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Key Points:

- Li partitioning in *A. lessonii* fundamentally differs from Mg and Sr partitioning
- The Li partitioning coefficient should be based on the seawater Li concentration
- A new cellular transport model for alkali metals is presented

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Li partitioning in the benthic foraminifera *Amphistegina lessonii*

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Abstract The shallow water benthic foraminifer *Amphistegina lessonii* was grown in seawater of variable Li and Ca concentration and shell Li/Ca was determined by means of LA-ICPMS. Shell Li/Ca is positively correlated to seawater Li/Ca only when the Li concentration of seawater is changed. If the seawater Ca concentration is changed, shell Li/Ca remains constant. This indicates that Li does not compete with Ca for incorporation in the shell of *A. lessonii*. A recently proposed calcification model can be applied to divalent cations (e.g., Mg and Sr), which compete for binding sites of ion transporters and positions in the calcite lattice. By contrast, the transport pathway of monovalent cations such as Li is probably diffusion based (e.g., ion-channels), and monovalent cations do not compete with Ca for a position in the calcite lattice. Here we present a new model for Li partitioning into foraminiferal calcite which predicts our experimental results and should also be applicable to other alkali metals.

1. Introduction

The reconstructions of physicochemical parameters of past oceans have benefited from the fact that many of these parameters are correlated to minor element to calcium ratios (Me/Ca) of the shells of marine calcifying organisms such as foraminifera [Fischer and Wefer, 1999]. The Mg/Ca ratio of foraminiferal shells has been extensively used to reconstruct temperature [Elderfield et al., 2006; Nürnberg et al., 1996]. Another important group of target parameters is the Me/Ca ratios of past ocean waters. The foraminiferal Sr/Ca, for instance, has been used to reconstruct seawater Sr/Ca [Lear et al., 2003]. The underlying assumption in these reconstructions is that the seawater Me/Ca is positively correlated to the shell Me/Ca. This assumption was experimentally tested three decades ago, and the authors concluded that it holds true for Sr and also Li [Delaney et al., 1985]. Subsequently, seawater Li/Ca was inferred from foraminiferal Li/Ca [Delaney and Boyle, 1986; Hathorne and James, 2006]. Besides the application of seawater-shell Me/Ca relationships in paleo-reconstructions, these relationships can also be used to refine conceptual calcification models which have been developed in the last two decades in order to put paleo-reconstructions on a firm theoretical footing [Elderfield et al., 1996; Erez, 2003; Nehrke et al., 2013].

A recently proposed model, henceforth called the mixing model, assumes that two different ion fluxes from seawater to the site of calcification determine the shell Me/Ca [Nehrke et al., 2013]. A refined version of the mixing model was successfully applied to Mg and Sr partitioning in *Ammonia aomoriensis* and *A. lessonii* [Mewes et al., 2015; G. Langer et al., manuscript in preparation, 2015]. This model predicts a positive correlation between the seawater Me/Ca and the shell Me/Ca, regardless of whether the Me concentration or the Ca concentration of seawater is changed. Since developed to explain the incorporation of divalent cations incorporated at the position of a Ca ion, it is questionable whether the mixing model in the present form is applicable to alkali metal ions such as Li. In inorganically precipitated calcite, Na/Ca, K/Ca, and Li/Ca are independent of the Ca concentration of the parent solution [Ishikawa and Ichikuni, 1984; Marriott et al., 2004]. This result was explained by the fact that, in contrast to divalent ions such as Sr, alkali metal ions do not compete with Ca for a position in the calcite lattice [Lorens, 1981; Ishikawa and Ichikuni, 1984; Busenberg and Plummer, 1985; Okumura and Kitano, 1986; Marriott et al., 2004]. If foraminiferal Li/Ca is independent of seawater Ca concentration, a new transport model would be required to describe the uptake of a monovalent ion such as Li. Here we determine the response of shell Li/Ca in the benthic foraminifer *A. lessonii* to changes in the seawater Li as well as Ca concentration.

2. Material and Methods

Specimens of the tropical benthic foraminifer *Amphistegina lessonii* were sampled from a coral reef aquarium at Burger's Zoo in Arnhem, Netherlands. Foraminifera were kept in stock cultures in the laboratory at 25°C. Adult specimen was picked from the stock cultures and isolated into well plates, in which they reproduced asexually. Offspring was isolated and used for the culture experiments. The use of offspring ensured that all chambers analyzed were grown under experimental conditions. Briefly, juveniles (2–3 chamber stage) were grown in Petri dishes to adult size. The culture medium was exchanged every other day in order to ensure quasi-constant carbonate chemistry and avoid bacterial contamination (for details, see Keul *et al.* [2013], Kaczmarek *et al.* [2015], and Mewes *et al.* [2015]). Two different types of culture experiments were performed. In one set, the Li concentration of the culture medium was altered. This was achieved by adding calculated amounts of LiCl to sterile filtered North Sea seawater, which was sampled off Helgoland (Germany) and off Mersea Island (UK). In the other set, the Ca concentration of the culture medium was changed. To this end, a mixture of 70% artificial seawater and 30% natural North Sea seawater was used (for details, see Mewes *et al.* [2015]). Adult specimens were harvested, rinsed in reverse osmosis water, dried, and analyzed by means of LA-ICPMS.

2.1. LA-ICPMS: Li/Ca Analyses

Li/Ca ratios of foraminiferal calcite were measured using a Laser Ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) system at the Department of Earth Science at the University of Cambridge. This high-resolution depth profiling technique employs Analyte G2 excimer laser (Teledyne Photon Machines Inc.) coupled with a Thermo i-CapQ ICPMS to measure trace metal elemental profiles through foraminiferal test walls. Sample preparation and analyses were carried following protocols discussed in Eggins *et al.* [2003] and Sadekov *et al.* [2008]. The isotopes 7Li, 11B, 24Mg, 25Mg, 43Ca, 44Ca, 55Mn, 88Sr, and 27Al were measured during each depth profile analysis and required around 60–120 s to acquire. We used 10–15 tests to obtain a representative average for each Li and Ca experiment. Three to four profiles were generated for each foraminiferal test. The Laser Ablation system was optimized for depth profiling by using a 80 μm ablation spot with 4 Hz frequency and 2 J/cm² laser fluence. The ICP-MS was optimized using NIST610 reference glass material for maximum sensitivity in the Li-Ca mass range and maintaining ThO/Th < 0.5% and Th/U ratio ~1. Data reduction involved initial screening of spectra for outliers, subtraction of the mean background intensities (measured with the laser turned off) from the analyzed isotope intensities, internal standardization to 43Ca, and external standardization using the NIST-SRM610 glass reference material [Eggins *et al.*, 2003]. NIST-SRM610 values were taken from Pearce *et al.* [1997]. NIST-SRM612 were used to monitor long-term standards reproducibility which is Li/Ca = 2.98 ± 0.04(2SE) mmol/mol.

2.2. Culture Medium Analysis

Li/Ca ratios of the *Amphistegina lessonii* culture media were determined by ICP-OES (Inductively-Coupled-Plasma-Optical-Emission-Spectroscopy) after dilution to a constant sodium concentration of 110 ppm, thereby exploiting the high-precision capability of simultaneous ICP-OES for element ratio determinations. Samples were run on a Varian Vista Axial ICP-OES using the 315.887 nm Ca and the 421.552 nm Sr emission lines. Calibration standards were prepared using IAPSO standard seawater to closely match the concentration matrix of the media solutions, spiked with Ca and Li (also Mg and Sr) to cover the concentration ranges in the experiments. Precision better than 0.5% (r.s.d) was achieved for Li/Ca, determined by replicate runs of a consistency standard containing 14.5 mmol/mol Li/Ca.

3. Results and Discussion

The benthic foraminifer *A. lessonii* was grown under different seawater Li as well as Ca concentrations. If the seawater Li concentration is changed there is a positive correlation between seawater Li/Ca and shell Li/Ca (Figure 1). This was also observed in the planktonic species *Globigerinoides sacculifer* [Delaney *et al.*, 1985]. The partitioning coefficient K_{DLi} can be inferred from a linear regression, and its value (0.005, Figure 1) tallies well with those of other foraminifera [Delaney *et al.*, 1985; Marriott *et al.*, 2004]. On the other hand, if the seawater Ca concentration is changed, the shell Li/Ca remains essentially constant (Figure 2). We do not have a definitive answer to the question why the shell Li/Ca corresponding to the lowest seawater Li/Ca is lower than all the other data points. This exceptional data point features the highest seawater Ca concentration,

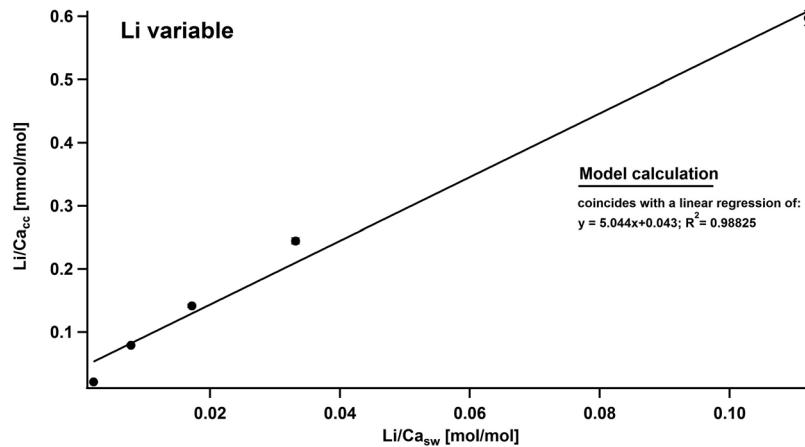


Figure 1. Shell Li/Ca versus seawater Li/Ca. The seawater Li/Ca was changed by changing seawater Li concentration. The line was calculated using equation (4), see section 3. The same line is obtained by a linear regression of the data. Error bars represent standard error.

which had a detrimental effect on the growth rate of *A. lessonii* [Mewes et al., 2015]. It might be hypothesized that the impaired physiological processes which are correlated to the lowered growth rate also affected Li partitioning. This hypothesis is supported by the fact that also Sr partitioning is unusual at this high seawater Ca concentration (Langer et al., manuscript in preparation, 2015). Please note that growth rate per se does not affect Li partitioning, because growth rate was also reduced at lowered seawater Ca concentration [Mewes et al., 2015]. This also implies that the seawater saturation state for calcite (omega calcite) does not affect Li partitioning (for values of omega calcite, see Mewes et al. [2015]). In this context, it is interesting that it was hypothesized that glacial-interglacial variations in Li/Ca of *Orbulina universa* are caused by changes in growth rate, which in turn are due to changes in seawater carbonate ion concentration [Hall and Chan, 2004]. If our results were applicable to *O. universa* the hypothesis of Hall and Chan [2004] would be wrong.

However, we claim that our conclusion, that shell Li/Ca is insensitive to changes in seawater Ca concentration, holds true. This conclusion has two important consequences. First, the partitioning coefficient K_{DLi} should be defined as $K_{DLi} = (Li/Ca_{CC})/[Li]_{sw}$ as opposed to $K_{DLi} = (Li/Ca_{CC})/(Li/Ca_{sw})$. This alternative K_{DLi} definition is in line with the description of alkali metal partitioning in inorganically precipitated calcite [Busenberg and Plummer, 1985; Okumura and Kitano, 1986]. Second, the mixing model, which successfully predicts the partitioning of divalent metal ions in foraminiferal calcite [Mewes et al., 2015; Langer et al., manuscript in preparation, 2015], cannot be applied to alkali metal ions. Therefore, we present a model for the coupled transport of Li and Ca, which does not assume a competition between Li and Ca (Figures 1 and 2). This

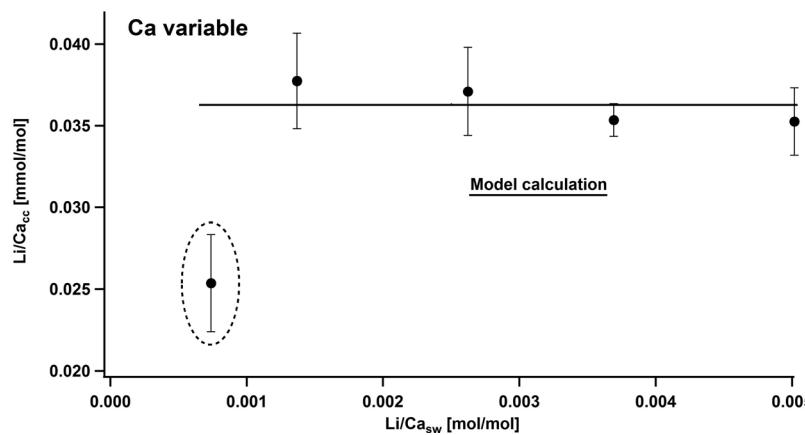


Figure 2. Shell Li/Ca versus seawater Li/Ca. The seawater Li/Ca was changed by changing seawater Ca concentration. The line was calculated using equation (5), see section 3. The encircled data point was neglected for reasons given in section 3. Error bars represent standard error.

model is based on the idea that calcification related ion transport is largely mediated by transmembrane transport [Nehrke *et al.*, 2013; Mewes *et al.*, 2015]. Please note that the partitioning coefficient of 0.005 as well as the relationships presented in Figures 1 and 2 can be explained in terms of inorganic precipitation from seawater. Given that foraminifera do not precipitate calcite directly from seawater [Erez, 2003; Nehrke *et al.*, 2013; Mewes *et al.*, 2015], the challenge is to explain how the relationships presented in Figures 1 and 2 can be described in terms of transmembrane transport. This is what our model attempts to do.

Li can enter the cell via Ca channels, the conductivity of which for Li depends on the presence of Ca [Hess *et al.*, 1986; Gallicchio, 1990], which means that the flux of Li is proportional to the concentrations of both Li and Ca:

$$F_{Li^+} = k [Li^+]_{sw} [Ca^{2+}]_{sw} \quad (1)$$

Due to its small size, the Li ion probably does not affect the transport of Ca significantly. Therefore, we describe the flux of Ca as:

$$F_{Ca^{2+}} = l [Ca^{2+}]_{sw} \quad (2)$$

This is valid for the channels as well as for a nonsaturated active transport process. The proportional constants k and l were introduced to convert concentration units into flux units. The Li/Ca_{CC} ratio of the precipitated calcite represents the Li/Ca ratio of the ion fluxes:

$$\left(\frac{Li^+}{Ca^{2+}} \right)_{cc} = \frac{F_{Li^+}}{F_{Ca^{2+}}} = \frac{k}{l} [Li^+]_{sw} = \frac{k}{l} [Ca^{2+}]_{sw} R_{sw} \quad (3)$$

where R_{sw} is the seawater Li/Ca. Equation (3) indicates that the Li/Ca_{CC} is positively correlated to R_{sw} only if the Li concentration of seawater is changed. From the last term in equation (3) follows the observed linear relationship between the shell Li/Ca and the seawater Li/Ca at constant seawater Ca concentration:

$$\left(\frac{Li^+}{Ca^{2+}} \right)_{cc} = \frac{k}{l} [Ca^{2+}]_{sw} R_{sw} = const \times R_{sw} \quad (4)$$

However, if the seawater Ca concentration is changed (instead of Li), the shell Li/Ca remains constant:

$$\left(\frac{Li^+}{Ca^{2+}} \right)_{cc} = \frac{k}{l} [Li^+]_{sw} = const \quad (5)$$

Hence, our model predicts the observed dependency of shell Li/Ca on seawater Li concentrations.

In summary, we have shown that Li partitioning in *A. lessonii* fundamentally differs from Mg and Sr partitioning. We conclude that the description of alkali metals in foraminifera should differ from that of divalent minor elements in two ways. First, the partitioning coefficient should be based on the seawater alkali metal concentration, as opposed to the seawater Me/Ca ratio. Second, a new transport model, which is not based on a competition between Me and Ca, is needed.

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