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Differences between potassium and sodium incorporation in foraminiferal shell carbonate

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The isotopic and elemental composition of the fossil shells of foraminifera are often used for reconstructing past environments and climates. These so-called proxy relations are based on the effect of environmental conditions (e.g. seawater temperature, pH) on the isotopic ratio (e.g. $\delta^{11}B$ or $\delta^{18}O$) or partitioning of elements (commonly expressed as El/Ca or D_{El}) during calcification. Whereas many studies focused on proxy-calibrations of divalent cations, incorporation of monovalent cations are less well constrained. Here we calibrate shell potassium content (K/Ca_{cc}) as a function of 1) seawater K^+ concentration, 2) the ratio of potassium and calcium in seawater (K/Ca_{sw}) and 3) temperature. Moreover, we analyze Na^+ incorporation into the calcite as a function of seawater K^+ and Ca^{2+} concentrations. First, we cultured specimens of the larger benthic foraminifer *Amphistegina lessonii* at four different seawater $[Ca^{2+}]$ and constant $[K^+]$, resulting in a range of K/Ca_{sw}. Secondly, we cultured specimens of the same species at four different $[Ca^{2+}]_{sw}$ and $[K^+]_{sw}$ while keeping the ratio between these two ions constant. Finally, we tested the effect of temperature (from 18 to 28°C) on K-incorporation in this species. Measured K/Ca_{cc} values are not notably affected by $[Ca^{2+}]_{sw}$, while seawater $[K^+]$ positively influences potassium incorporation, resulting in a positive correlation between seawater K/Ca values and K/Ca_{cc}. Although the $[Na^+]$ in the culture media was constant throughout both experiments, incorporated Na responded positively to decreasing $[Ca^{2+}]_{sw}$, resulting in a positive correlation between sea water Na/Ca and Na/Ca_{cc}. The difference in the controls on K- and Na-incorporation suggests that the (biological) control on these ions differs. Part of the observed variability in element partitioning may be explained by differences in chemical speciation and crystallographic coordination in the calcite lattice.

KEYWORDS

foraminifera, biomineralization, K/Ca, Na/Ca, proxy, culture experiment

1 Introduction

Our climate is rapidly changing as a consequence of anthropogenic greenhouse gas emissions to the atmosphere. Predicting the effects of increases in atmospheric CO_2 levels are greatly helped by reconstructions of past climate change. Such reconstructions, in turn, can be derived from the chemical composition of the shells of foraminifera: the boron isotopic composition of their calcite reflects primarily seawater pH (Sanyal et al., 1995), while for example the Mg/Ca can be used to reconstruct past seawater temperature (Nürnberget al., 1996; Holland et al., 2020). Incorporation of elements is usually also affected by biological control during calcification. This is apparent from the large deviation in El/Ca between species (Bentov and Erez, 2006; De Nooijer et al., 2023), within species (De Nooijer et al., 2014; Sadekov et al., 2016) and even within single chamber walls (Kunioka et al., 2006; Fehrenbacher et al., 2017; Levi et al., 2019). These observations have prompted investigating the physiological controls acting on ion uptake by foraminifera during calcification (Erez, 2003; De Nooijer et al., 2014; Schmidt et al., 2016; Evans et al., 2018; Tyszka et al., 2019). The active proton pumping (Bentov et al., 2009; De Nooijer et al., 2009) and calcium uptake (Toyofuku et al., 2017) may be the key in understanding divalent cation uptake and incorporation and at the same time may affect reconstruction of such elements' concentrations.

Concentrations of the major ions in seawater (Na^+, Mg^{2+}, Ca^{2+}, K^+) are not constant on geological time scales with residence times of 1.1 to 100 Myrs (Horibe et al., 1974; Hardie, 1996; Lécuyer, 2016; Zeebe and Tyrrell, 2018; Hauzer et al., 2021). The changes of $[Ca^{2+}]_{sw}$ result in changes in the incorporation of other elements into the calcite of foraminifera, likely as a result of competition of these ions with Ca^{2+} for a place in the crystal lattice (Dueñas-Bohórquez et al., 2011; Mewes et al., 2015a; Hauzer et al., 2018). In theory, past concentrations of calcium in seawater may be estimated from foraminiferal El/Ca ratios of elements that have a higher residence time than calcium (Na; (Hauzer et al., 2018). This, however, requires calibration of El/Ca as a function of $[Ca^{2+}]$. For Mg^{2+} incorporation, a non-linear response to $[Ca^{2+}]$ is described (Segev and Erez, 2006; Hauzer et al., 2018), It has been described linear correlations for Li/Ca_{cc} versus Li/Ca_{sw}, Sr/Ca_{cc} versus Sr/Ca_{sw} (Mewes et al., 2015b; Hauzer et al., 2018) and Na/Ca_{cc} versus Na/Ca_{sw} (Hauzer et al., 2018).

One of the major elements in seawater is K^+ with an average concentration of 380 mg/L (Wang et al., 2020) and a residence time of ~12 Myrs (Culkin and Cox, 1966). The 2 main sources for potassium in seawater are continental runoff and hydrothermal fluxes, while K is removed from seawater by pore-water entrapment or adsorption into clay minerals (Kronberg, 1985; Sun et al., 2016). However, K^+ incorporation into foraminiferal calcite and its potential dependency on environmental parameters are at the first steps with only a few publications. Culturing experiments with benthic foraminifera suggested both foraminiferal K/Ca_{cc} and Na/Ca_{cc} as a potential proxy for seawater $[Ca^{2+}]$ (Hauzer et al., 2018; Nambiar et al., 2023). Such reconstructions are important as they can reveal long-term changes in the oceans' major ion composition and thereby allow studying changes in the rates of geological processes including weathering, seafloor spreading and authigenic mineral formation (Horita et al., 2002; Fantle and DePaolo, 2005).

Compared to other major elements in seawater, K^+ has a large ionic radius and can interfere with the structure of proteins, requiring cells to regulate the concentration of this ion. Studies looking at the impact of temperature showed no apparent effect on K/Ca in a variety of organisms (Li et al., 2021) and suggest that K-incorporation is correlated only to the concentration of K^+ in the medium during inorganic precipitation experiments (Ishikawa and Ichikuni, 1984). Another very well-known monovalent ion in seawater is Na^+, with an average concentration of 10.6 g/L (Duxbury et al., 2024). Na/Ca_{cc} has being studied as a proxy before for changes in salinity in the past (Wit et al., 2013; Geerken et al., 2018), although this was debated to be the case by Hauzer et al. (2021). In addition, there is no effect of temperature on Na-incorporation (Allen et al., 2016).

Incorporation of monovalent cations and whether these elements are affected by the so-called vital effects of foraminifera remain largely unknown. Incorporation of K^+ by skeleton of corals has been shown to be related to incorporation of Na^+ and explains the similarity in the way they are incorporated (Mitsuguchi and Kawakami, 2012). Moreover, using the incorporation of divalent cations such as Mg^{2+} and Sr^{2+} as proxies also requires known sea water element to calcium ratios, which is on geological time scales can rely on changes in seawater $[Ca^{2+}]$. It is also vital to understand the inter-species' effect of environmental parameters on element incorporation. Finally, it is necessary to quantify the interaction between incorporated ions, for example Na^+ and K^+, to correct fossil El/Ca for changes in the composition of the seawater's major ion inventory.

In this study, we report the results of a set of experiments to calibrate K^+ incorporation in the benthic foraminifer *Amphistegina lessonii* as a function of $[Ca^{2+}]$, $[K^+]$and $[Ca^{2+}]$ and temperature. We set up controlled growth experiments to decouple the effect of these variables on calcitic K/Ca, which are inherently correlated in nature to deconvolve the underlying processes involved in K^+ and Na^+ uptake. Hence, grown specimens were also used to analyze their Na/Ca to test potential impacts of $[Ca^{2+}]$, $[K^+]$ and temperature on sodium incorporation. Accordingly, we aim to evaluate the potential of foraminiferal K/Ca and Na/Ca values as a proxy for $[Ca^{2+}]_{sw}$ and seawater chemistry in general.

2 Materials and methods

Three sets of controlled growth experiments were performed (Table 1). In the first set only the seawater's calcium concentration (i.e. $[Ca^{2+}]_{sw}$) was varied. In the second set of experiments, we varied both $[K^+]_{sw}$ and $[Ca^{2+}]_{sw}$, while keeping K/Ca_{sw} constant. These two sets of experiments were done under identical, constant temperature, salinity, and inorganic carbon chemistry. Finally, a set of experiments was conducted with varying temperatures, while keeping element concentrations, salinity and inorganic carbon chemistry constant.

TABLE 1 Three different culture experiments with *A. lessonii*.

Manipulated parameter	Temperature °C	$[Ca^{2+}]_{sw}$ (mmol/kg)	$[K^{+}]_{sw}$ (mmol/kg)	K/Ca_{sw} (mol/mol)	$Na/Ca_{sw} * 10^{-3}$ (mol/mol)
$[Ca^{2+}]_{sw}$	24 (constant)	7.63 - 19.93	8.4 (constant)	0.44 - 1.01	23.8 - 58.52
$[K^{+}]_{sw}$, $[Ca^{2+}]_{sw}$	24 (constant)	7.84 - 15.36	6.78 - 13.86	0.87 (constant)	33.25 - 67.47
Temperature °C	18, 22, 26 and 28	9.97 (constant)	9.72 (constant)	0.95 (constant)	26 (constant)

2.1 Culture set-up: $[Ca^{2+}]_{sw}$, and $[K^{+}]_{sw}$ and $[Ca^{2+}]_{sw}$

For the two experiments in which Ca- and/or K-concentrations were varied, specimens of *A. lessonii* were isolated from coral rubble retrieved from the tropical aquarium of Burgers' Zoo [Arnhem, the Netherlands; (Ernst et al., 2011)]. Approximately 100 living specimens were selected and transferred to Petri dishes and placed at 26°C with a light/dark cycle of 12h/12h to stimulate asexual reproduction. Within 2 weeks, between 80 and 90 juveniles were released from several adults that were incubated in pre-made culture media.

For these two sets of experiments, the amounts of salts were added following the recipes of (Kester, 1967) and (Wit et al., 2013), however changing the concentrations of $CaCl_2$ and KCl (Supplementary Tables S4, S5). We mixed the artificial seawater with filtered (< 2 µm) North Sea Water, using a ratio of 1 to 5 (20% North Sea Water and 80% artificial seawater) and we measured and controlled the salinity (within +/-0.1 salinity units) at the start and at the end of the experiment using a conductometer.

The prepared media were divided over culture flasks (De Goeyse et al., 2021) that were placed in a cabinet with a controlled atmospheric pCO_2 of 600 ppm and a light/dark cycle of 12h/12h. Evaporation of the culture media was minimized by saturating the atmosphere inside the cabinet with water vapor. The culture media were subsampled for DIC and TA by filling replicate 5mL vials, pre-poisoned with $HgCl_2$, and storage at 4°C until analyses using a Continuous Segmented Flow Analyzer (QuAAtro). For DIC the method was the same as the one used in the temperature experiment (2.1.1) but for TA an adapted method from (Sarazin et al., 1999) was used, changing the organic acid from formic acid to Phthalic acid, keeping the same indicator Bromo Phenol Blue which is blue at a pH of 3.7 and giving a green color at more alkaline phases having an absorbance at 590nm (Supplementary Tables S1, S2). *A. lessonii* was grown under these pre-set conditions for six weeks. Almost all replicates had sufficient material to have one or two analysis per replicate for K/Ca_{cc} using ICP-MS (Supplementary Tables S1, S2). Every batch of foraminifera measured contained between 10-25 individuals per condition. The specimens that were selected for analysis were fully grown (i.e. consisted of more than 15 chambers) to minimize the contribution to the chemical signal by the first 1 or 2 chambers that were built before the experimental incubation a correlation with weight of Ca against K/Ca_{cc} was plotted to ensure there was no correlation and hence no effect of growth rate when K and Na incorporated into the calcite (Supplementary Table S12, Supplementary Figure S2) The mortality rate during the experiments was derived from the temperature experiment and equaled 22% (i.e. 78% of the incubated specimens were alive at the end of the experiment).

2.2 Culture set-up: temperature experiment

The procedure for selecting specimens, feeding, and subsampling of the culture media were identical to that in the first two sets of experiments. Juveniles derived from asexual reproduction events were divided into 4 equal groups, with at least 20 juveniles per group, which were transferred to Petri dishes with filtered (< 2 µm) North Sea water. At this stage, the juveniles had not more than seven chambers. Three or four replicates (depending on the number of juveniles available per condition) were subsequently incubated at each of the four different temperatures: 18°C, 22°C, 26°C, and 28°C (Table 1). All incubations used a light/dark cycle of 12h/12h and a light intensity of approximately 180 µmol photons m^{-2} s^{-1} for a total of eight weeks. During the experiment, the foraminifera were observed weekly to monitor how many of the incubated specimens were alive. Every week, culture media were replaced and the foraminifera were fed freeze-dried algae *Dunialiella salina* (Van Dijk et al., 2017a) suspended in precleaned water (cleaned by rinsing the Falcon tubes with Milli-Q water three times).

To monitor potential changes in inorganic carbon chemistry, culture media were subsampled for dissolved inorganic carbon (DIC) and total alkalinity (TA) (Supplementary Table S3). Vials for these sub-samples were pre-poisoned with $HgCl_2$ and stored at 4°C until they were analyzed. DIC samples were acidified, and the CO_2 was dialyzed to reduce the phenolphthalein indicator and spectrophotometrically measured at 550nm using Continuous Segmented Flow Analyzer (QuAAtro); TA was measured by using an acid buffered solution of formic acid and was measured spectrophotometrically (Sarazin et al., 1999) using a QuAAtro. For the temperature experiments salinity of the culture media was monitored using a refractometer and was always 36 +/- 0.5. Because we used the same culture water for the different temperature experiments, we do not expect offsets between these experiments. Measured values for DIC and TA together with the temperature and salinity were used to calculate pH, pCO_2, $[HCO_3^{-}]$, $[CO_3^{2-}]$ and the saturation state with respect to calcium (Ω_{Ca}) using PyCO2SYS (Humphreys et al., 2022) (Supplementary Table S3).

2.3 Element/Ca ratios

2.3.1 Element/Ca in seawater

To analyze the El/Ca values of the culture media, we subsampled the culture media from every replicate of the two experiments (2.1.1). Samples were diluted 900 times in 2 steps using a 30x dilution with 1M HNO_3 sub boiled distilled quality acid, with a standard element mix containing Sc, Rh and In added to it. Rhodium was used as an internal standard to correct instrumental drift during the analysis of the mass spectrometer. Samples were measured on a sector field SF-ICPMS (ThermoFisher Scientific, Element-2) at the Royal NIOZ. Resolutions for the measurements were based on 3 slits, measuring at high resolution: 10000; medium resolution: 4000; low resolution: 300. To fully separate the ^{39}K-signal from ^{38}Ar^{1}H, potassium was measured in high resolution. This strategy was based on the ratio of the mass over the mass difference: ^{39}K has an atomic mass (M) of 38.96371 and ^{38}Ar^{1}H has an M of: 38.97056. Dividing the M of potassium over the difference in M, gives 5688 > 4000, which requires the high-resolution settings of the detector (Supplementary Figure S1). Similarly, measuring in medium resolution is also necessary for ^{32}S due to interference from ^{16}O^{16}O, dividing the M of sulfur over the difference in M gives 479 > 300. ^{11}B, ^{23}Na, ^{25}Mg, ^{43}Ca, ^{88}Sr and ^{103}Rh were all measured in low resolution (Tables 2, 3) and values El/Ca$_{sw}$ (Tables 4, 5).

2.3.2 Foraminiferal element uptake

2.3.2.1 Cleaning procedure for shells from the culture experiments

Even though the foraminifera were all derived from culture experiments in which no sediment was present, all samples were carefully cleaned prior to element analyses. We followed a cleaning procedure based on the protocol from Barker et al. (2003). The foraminifera were not crushed, because the specimens do not contain sedimentary infillings. Crushing or over-crushing can lead to losses of carbonate material (Barker et al., 2003). First organic matter was removed using a 1% H_2O_2 buffered with a NH_4OH solution, adding 250 µL to each 500 µL Eppendorf, which was then transferred to a pre-warmed water-bath at 95°C for 10 minutes and ultrasonicated. Afterwards, the solution was removed with a 0.1 ml pipette. This procedure was repeated twice and the uncrushed foraminifera and buffered H_2O_2 solution probably gave a neglectable loss of carbonate during this organic removal step. After this step, the foraminifera were rinsed three times with ultrapure water (Milli-Q, >18.2 MΩ) by filling the tube fully with ultrapure water and removing after fully settling of the foraminifera. Possible remaining contaminants at the surface of the foraminiferal shells were finally removed by a leaching step with diluted HNO_3 (250µL 0.001 M) and concurrent gentle ultrasonication for 30 seconds. The HNO_3 was removed, and samples were cleaned with ultrapure water. The cleaned foraminifera were dissolved in 0.5 ml 0.1M ultra-pure HNO_3 (two times sub-boiled analytical grade acid in the NIOZ clean lab). To enhance the dissolution, vials were placed in an ultrasonic bath for 15 min and visually inspected to ensure complete dissolution.

2.3.2.2 SF-ICPMS analyses

For all solutions with dissolved calcium carbonate, the [Ca^{2+}] were pre-determined in medium resolution with the SF-ICPMS against a 5-point external calibration line using ^{45}Sc as an internal standard. Based on this data, samples were diluted to obtain a 100 ppm Ca matrix for each sample, minimizing mass bias effects between samples and standards. To determine foraminiferal element to calcium ratios with the SF-ICPMS, a ratio calibration method (de Villiers et al., 2002) was employed using standards with similar matrices as the samples. Samples (between 20-40 individuals per condition) were divided to obtain a minimum weight of 300µg. Samples were measured in triplicate using a low sample flow of 50µl/min (ESI, microFAST). To monitor accuracy, JCp-1 (Geological Survey of Japan, coral; *Porites* sp (Okai et al., 2004), JCt-1 (giant clam), and NFHS-2NP (Boer et al., 2022) were included in the analyses. NFHS-1(NIOZ Foraminifera House Standard; (Mezger et al., 2016) was used as a drift standard. Accuracies are listed in (Supplementary Table S6).

2.4 Statistical analysis

To analyze (potential) correlations between seawater temperature/chemistry and foraminiferal calcite composition, a bootstrap method was applied. This allows calculating confidence intervals for potential correlations through iterative resampling of the dataset generating distinct simulated sub-sets of samples (in this case 1000 iterations were used). The results of these regressions are only shown when p-values< 0.05. Confidence intervals displayed in the figures were taken from the means and standard deviations obtained from the bootstrap analysis. Analyses were performed using a standard package available for Python: scipy.stats (Virtanen et al., 2020).

TABLE 2 Elements in the seawater (mean +/- SD) after mixing with North Sea water and measured with SF-ICPMS in the [Ca^{2+}]$_{sw}$ experiment. Low resolution analysis (LR), Medium resolution analysis (MR), High resolution analysis (HR).

Ca (LR)	K (HR)	B (LR)	Na (LR)	Mg (LR)	Sr (LR)	S (MR)
(mmol/kg)	(mmol/kg)	(µmol/kg)	(mmol/kg)	(mmol/kg)	(µmol/kg)	(mmol/kg)
7.76 ± 0.13	7.98 ± 0.03	408.77 ± 2.5	447.22 ± 0.83	49.81 ± 0.04	94.79 ± 0.45	25.81 ± 0.27
15.33 ± 0.05	8.48 ± 0.09	432.77 ± 2.72	469.86 ± 2.16	52.46 ± 0.08	101.89 ± 0.55	27.44 ± 0.14
17.1 ± 0.13	8.39 ± 0.06	426.83 ± 3.34	452.23 ± 0.63	51.52 ± 0.09	100.56 ± 0.46	27.04 ± 0.14
19.76 ± 0.18	8.74 ± 0.09	443.62 ± 3.89	470.09 ± 4.01	53.89 ± 0.54	105.8 ± 0.47	28.47 ± 0.35

TABLE 3 Elements in the seawater (mean +/- SD) after mixing with North Sea water and measured with SF-ICPMS in the $[Ca^{2+}]_{sw}$ and $[K^{+}]_{sw}$ experiment. Low resolution analysis (LR), Medium resolution analysis (MR), High resolution analysis (HR).

Ca (LR)	K (HR)	B (LR)	Na (LR)	Mg (LR)	Sr (LR)	S (MR)
(mmol/kg)	(mmol/kg)	(µmol/kg)	(mmol/kg)	(mmol/kg)	(µmol/kg)	(mmol/kg)
7.9 ± 0.03	6.81 ± 0.04	418.85 ± 4.93	531.01 ± 3.87	50.98 ± 0.07	91.22 ± 0.44	26.75 ± 0.28
9.88 ± 0.08	8.67 ± 0.07	424.62 ± 2.71	470.25 ± 3.7	51.91 ± 0.55	93.24 ± 0.87	27.5 ± 0.03
11.38 ± 0.16	9.82 ± 0.37	421.17 ± 8.33	461.78 ± 5.28	51.17 ± 0.55	91.72 ± 1.29	26.72 ± 0.41
15.24 ± 0.09	13.67 ± 0.27	421.36 ± 1.05	506.16 ± 1.68	51.35 ± 0.04	93.5 ± 0.05	26.54 ± 0.4

2.5 Element partitioning

The incorporation of elements is often presented as the El/Ca (where El is the element analyzed) or D_{EL}, known as the partition coefficient:

$$\mathbf{[El]_{cc}/[Ca^{2+}]_{cc} = D*([El]_{sw}/[Ca^{2+}]_{sw}}$$

When D > 1 the element is more concentrated in the shell than in the seawater and when D< 1 the element is excluded from the shell (Lea, 2003). As it is explained by (Lea, 2003) this relation is not strictly following thermodynamic properties, but also affected by biology. Nevertheless, expressing element incorporation into the calcite in terms of D allows better comparison between different ocean chemistries and also between experiments.

3 Results

3.1 Experiment $[Ca^{2+}]_{sw}$

In the first experiment, both $[K^{+}]_{sw}$ and $[Na^{+}]_{sw}$ were kept constant and therefore variability in foraminiferal calcite composition must be related to changes in $[Ca^{2+}]_{sw}$ (Supplementary Table S7). The K/Ca_{cc} values of the different conditions used are statistically the same. The K/Ca_{cc} at the lowest K/Ca_{sw} appear higher than at higher K/Ca_{sw}, but this is likely caused by the contribution of pre-existing calcite (see also discussion, 4.1). Na/Ca_{cc}, however, increases with increasing Na/Ca_{sw} values (and hence decreasing $[Ca^{2+}]_{sw}$) with a significant offset between the lower and the higher Na/Ca_{cc} conditions used in the experiments (Figure 1B; bootstrap analysis, p<0.05). Also clear from these figures is that the partitioning coefficients does not remain constant with changing $[Ca^{2+}]_{sw}$, for both K and Na incorporation.

3.2 Experiment $[Ca^{2+}]_{sw}$ and $[K^{+}]_{sw}$

When varying both $[K^{+}]_{sw}$ and $[Ca^{2+}]_{sw}$ and keeping K/Ca_{sw} constant, K/Ca_{cc} increases linearly (Figure 2A). In the same cultured foraminifera, the Na/Ca_{cc} also increases significantly with higher seawater Na/Ca ratios (Figure 2B). When directly comparing these results with those from the first experimental set, it is clear that K-incorporation depends not on $[Ca^{2+}]$ but does respond when both $[K^{+}]$ and $[Ca^{2+}]$ are varied (Figure 2C). Na-incorporation, on the other hand, does react to changes in $[Ca^{2+}]_{sw}$, irrespective of changes in $[K^{+}]$ (Figure 2, Supplementary Table S8).

TABLE 4 El/Ca in the seawater after mixing with North Sea water and measured with SF-ICPMS in the $[Ca^{2+}]_{sw}$ experiment.

K/Ca	B/Ca	Na/Ca	Mg/Ca	Sr/Ca	S/Ca
(mol/mol)	(mol/mol)	(mol/mol)	(mol/mol)	(mol/mol)	(mol/mol)
1.01	0.05	56.78	6.31	12.07	3.31
1.05	0.05	58.52	6.53	12.37	3.35
0.56	0.03	30.66	3.41	6.66	1.79
0.56	0.03	30.66	3.41	6.66	1.79
0.54	0.03	30.55	3.43	6.64	1.78
0.56	0.03	30.68	3.43	6.62	1.80
0.49	0.02	26.11	2.99	5.85	1.58
0.49	0.03	26.61	3.02	5.89	1.58
0.49	0.03	26.61	3.02	5.89	1.58
0.44	0.02	23.79	2.73	5.33	1.45
0.44	0.02	23.80	2.72	5.38	1.44

TABLE 5 El/Ca in the seawater (mean +/- SD) after mixing with North Sea water and measured with SF-ICPMS in the $[Ca^{2+}]_{sw}$ and $[K^+]_{sw}$ experiment.

K/Ca (mol/mol)	B/Ca (mol/mol)	Na/Ca (mol/mol)	Mg/Ca (mol/mol)	Sr/Ca (mol/mol)	S/Ca (mol/mol)
0.86	0.05	67.22	6.44	11.43	3.44
0.88	0.05	66.80	6.48	11.69	3.40
0.86	0.05	67.47	6.45	11.55	3.35
0.86	0.05	67.47	6.45	11.55	3.35
0.86	0.04	47.62	5.28	9.33	2.76
0.88	0.04	47.65	5.26	9.52	2.79
0.88	0.04	47.65	5.26	9.52	2.79
0.88	0.04	47.61	5.24	9.40	2.81
0.86	0.04	40.22	4.45	8.03	2.36
0.89	0.04	40.80	4.52	8.09	2.34
0.83	0.04	40.69	4.51	8.05	2.35
0.86	0.03	33.10	3.35	6.09	1.76
0.91	0.03	33.26	3.38	6.16	1.73
0.91	0.03	33.26	3.38	6.16	1.73

3.3 Temperature experiment

Both K/Ca_{cc} and Na/Ca_{cc} of the cultured *A. lessonii* do not show consistent changes with varying temperature (Figures 3A, B), although the average K/Ca_{cc} was slightly higher at the lowest temperature (0.21 +/- 0.06 mmol/mol) (Supplementary Table S9). Variability observed for K/Ca_{cc} was higher than that of Na/Ca_{cc} but does not change consistently between the four temperature conditions using a regression analysis giving for both plots (Figure 3) p-values > 0.05.

3.4 K/Ca_{cc} versus Na/Ca_{cc}

Combining all data, Na/Ca_{cc} and K/Ca_{cc} of the cultured *A. lessonii* do not correlate with each other (Figure 4) when varying temperature or changing only $[Ca^{2+}]$. However, when considering the experiments in which both $[K^+]$ and $[Ca^{2+}]$ varied with a constant K/Ca_{sw} K- and Na-incorporation were negatively correlated, this correlation is due to the difference in $[Ca^{2+}]_{sw}$ that changes the Na incorporated, and not because of a Na^+ and K^+ compete for the same spot in the calcite crystal lattice during incorporation.

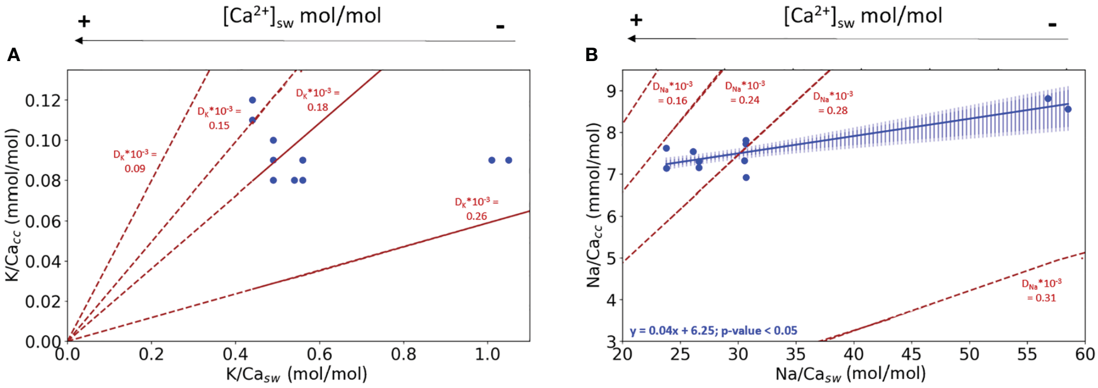

FIGURE 1
(A) K/Ca_{cc} in cultured *A. lessonii* versus K/Ca_{sw} from the experiment with varying $[Ca^{2+}]$, keeping $[K^+]$ constant; **(B)** Na/Ca_{cc} from the same specimens versus $Na/Ca_{sw,}$ keeping $[Na^+]_{sw}$ constant. Blue dots are the measured El/Ca_{cc}, the blue line in **(B)** indicates the linear correlation between Na/Ca in the culture media and the foraminiferal calcite. The shading surrounding this correlation represents the confidence interval (0.99 darker blue and 0.95 lighter shade of blue) based on a bootstrap analysis (1000 iterations). In both plots, lines with constant partition coefficients (D_K and D_{Na}) are plotted (dashed red lines) to facilitate interpretation of the observed changes in the relative incorporation of elements. The standard deviation for every replicate using the internal error from the SF-ICPMS was very small making it imperceptible in the plotted data (Supplementary Table S10).

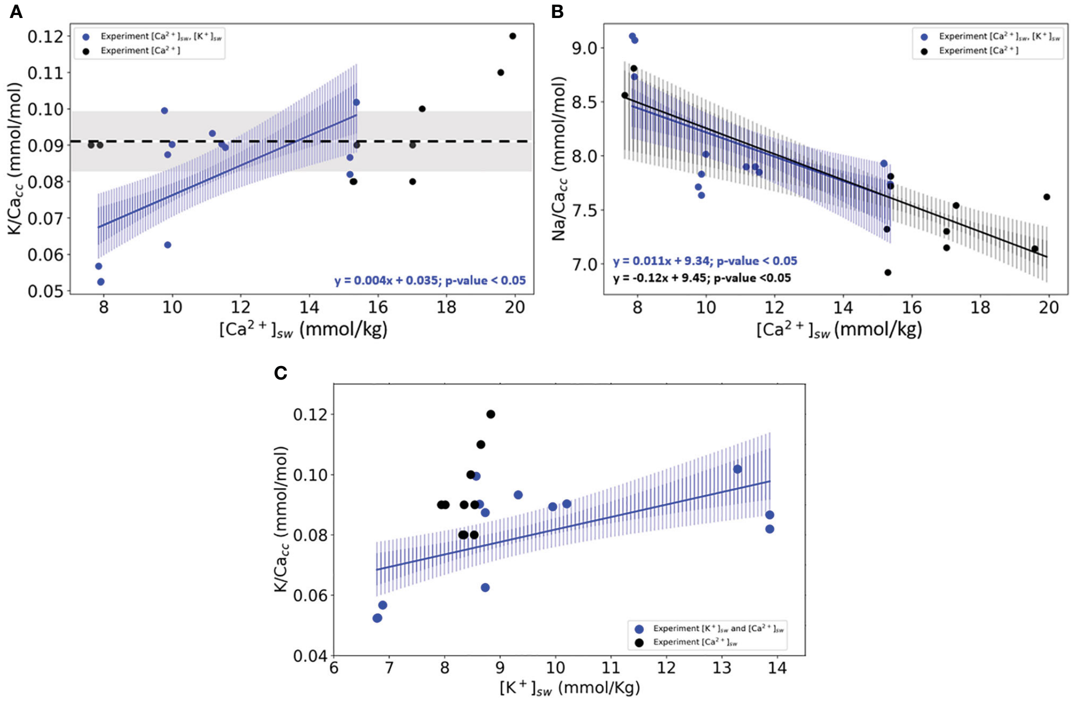

FIGURE 2
(A) K/Ca$_{cc}$ in cultured specimens of **(A)** lessonii as a function of the culture's media [Ca^{2+}]$_{sw}$. **(B)** Na/Ca$_{cc}$ of the same specimens versus [Ca^{2+}]$_{sw}$. **(C)** K/Ca$_{cc}$ versus [K$^+$]$_{sw}$. In panels **(A, B)**, blue dots and lines are the results from the experiment in which both [Ca^{2+}] and [K$^+$] were varied. In black are the results from the experiments (Figure 1) where only [Ca^{2+}] was varied. Lines indicate the linear correlations (both with p-values<0.05) based on the bootstrap analysis, for which the confidence intervals are added as envelopes (0.99 darker blue and 0.95 lighter shade of blue). The standard deviation for every replicate using the internal error from the SF-ICPMS was very small making it imperceptible in the plotted data (Supplementary Table S10). Panel **(C)** shows the same statistical analysis for both experiments axys X changes, and instead of [Ca^{2+}]$_{sw}$, the results are plotted against [K$^+$]$_{sw}$.

4 Discussion

4.1 Consistency of the data, the effect of temperature and the proxy value of K/Ca and Na/Ca

The K/Ca$_{cc}$ values obtained for *A. lessonii* in all experiments ranged between 0.05 and 0.26 mmol/mol (Supplementary Table S9), without a noticeable effect of temperature (Figure 3A). The total amount of calcite added per treatment, either when changing [Ca^{2+}]$_{sw}$ or temperature did not correlate to K/Ca$_{cc}$ (Supplementary Figures S2 and S3, respectively). This means that the average K/Ca$_{cc}$ does not depend on growth rate and changes therein reflect directly the effects of temperature or seawater chemistry. The relatively high variability observed for K/Ca$_{cc}$ at the lowest temperature (Figure 3A) may be explained by uneven growth of foraminiferal specimens across temperatures. At the lowest temperature (18°C) on average fewer chambers were added per specimen than at higher temperatures (Supplementary Tables S13, S14). As this increases the relative contribution of pre-existing carbonate (i.e. from before the actual

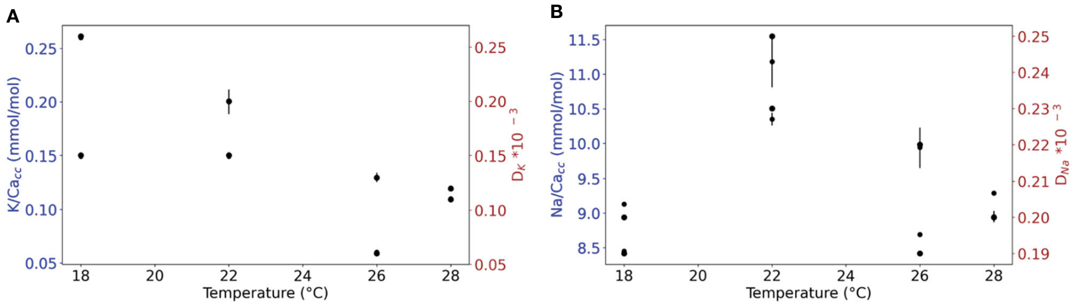

FIGURE 3
(A) K/Ca$_{cc}$ and D$_K$ versus temperature. **(B)** Na/Ca$_{cc}$ and D$_{Na}$ versus temperature. The RSD for every replicate using the internal error from the SF-ICPMS are plotted with black lines (Supplementary Table S11). For either of the elements, a regression analysis shows no significant correlation between El/Ca$_{cc}$ and temperature ($p < 0.05$).

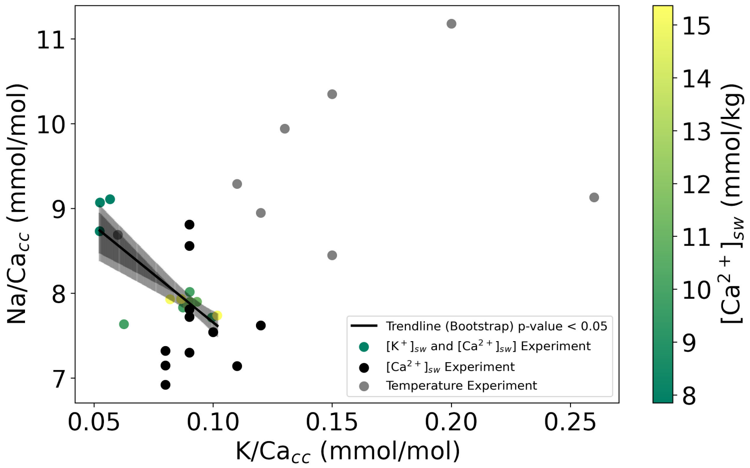

FIGURE 4
Na/Ca_{cc} versus K/Ca_{cc} for the three experiments. Solid lines indicate the linear correlations (both with p-values<0.05) based on the bootstrap analysis, for which the confidence intervals (0.99 darker black and 0.95 lighter black) are added as shading. The color-scale in experiment $[K^+]_{sw}$ and $[Ca^{2+}]_{sw}$ shows the $[Ca^{2+}]_{sw}$ from green (higher $[Ca^{2+}]_{sw}$ to yellow (lower $[Ca^{2+}]_{sw}$).

experiment) this would add to the variability in the data. The contribution of chambers formed before start of the incubation may have also biased average K/Ca and Na/Ca values, with a larger impact for specimens that added less chambers during the experiment.

The potassium-to-calcium ratio in *A. lessonii* (0.10 – 0.26; Figure 1A) overlap with those established for inorganically precipitated calcites (Ishikawa and Ichikuni, 1984); K/Ca_{cc}: 0.01-0.1 and (Okumura and Kitano, 1986). Still, it is challenging to compare these coefficients directly as the overall composition of the culture media (artificial seawater) in our experiment differed considerably from that used in the inorganic precipitation experiments, which only contained few elements.

The only other report on foraminiferal K/Ca_{cc} indicated similar ratios for the benthic *O. ammonoides* (0.12-0.30; Nambiar et al., 2023), as those reported here (Supplementary Tables S10, S11). The small offset in the average ratios could be caused by differences in culturing conditions or by inter-species differences in El/Ca values as observed for many elements (Bentov and Erez, 2006). Although we used a slightly different analytical approach (higher mass resolution) this is unlikely to have resulted in appreciable offsets between studies (methods and Supplementary Figure S1).

The average and range in Na/Ca_{cc} of cultured specimens (Supplementary Tables S9-S11) are similar to ratios reported previously for this genus (Geerken et al., 2019; Levi et al., 2019). The Na/Ca_{cc} in specimens cultured from 18 to 28°C vary between 8.8 and 11 mmol/mol (Supplementary Table S9) and are not correlated to temperature, which is in line with previous reports (Allen et al., 2016; Geerken et al., 2019). In the experiment with temperatures ranging from 18 to 28°C (Supplementary Table S9, Figure 3), K/Ca_{cc} values show no significant differences between different temperature conditions, agreeing with the field data from (Nambiar et al., 2023). The absence of an effect of temperature on either K/Ca_{cc} or Na/Ca_{cc} underscores the potential for applying these ratios in reconstructing (long-term) changes in seawater composition.

Element/Ca ratios vary greatly between genera and species and generally show elevated ratios for multiple elements in the same taxon (Evans et al., 2015; Mewes et al., 2015a; Hauzer et al., 2018; Van Dijk et al., 2019; Dämmer et al., 2021). The magnitude by which the different elements vary among species, however, is not constant. For K/Ca_{cc}, ratios are on average slightly higher in *O. ammonoides* (Nambiar et al., 2023) than in *A. lessonii.* (Figures 1–3), which is in line with the observed difference in Mg/Ca_{cc} between these species. Mg/Ca_{cc} is approximately 140 mmol/mol for *O. ammonoides* (Evans et al., 2015) and varies between 25 and 30 mmol/mol for *Amphistegina* sp (De Nooijer et al., 2017). Similarly, Na/Ca_{cc} in *A. lessonii* varies between 7 and 11 mmol/mol (Figures 1B, 2B and 3B; (Van Dijk et al., 2017c) and around 20 - 25 mmol/mol in *O. ammonoides* (Hauzer et al., 2018). In contrast, interspecific differences in Sr/Ca are relatively small [~1.7 versus ~2.6 mmol/mol for *Amphistegina* and *Operculina*, respectively; (Geerken et al., 2019; Hauzer et al., 2021)], but still, as for the other elements, they are all higher in *Operculina* than in *Amphistegina*. The consistent offsets, albeit with different magnitudes, suggest that differences in biomineralization pathways, e.g. Ca^{2+} pumping rate, between genera and species are reflected in element incorporation (De Nooijer et al., 2023). These inter-specific differences in element uptake are consistent with the reported relatively low K/Ca_{cc} values for planktonic foraminiferal species [0.06-0.12 mmol/mol; (Li et al., 2021)], as these are also known to have low values for Mg/Ca (1-5 mmol/mol; (Nürnberg et al., 1996; Anand et al., 2003) compared to *Amphistegina* and *O. ammonoides* (Figure 5). More recently (Nambiar et al., 2023), however, showed ratios (about 0.25 mmol/mol) for *G. ruber* comparable to those reported here and for *A. lessonii* (Nambiar et al., 2023).

Recently, foraminiferal Na/Ca_{cc} was suggested to act as a proxy for seawater $[Ca^{2+}]$ (Hauzer et al., 2018) in addition to its potential to reconstruct salinity (Wit et al., 2013; Mezger et al., 2019). Our results confirm that foraminiferal Na/Ca$_{cc}$ is responsive to changes in [Ca^{2+}] (Figures 1, 2) and the salinity range in Tables 2 and 4 in this case, show no significant effect in the Na or K incorporation, due to [Ca^{2+}]$_{sw}$ differences act as the main driver where they are incorporated. Here we show that foraminiferal K/Ca$_{cc}$ may be used to reconstruct past seawater [K^{+}], adding to our understanding of the long-term cycling of the oceans' major ions as was suggested by Nambiar et al., 2023). For seawater potassium concentrations, such a reconstruction may indicate rates of continental weathering (Kronberg, 1985; Sun et al., 2016) and indirectly, may reflect long-term changes in total alkalinity. Alternatively, seawater potassium concentrations may reflect rates of oceanic crust formation due to the difference between seawater and the mantle (Bloch and Bischoff, 1979).

4.2 Incorporation of potassium in foraminiferal calcite

K/Ca$_{cc}$ in *A. lessonii* does not vary consistently with [Ca^{2+}]$_{sw}$ (and hence K/Ca$_{sw}$; Figure 1A). Conversely, K/Ca$_{cc}$ increases when [Ca^{2+}] and [K^{+}] both increase (and K/Ca$_{sw}$ remains similar; Figure 2A). The absence of an effect of seawater Ca^{2+} and a positive effect of the combined K^{+} and Ca^{2+} elevation suggests that seawater [K^{+}] is the main driver of K-incorporation into foraminiferal calcite (Figure 2C), whereas it is not affected by [Ca^{2+}]. This resembles results from inorganic experiments in which K-incorporation was found to depend on solution [K^{+}] (Ishikawa and Ichikuni, 1984; Okumura and Kitano, 1986). Such a dependency is hence fundamentally different from that observed for many divalent cations like Ba^{2+}, Mn^{2+}, Mg^{2+}, or Sr^{2+}, for which the concentration in seawater relative to [Ca^{2+}]$_{sw}$ directly translates into a calcitic El/Ca ratio (Okumura and Kitano, 1986; Alkhatib et al., 2022). Such an incorporation pattern is caused by the competition of these ions with Ca^{2+} for a place in the calcite crystal lattice: for the monovalent cation incorporation is not governed by competition with Ca^{2+}. However, incorporation of monovalent ions (Li^{+}, Na^{+}, K^{+}, etc.) may be affected by different processes such as crystal surface sorption, speciation, and crystal growth rate, which complicates a straightforward interpretation of the environmental controls on element partitioning during calcification. Most likely a combination of all these effects impacts the uptake of monovalent cations.

More precisely, incorporation of an element into foraminiferal calcite is at least a two-step process (Figure 6; Bentov and Erez, 2006). There is the biological activity that configures the size and shape of the calcifying space and sets the composition of the fluid from which CaCO$_3$ precipitates (Erez, 2003; Bentov and Erez, 2006; Bentov et al., 2009; De Nooijer et al., 2014). The exact controls are only partly characterized and may vary between species, but include selective ion transport (Nehrke et al., 2013; Toyofuku et al., 2017), pH manipulation (Bentov et al., 2009; De Nooijer et al., 2009; Glas et al., 2012) and production of organic templates (Branson et al., 2016; Tyszka et al., 2019). Secondly, there are various (physico-) chemical processes that operate within the calcifying space that determine how much of each ion in the fluid is incorporated into the shell. Relevant processes include Rayleigh fractionation (Elderfield et al., 1996; Evans et al., 2018), kinetics (Uchikawa and Zeebe, 2012; Devriendt et al., 2021), CaCO$_3$ phase-transformations (Gray and Evans, 2019), chemical speciation (Van Dijk et al., 2017b) and configuration of ions within the crystal lattice (Branson et al., 2015) (Figure 6). For K one would expect a different trend as K uptake does not depend on Ca concentration (Figures 1, 2), but should reflect K concentration at the site of calcification (SOC). Nambiar et al. (2023), however, suggested an effect of [Ca^{2+}] on K-incorporation, as was observed in corals (Ram and Erez, 2021). The within chamber wall K profiles of Geerken

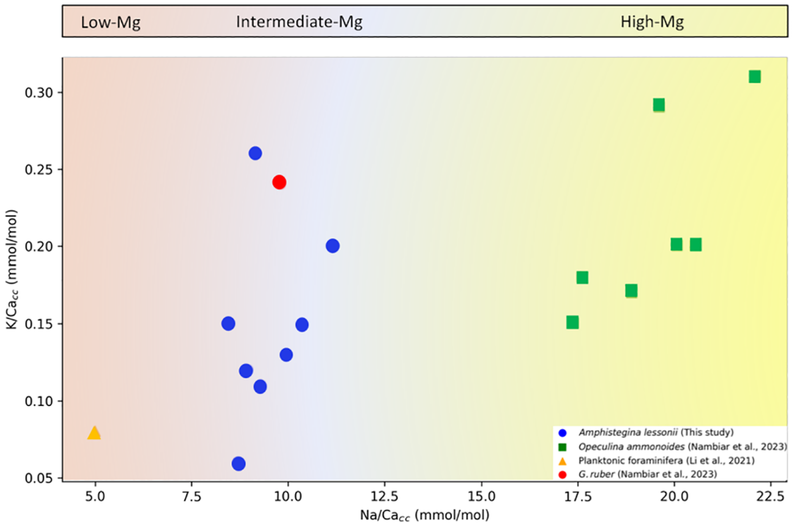

FIGURE 5
K/Ca$_{cc}$ versus Na/Ca$_{cc}$ for groups with different average Mg/Ca$_{cc}$. Low-Mg/Ca (<40 mmol/mol), Intermediate-Mg/Ca (40 – 100 mmol/mol) and High-Mg/Ca (>100 mmol/mol) (Blackmon and Todd, 1959).

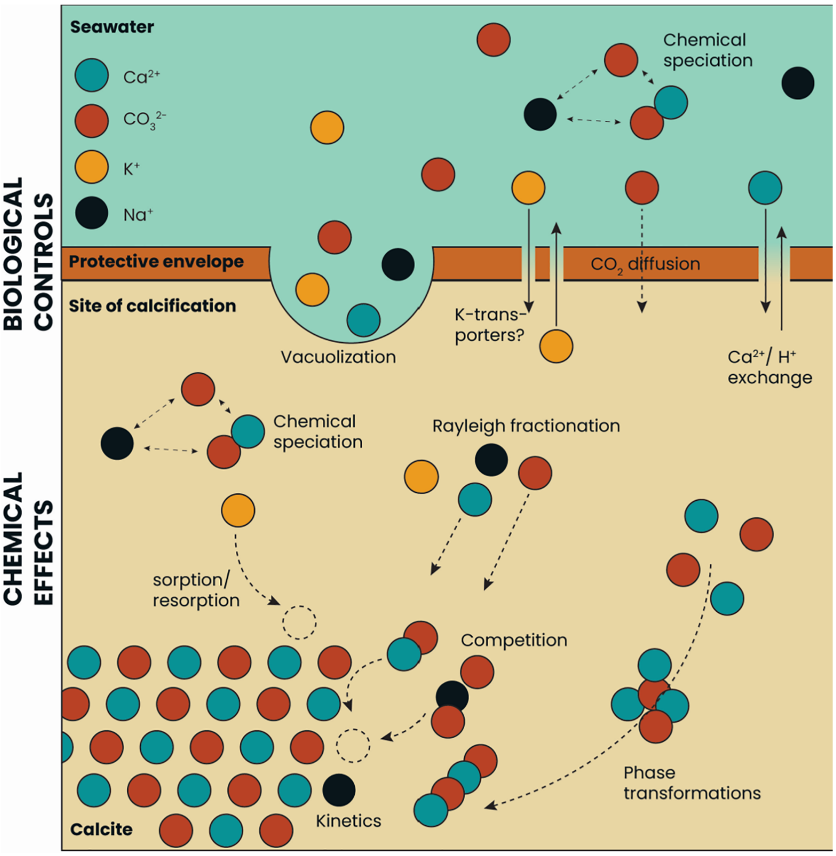

FIGURE 6
Simplified calcification scheme for rotaliid foraminifera. Biological and chemical processes at the site of calcification are presented, with a focus on the differences between Na^+ and K^+ incorporation into the calcite.

et al. (2019) actually show a gradual increase towards the end of a low concentration band (i.e. towards the outer surface of the shell wall). Other studies, however, have shown a tight correlation between the alternating high- and low-K bands with those of other elements (e.g. Mg) in *Amphistegina lobifera* and *A. lessonii* (Levi et al., 2019), which hints at a similarity in their incorporation dynamics. In addition, phosphorus is present in relatively narrow bands, similar to those of potassium, which hints to a coupling in their incorporation mode.

The observed relation between a solution's El/Ca and the calcitic El/Ca is likely affected by both biological and 'chemical' steps during foraminiferal biomineralization. Transport of K-ions over a cell membrane is not likely facilitated by Ca-transporters, while an occasional Mg-ion may well pass a Ca-pump (e.g. Dudev and Lim, 2013). For the precipitation dynamics, the monovalent K ion may occupy the interstitial sites in the calcite lattice (Ishikawa and Ichikuni, 1984), in the organic phases, or be incorporated in amorphous K_2CO_3 (Li et al., 2021). It is likely that all or most of these processes together determine the eventual K/Ca_{cc} and Na/Ca_{cc} of the foraminiferal calcite (Figure 6).

Our results show that the seawater's $[K^+]$, rather than $[Ca^{2+}]$ is the main driver for K partitioning. This is in line with free K^+ being the main species present in seawater (Johnson and Pytkowicz, 1979), with K sorption at the crystal lattice being the primary way K is incorporated. It should be noted however, that the chemical speciation of potassium in the calcifying fluid may differ from that in seawater due to the foraminfer's biological control on that fluid's composition (Erez, 2003; Bentov and Erez, 2006; De Nooijer et al., 2014) In contrast, for Na-incorporation, our results, and the dependence of Na/Ca_{cc} on the solution's Na/Ca (Figure 2) suggest that sodium and calcium compete for the same place in the crystal lattice. This would imply that sodium incorporation substitutes by replacement of two Na ions for one Ca ion (Devriendt et al., 2021) in the calcite and form a quadratic relationship. Since we do not observe this, alternatives including lattice vacancies can be filled by other divalent elements such as Mg^{2+} or Sr^{2+} may also play a role in the calcite's El/Ca.

Although our results cannot exclude that K-incorporation at interstitial sites is responsible for a (minor) part of the foraminiferal K/Ca_{cc}, (Nambiar et al., 2023) showed an increasing K/Ca_{cc} with K/Ca_{sw} for *O. ammonoides* with similar conditions as the one show in the $[Ca^{2+}]_{sw}$ experiment from this study. This may indicate that the crystallographic orientation of potassium differs between foraminiferal species but may also indicate that biological uptake of potassium ions varies among species. The presence of specialized K-transporters in addition to Ca-transporters (Toyofuku et al., 2017) promoting K-incorporation into the shell would imply an advantage of higher K/Ca, which is not immediately apparent. Alternatively, inward K-transport into the site of calcification may result from the organismal need to accompany inward transport of a negatively charged ions and/or to counter the outward transport of another positively charged ion in the calcifying fluid. Major anions are SO_4^{2-}, Cl^-, but both do not seem to be enriched in foraminiferal calcite compared to seawater and inorganically precipitated calcite (Kontrec et al., 2004; Van Dijk et al., 2017b; Roepert et al., 2020). Cations that are pumped out during calcification include H^+ (Glas et al., 2012) and are hypothesized to be coupled to an inward Ca^{2+} pumping (De Nooijer et al., 2017). The outward pumping of H^+ may sometimes also affect Na^+- and/or K^+-transport. With it is considerably larger ionic radius K^+ (152 pm) is less likely to be 'accidentally' transported through a transporter designed for H^+ (ionic radius of 66 pm) compared to Na^+ (116 pm).

When pumping of K^+ by the foraminifer is somehow affecting the K/Ca at the site of calcification incorporation of potassium in foraminiferal calcite may be impacted by an intracellular role of $[K^+]$. Potassium is often used as an agent to regulate osmosis and is found in cells at $[K^+]/[Na^+]$ ratios in the 0.1–1.0 range (Dibrova et al., 2015). Sodium ions form relatively strong hydrogen bonds, therefore attract water, and disrupt intracellular processes. For this reason, many (marine) cells have $[K^+]/[Na^+]$ antiporters (Nakamura et al., 1992; Shabala et al., 2009). Such a transport mechanism may (partly) explain the observed difference in Na/Ca and K/Ca in foraminifera when compared to inorganically precipitated calcite. The partition coefficients for potassium are relatively similar between inorganic and foraminifera calcite, while the partition coefficients for sodium are much lower in inorganically precipitated calcite (compared to foraminiferal shells). Overall, this makes K uptake in foraminiferal calcite a much more reliable proxy for reconstructing past sea water major ion composition.

5 Conclusions

Potassium in the shells of the benthic foraminifera *A. lessonii* was found at concentrations of 0.05-0.26 mmol/mol Ca. The incorporation of potassium was found not to depend on temperature, nor on seawater $[Ca^{2+}]$. This also implies a fundamental difference in uptake compared to that of Na, the other major monovalent cation in sea water. Experiments in which $[K^+]$ and $[Ca^{2+}]$ varied simultaneously, resulted in a change in the foraminifer's K/Ca, indicating the direct and unique effect of seawater $[K^+]$ on potassium partitioning during calcification. This implies that fossil foraminiferal K/Ca may directly reflect changes in seawater $[K^+]$, without being affected by changes in $[Ca^{2+}]$. We did find an effect of $[Ca^{2+}]_{sw}$ on Na- incorporation, highlighting the potential to use these two elements combined to reconstruct both seawater potassium and calcium concentrations.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding authors.

Ethics statement

The manuscript presents research on animals that do not require ethical approval for their study.

Author contributions

LP: Conceptualization, Data curation, Formal Analysis, Investigation, Writing – original draft, Writing – review & editing. LD: Conceptualization, Formal Analysis, Methodology, Project administration, Supervision, Writing – original draft, Writing – review & editing. WB: Data curation, Methodology, Writing – original draft, Writing – review & editing. G-JR: Conceptualization, Formal Analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – original draft, Writing – review & editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2024.1385347/full#supplementary-material

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