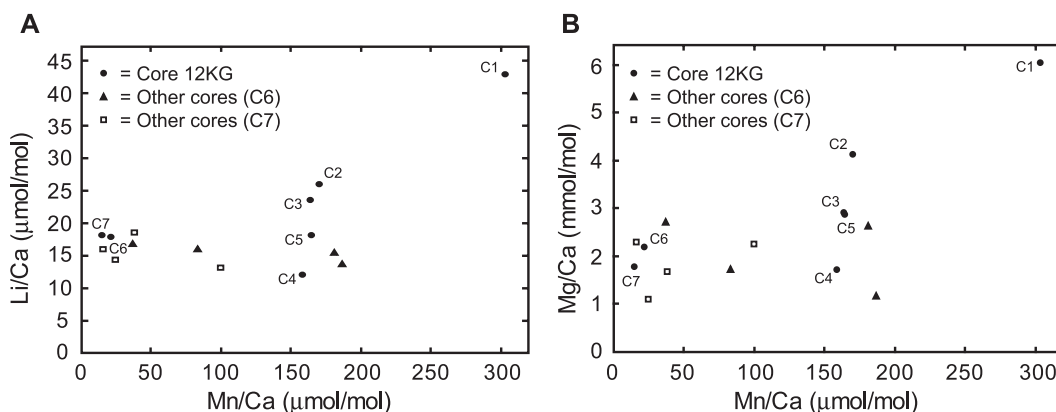


Fig. 2. Li/Ca, Mg/Ca, and Mn/Ca results for a single sample cleaned by seven different techniques, and for samples from other cores cleaned using the two most comprehensive of these techniques (C6—triangles; and C7—open squares). Filled circles are 0.5-mg subsamples from Core 12KG and are labelled with the cleaning approach used, as described in Section 2.2. Note that full reductive cleaning (C7) gave the lowest Mn/Ca.

3. Results

Inorganic and biogenic samples were analysed for Li/Ca and Li isotopes using techniques identical to those of Marriott et al. (2004). Aliquots of dissolved samples were diluted to 10 ml with 1% HNO₃ and doped with 0.2 ml of 500 ppb indium standard solution. Li/Ca ratios were then measured by ICP-MS using a Perkin Elmer Elan 6100DRC to a precision of $\pm 2\%$ (2σ) using an indium standard referencing technique to correct for instrumental drift. Li for isotope analysis was first purified using a mixed-media methanol-acid chemistry with 100% yield (Pistiner and Henderson, 2003), and then measured on a Nu Instruments MC-ICP-MS using a standard-bracketing approach with the NIST Li isotope standard, L-SVEC (Marriott et al. 2004). Precision of the isotope analysis was assessed by repeated measurement of a second standard and was typically between 0.3‰ and 1.0‰ (2σ) during a day of analysis.

3.1. Inorganic samples

Measured Li/Ca values have been converted into distribution coefficients (D) according to the equation, $D_{(Li/Ca)} = [(Li/Ca)_{\text{carbonate}} / (Li/Ca)_{\text{solution}}]$. Li/Ca in the carbonate was corrected for the mass of Ca present in the seed calcite prior to calculating $D_{(Li/Ca)}$ and Li/Ca ratios measured in the final solutions were used in each case (Table 2). Calculated $D_{(Li/Ca)}$ values for the five aragonites show no statistically significant trend with salinity, but those for the five calcites show a dramatic factor-of-four increase from 0.0008 at 10‰ to 0.0031 at 50‰ (Table 2, Fig. 3). This indicates a sensitivity of D of $6 \pm 1 \times 10^{-5}$ per ‰ salinity change.

The $\delta^7\text{Li}$ of inorganically precipitated calcite and aragonite are significantly different from one another, but there is no systematic relationship between salinity and $\delta^7\text{Li}$ for either mineral (Table 2). Calcite is offset from the growth solution by $\approx -3\%$ and aragonite by $\approx -12\%$.

3.2. Benthic foraminifera

All foraminifera samples cleaned with the full reductive cleaning (C7) yield Mn/Ca ratios of 100 $\mu\text{mol/mol}$ or less. The four *Uvigerina* spp. samples

Table 2

Li/Ca and $\delta^7\text{Li}$ for inorganically grown carbonates, together with Li/Ca ratios of solution initially and finally (initial value identical for all samples of each mineral)

Salinity (psu)	Li/Ca carbonate ($\mu\text{mol/mol}$)	Li/Ca solution (mmol/mol)	$D_{(Li/Ca)}$	$\delta^7\text{Li}$ (‰)
<i>Aragonite</i>				
Initial solution		27.3		
10	65.7	15.2	0.0043	-10.9
20	58.9	22.7	0.0026	-12.0
30	71.4	21.4	0.0033	-11.9
40	74.3	25.2	0.0030	-11.9
50	69.7	23.2	0.0030	-11.8
<i>Calcite</i>				
Initial solution		21.8		
10	14.5	19.4	0.0008	-2.4
20	28.2	18.2	0.0016	-3.0
30	40.4	21.8	0.0019	-3.1
40	54.4	22.6	0.0024	-2.5
50	62.9	20.0	0.0031	-1.9

Distribution coefficients D are calculated having taken Ca in seed calcite into account, and using the final solution Li/Ca ratio. Precision on the trace element ratios are $\pm 2\%$, and on $\delta^7\text{Li}$ are $\pm 0.8\%$ (2σ).

show a systematic variation of Li/Ca with depth, and therefore with temperature (Table 1). Li/Ca increases from 13.1 $\mu\text{mol/mol}$ at 96 m to 18.5 $\mu\text{mol/mol}$ at 992 m, a depth range corresponding to a temperature decrease of 14 °C. This is equivalent to a change in $D_{(Li/Ca)}$ from 0.006 to 0.0075, or $2.5 \pm 0.8\%$ per °C (Fig. 1). The salinity of growth for these four samples varies by less than 1‰ suggesting that only a very small portion of the observed Li/Ca variation is caused by salinity. The Li/Ca for the one deep *Euvigerina* spp. sample falls below this temperature trend, suggesting a species-specific effect. Reinspection of the foraminifera from this core suggested the presence of secondary mineral overgrowths that might also be responsible for this different chemistry. With only one sample of this species, further interpretation is not possible and this sample is therefore discounted from further discussion.

The Li isotope composition of the four *Uvigerina* spp. samples range by 2.8‰, from 24.7 to 27.5 (Fig. 1) and are approximately 5‰ lighter than the seawater from which they grew. They show no systematic relationship with temperature. The $\delta^7\text{Li}$ of the

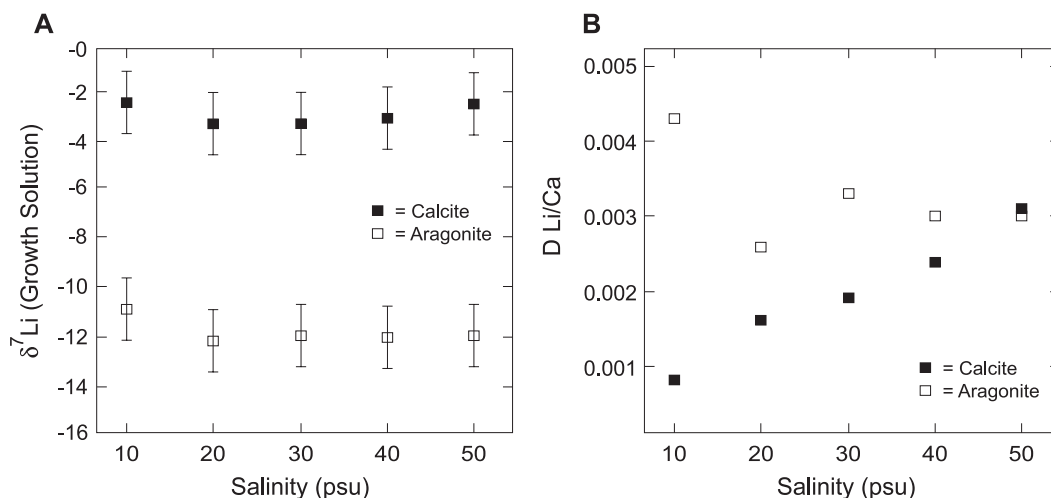


Fig. 3. $\delta^7\text{Li}$ and $D_{\text{Li/Ca}}$ for calcite and aragonite precipitated inorganically over a range of salinity from 10‰ to 50‰. Precision on the trace element ratios are $\pm 2\%$ (2σ), and on $\delta^7\text{Li}$ are $\pm 0.8\%$ (2σ). $\delta^7\text{Li}$ values are calculated relative to the growth solution composition which, in these experiments, was identical to that of L-SVEC.

Euvigerina sample is significantly lighter at 21.1, again perhaps due to secondary mineralization of this sample.

4. Discussion

4.1. Salinity control on Li/Ca in calcite and aragonite

The fivefold increase in salinity (or ionic strength) of the growth solutions causes changes in the activity coefficients (γ) of Li and Ca in the growth solution. To assess the significance of a change in $\gamma_{\text{Li}}/\gamma_{\text{Ca}}$ with changing salinity, the extended Debye–Huckel equation was used, via the computer programme Visual MINTEQ 2.15. This analysis demonstrated that $\gamma_{\text{Li}}/\gamma_{\text{Ca}}$ increased by only about 10% from the 10‰ salinity solution to the 50‰ salinity solution. Although the extended Debye–Huckel equation becomes somewhat inaccurate at the ionic strengths of the high-salinity experiments in this study, it is sufficiently precise to demonstrate that changes in activity coefficients are too small to explain the large variations in Li/Ca observed in the calcium carbonates grown within this study.

In many investigations of trace metal (X) incorporation into calcium carbonate, the X/Ca ratio in the growth solution is adjusted by changing the concen-

tration of X. This approach makes it difficult to deduce whether it is the ratio X/Ca in the growth solution, or simply the concentration of X, that is responsible for any observed changes in X/Ca of the mineral. In this study, by attempting to keep the ratio of elements identical to one another while changing their total concentration, the role of concentration changes can be isolated from changes in X/Ca. Adjusting the total concentration by dilution in this way is identical to the processes causing changes in salinity in the ocean and is therefore of particular relevance to assessment of the importance of such salinity changes for calcium carbonates grown from seawater.

In the inorganically grown calcium carbonates of this study, it is striking that mineralogy plays such a big role in the sensitivity of Li/Ca to salinity (Fig. 3). The ratio is approximately constant in aragonite, regardless of salinity, while it increases dramatically with increasing salinity in calcite. This difference in behaviour probably reflects the different incorporation mechanisms of Li in calcite and aragonite. Previous work has demonstrated that the alkali metals, including Li, are incorporated in an interstitial location in calcite, but are substituted into the Ca^{2+} site in aragonite (Okumura and Kitano, 1986). For aragonite, Li is therefore competing with Ca to enter the site so that it is the Li/Ca ratio in the solution which is of

prime importance in controlling the Li/Ca ratio of the grown mineral. For calcite, no such competition occurs and it is simply the concentration of Li in the solution that controls the amount of Li incorporated interstitially within the mineral.

A similar dependence of Na/Ca in calcite on the Na concentration of the growth solution has been indicated (Ishikawa and Ichikuni, 1984) suggesting that this relationship with salinity might be general for the alkali metals. The control on Na content of calcite is, however, also known to depend on the number of defects in the mineral which is, in turn, controlled by variables such as growth rate (Busenberg and Plummer, 1985). By analogy, the Li/Ca ratio in carbonates is unlikely to be controlled only by the salinity of the growth solution, although it is clear that salinity is a significant variable.

If natural calcium carbonates demonstrate the same sensitivity to salinity as the inorganic samples of this study then an increase in Li/Ca of $\approx 3\%$ per ‰ salinity increase is expected (at $\approx 35\%$). Given present analytical ability, changes in Li/Ca during, for instance, glacial–interglacial cycles, should result in observable changes in calcite Li/Ca. Whether such changes could be used as a robust proxy is questionable, given the other likely controls on Li/Ca, but it is possible that Li/Ca might act as a salinity proxy in regions where the signal is large, such as estuaries.

4.2. Li isotope fractionation during calcite and aragonite growth

The consistency of $\delta^7\text{Li}$ observed for each of the two minerals grown here (Fig. 3) suggests a consistent incorporation mechanism within each crystal structure, regardless of the salinity of the growth medium. The difference in $\delta^7\text{Li}$ between the two minerals, however, suggests a difference in Li incorporation mechanism between calcite and aragonite. The general tendency for $\delta^7\text{Li}$ to be more fractionated from the growth medium in aragonite than in calcite is observed, not only in our inorganically grown calcium carbonates, but also in those formed biogenically in nature (Fig. 4). This similarity of isotope fractionation in inorganic and biogenic samples, and across a factor of four change in Li/Ca ratio, suggests an equilibrium rather than kinetic control on Li isotope incorporation into calcium carbonate.

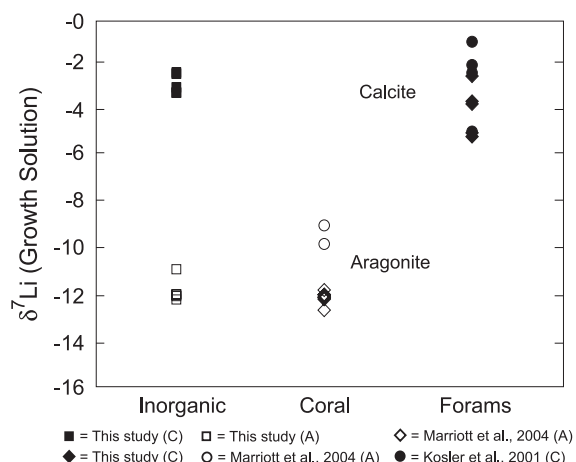


Fig. 4. $\delta^7\text{Li}$ measurements (calculated relative to composition of growth solution) from this and previous studies for carbonates grown from seawater-like solutions. Open symbols are aragonite (A) and closed are calcite (C). Data is from this study unless otherwise noted. Note the distinct difference in $\delta^7\text{Li}$ between inorganic aragonite and calcite. Biogenic aragonite (corals) and biogenic calcite (foraminifera) show similar values to those in the inorganically precipitated minerals. Precision on $\delta^7\text{Li}$ in this study is $\pm 0.8\%$ (2σ).

Equilibrium fractionation of Li during mineral growth from an aqueous medium is likely to result in a mineral isotopically lighter than the growth solution (Teng et al., in press). This is because Li is bound strongly in tetrahedral coordination with four waters while in solution, but is generally more weakly bound in higher coordination sites within minerals (Yamaji et al., 2001). When substituting for Ca^{2+} in the aragonite structure, Li is entering a ninefold coordination site where it is reasonably weakly bound so that the lighter isotope is preferentially incorporated. This may explain the large $\delta^7\text{Li}$ offset observed during growth of aragonite ($\approx 11\%$). By contrast, the $\delta^7\text{Li}$ offset during calcite growth is quite small ($\approx 4\%$). Because the reduced partition function for Li is expected to be reasonably similar for ninefold coordination and sixfold coordination (Yamaji et al., 2001) this smaller offset is unlikely to reflect incorporation of Li in the six coordinated Ca^{2+} sites in calcite. The smaller offset is more consistent with Li incorporation into some interstitial position with reasonably strong bonds. Incorporation in its hydrated form, for instance, might explain such strong bonding.

The lithium isotope composition of calcium carbonates is not only governed by the mineralogy.

Calcite grown inorganically in pure water without the presence of other trace elements, for instance, had $\delta^7\text{Li}$ offset some -8% from the growth medium (Marriott et al., 2004). This large offset (compared to those observed for the calcites in this study) is unlikely to be a kinetic overprint, because the growth conditions of those calcites and the inorganic calcites of this study are very similar. Inorganically precipitated calcite from Mono Lake, however, was found to be offset by only $\approx -2\%$ from the lake water (Tomascak et al., 2003), a rather similar offset to that found in this study. These results are probably best explained by competition between ions altering the nature of Li bonding during incorporation and thereby changes the isotope fractionation. The chemistry of the growth solution would therefore be an important determinant for the isotope composition of the precipitated mineral. One previous measurement of inorganically precipitated aragonite, from the Dead Sea, had a large offset of $\approx -20\%$ from the lake water (Huh et al., 1998), consistent with the idea that aragonite growth causes larger isotope fractionation than calcite, but that ion competition may also play a role in the precise fractionation observed. All of the samples shown in Fig. 4 formed from seawater (or a solution with similar composition to seawater) so that the complexity of growth solution chemistry is avoided and the significance of mineralogy for Li isotope fractionation is isolated.

4.3. Li in foraminifera

The $\delta^7\text{Li}$ of calcitic foraminifera measured here and in a previous study (Kosler et al., 2001) range from -5.2 to -1.2 relative to the growth solution, close to the offset observed for inorganic calcite. This similarity suggests that the process of biomineralization plays no major role in Li incorporation. If, for instance, Li was being depleted from an internal pool in the foraminifera, then its $\delta^7\text{Li}$ would be expected to be less offset from seawater than inorganic calcite. Or, if Li was being actively pumped by the foraminifera, then $\delta^7\text{Li}$ would be expected to be altered by kinetic fractionation. The similarity therefore suggests that Li is incorporated into foraminiferal calcite passively without significant biological interference. This is not surprising because Li has no known biological function, and occurs at such low concentrations in

seawater that it is unlikely to interfere with biological processes such as biomineralization.

The lack of a significant biological fractionation in foraminifera suggests that foraminiferal calcite can be used to reconstruct a history of past ocean $\delta^7\text{Li}$ without danger of a changing offset between the foraminifera and seawater. Such a history might provide valuable new information about the nature of past inputs to the oceans and, particularly, about the style of past weathering (Huh et al., 2001; Pistiner and Henderson, 2003) or of hydrothermal fluxes (Elderfield and Schultz, 1996).

In the absence of a biological control on Li incorporation, how are we to explain the changes in Li/Ca observed both within species and between species of foraminifera? It has previously been demonstrated that temperature plays a role in controlling Li/Ca, with all analysed species tending towards higher Li/Ca at lower temperatures (Hall and Chan, 2004) (Fig. 5). But both the absolute Li/Ca, and the temperature sensitivity vary significantly between species (Delaney et al., 1985; Hall and Chan, 2004) and differ from that observed in other low-Mg calcites such as brachiopods (Delaney et al., 1989) or those precipitated inorganically (Marriott et al. 2004). The inorganic calcites demonstrate that salinity also plays a role in controlling Li/Ca, but the range of salinity observed in the oceans is insufficient to explain the large range of Li/Ca observed between species of foraminifera. Growth rate, as controlled by carbonate ion concentration, has also been suggested as a possible control (Hall and Chan, 2004). Such a control might be expected because faster growth rate of minerals generally encourages the presence of crystal defects which are required for the interstitial substitution of Li in calcite.

Hall and Chan (2004) have also presented data demonstrating that the increase in Li/Ca observed in glacial foraminifera (relative to Holocene samples of the same species) is too large (up to 50%) to be explained by any reasonable temperature change. An even larger glacial increase in Li/Ca has also been observed in *Globorotalia menardii* from a Bay of Bengal core (Burton and Vance, 2000). A portion of such changes might be explained by higher salinities during the glacial. Although the average ocean had salinity only $\approx 1\%$ higher than at present during the glacial, areas such as the Bay of Bengal experienced

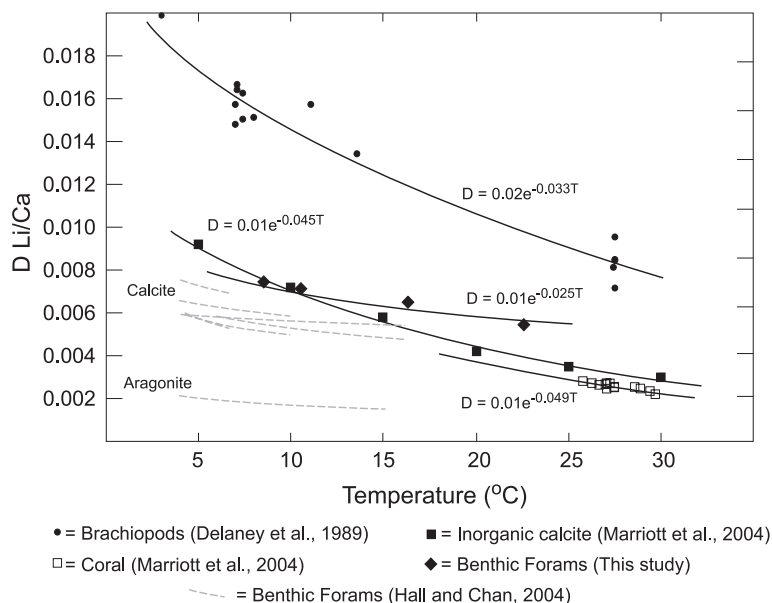


Fig. 5. The temperature (T) dependence of Li/Ca incorporation into inorganic calcite, coralline aragonite, benthic foraminifera, and brachiopods. Errors on the exponent are 95% confidence based on the scatter of data about the best-fit exponential curve shown. Dashed lines represent the best fit to data for seven species of benthic foraminifera analysed by Hall and Chan (2004). Exponents for those seven species are -0.022 ± 0.054 , -0.016 ± 0.021 , -0.005 ± 0.006 , -0.028 ± 0.005 , -0.020 ± 0.038 , -0.017 ± 0.026 , and -0.021 ± 0.006 . Although the variation with temperature is not generally statistically significant, it is striking that all seven species tend to have higher Li/Ca at lower temperature as found in this study for *Uvigerina* spp. and for all other types of calcium carbonate.

larger salinity increases due to changing precipitation patterns (Duplessy, 1982). Based on the inorganic experiments of this study, a 3‰ higher salinity at the glacial might explain a corresponding increase in Li/Ca of 9%. Even coupled with a substantial lowering of temperature at the glacial, such a change is still insufficient to explain the very high observed Li/Ca. This clearly indicates that a further control, apart from temperature and salinity, must influence foraminiferal Li/Ca.

5. Conclusions

Inorganic precipitation experiments demonstrate significantly different behaviour of Li and its isotopes during aragonite growth compared to that during calcite growth. A strong relationship between Li/Ca and salinity in calcite probably reflects the interstitial incorporation of Li^+ in calcite so that the Li concentration in the growth solution plays a key role in controlling the final Li/Ca ratio. The lack of a

similar salinity dependence for aragonite reflects the substitution of Li^+ for Ca^{2+} in that mineral.

Both inorganic and biogenic calcites fractionate Li isotopes by a rather constant -2% to -5% relative to seawater-like growth media, while inorganic and biogenic aragonites also exhibit a constant fractionation but with an offset of $\approx -11\%$. These offsets are most readily explained by equilibrium isotope fractionation, with their magnitude related to the type of bonding in the two minerals. The small size of these offsets and their low sensitivity to temperature and salinity mean that natural calcium carbonates will provide a good archive of the Li isotope composition of seawater in the past.

Li/Ca in foraminifera show an inverse relationship to temperature. The difference in absolute Li/Ca values and of temperature sensitivity between species suggests that other variables apart from temperature and salinity must play a role in controlling Li/Ca in natural calcites. This will make the application of Li/Ca as an environmental paleoproxy difficult, except in settings where one variable is known to dominate the signal.

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