



The impact of Mg contents on Sr partitioning in benthic foraminifers



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ABSTRACT

Foraminiferal calcite Mg/Ca (Mg/Ca_{CC}) is used in paleoceanographic studies to reconstruct temperature. Furthermore, the Mg/Ca_{CC} is influenced by different seawater Mg/Ca (Mg/Ca_{SW}). Foraminiferal calcite Sr/Ca (Sr/Ca_{CC}) can potentially be used to reconstruct Sr/Ca ratios of seawater (Sr/Ca_{SW}). As these elements are the most abundant of all elements incorporated into the calcium carbonate of the foraminiferal tests, they potentially might affect each other's incorporation. To investigate the effects of the Mg concentration in the test on Sr incorporation, we conducted a culture study with two species of benthic *foraminifera* producing carbonate tests with different Mg content. Foraminifers grew under controlled conditions in different Mg/Ca_{SW} , whereas Sr/Ca_{SW} was kept constant. By analyzing Sr/Ca_{CC} of cultured specimens with laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS), we show that Sr/Ca_{CC} increases with increasing Mg/Ca_{CC} . We explain this observation by a stress in the crystal lattice, caused by elevated Mg/Ca_{CC} , which may be compensated for by the additional incorporation of Sr. We discuss this finding in the context of biomineralization and evaluate the reliability of Sr/Ca_{CC} as a possible Sr/Ca_{SW} proxy.

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1. Introduction

Element to calcium ratios of foraminiferal calcium carbonate tests, ubiquitous in marine sediments, are widely used as proxies to reconstruct past seawater parameters. For example, the incorporation of Mg has been shown to reflect seawater temperature (Nürnberg et al., 1996; Lear et al., 2003) and trace elements, like barium and cadmium, reflect seawater nutrient levels (e.g. Boyle, 1988). Furthermore, foraminiferal Sr/Ca has been shown to vary with varying seawater Sr/Ca (e.g., Lear et al., 2003). Although this relationship is influenced by pressure (Elderfield et al., 1996), temperature and carbonate ion concentrations (Russell et al., 2004; Rosenthal et al., 2006) and therefore not straightforward, Sr/Ca_{CC} is handled as a potential proxy for seawater Sr/Ca (e.g., Yu et al., 2014). These proxy relationships are, however, complicated by so called vital effects (Urey et al. 1951, Weiner and Dove 2003, Erez, 2003), which encompass the biological processes involved in calcite precipitation affecting incorporation of elements into the calcium carbonate tests (De Nooijer et al., 2014a, 2014b). Hence, it is necessary to understand and reveal these biological processes involved in calcite precipitation to improve the reliable use of minor and

major elements in foraminiferal tests as paleo-proxies. Over the last decades, a number of studies aided the identification of the underlying processes responsible for foraminiferal biomineralization and their potential imprint on trace metal incorporation (e.g. Angell, 1967, 1979; Bé et al., 1979; Hemleben et al. 1986; Ter Kuile and Erez, 1988; Spero, 1988; Ter Kuile et al., 1989; Erez, 2003; Bentov and Erez, 2005; Segev and Erez, 2006; Bentov et al., 2009; De Nooijer et al., 2009a,b; De Nooijer et al., 2009b; De Nooijer et al., 2014a, 2014b).

Metals incorporated into foraminiferal calcium carbonate may affect each other during biomineralization, analogous to the mutual impact of incorporation of Mg^{2+} and Sr^{2+} in abiotically formed calcite. A clear trend is observed of increasing Sr content with increasing Mg content (Ohde and Kitano, 1984; Carpenter and Lohmann, 1992). At least for inorganic calcite this does not only hold for samples taken from seawater with constant seawater Mg/Ca_{SW} and Sr/Ca_{SW} , as Mucci and Morse (1983) observed increasing Sr contents in inorganic calcite when the Mg concentration of seawater increased. If such an effect would also been shown to impact the Mg-content of foraminiferal calcite, we have to consider its impact for paleo-reconstructions and assess how such effects can be reconciled with biomineralization models. Here we assess the effect of varying seawater Mg^{2+} and Ca^{2+} on Sr partition in foraminifers by analyzing Sr/Ca in foraminiferal specimens grown under a range of seawater Mg/Ca values. This allows assessing: (1) the

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(biological) controls on Sr incorporation during foraminiferal calcification and, (2) the reliability of Sr/Ca_{CC} as a possible Sr/Ca_{SW} proxy.

2. Material and methods

Specimens of the benthic intertidal foraminifer *Ammonia aomoriensis*, precipitating low Mg-calcite (0.4–4 mmol/mol), were sampled from the Wadden Sea near Dorum Neufeld, Germany (53.7416° north, 8.5159° east). Specimens of the tropical benthic foraminifer *Amphistegina lessonii*, precipitating intermediate Mg-calcite (40–60 mmol/mol) were sampled from a coral reef aquarium at Burger's Zoo in Arnhem. Both species were stored in stock cultures in the laboratory. Adult specimen were picked from stock cultures and placed in well plates. Probably due to evaporation salinity increased, which induced asexual reproduction. Offspring were isolated from the mother cell and used for the culture experiments. The use of offspring ensured that all chambers analyzed were grown under controlled conditions. Two different culture experiments were performed, in which juveniles were grown in artificial seawater at different seawater Mg/Ca. The Mg/Ca_{SW} values chosen here represent both today's and hypothesized extremes in past natural variations in seawater Mg/Ca for the last 100 Ma. This is also the maximum range which can be achieved in a culture experiment without inducing inorganic precipitation of calcium carbonate or magnesium hydroxide. Lowering Ca or Mg concentrations even further might also be detrimental to physiology (including processes unrelated to calcification). Artificial seawater was prepared based on the recipe by Kester et al. (1967). In the first experiment, seawater Mg/Ca was varied by changing [Mg²⁺] (for details see Mewes et al., 2014a), in the second experiment via varying [Ca²⁺] of the culture media (for details see Mewes et al., 2014b). All other seawater parameters (e.g. TA, pH, salinity) were kept constant. Seawater [Sr²⁺] was also constant in both experiments at ~0.1 mM. To determine Sr/Ca_{SW} and Mg/Ca_{SW}, seawater [Sr²⁺], [Mg²⁺] and [Ca²⁺] were analyzed with inductively coupled plasma optical emission spectrometry (ICP-OES). For details of the culture media in the two different experiments see Table 1. The total duration of the first experiment was approximately 4 weeks, the one of the second experiment ~7 weeks. Juveniles were cultured in Petri dishes. For each treatment duplicates or triplicates were cultured and juveniles stem from 2–4 different asexual reproduction events. Laser ablation-inductively coupled plasma–mass spectrometry (LA-ICP-MS) was used to determine Mg and Sr concentrations in the foraminiferal tests (Reichert et al., 2003). A GeoLas 200 Q Excimer 193 nm deep ultra violet laser (Lambda Physik) was used to ablate craters of 40–80 μm in diameter. Energy density at the sample surface was approximately 1.2 J/cm² and all samples were ablated with a repetition rate of 7 Hz in a He atmosphere. The sector field mass spectrometer (Element 2, Thermo Scientific) was run in low-resolution mode and masses monitored included ²⁴Mg, ²⁶Mg, ⁴³Ca, ⁴⁴Ca and ⁸⁸Sr. Calibration was performed against SRM NIST610 glass standard (using values from Jochum et al., 2011), using ⁴³Ca as an internal standard. Due to different material properties, the glass standard was ablated at higher energy density. Concentrations of Mg and Sr in the foraminiferal shell were calculated for each individual laser measurement based on count rates for ²⁴Mg, ²⁶Mg and ⁸⁸Sr, using ⁴³Ca as an internal standard. Relative precision based on analyses of standard material was below ~5% for ²⁴Mg, ²⁶Mg and ⁸⁸Sr. Concentrations of these elements and their respective confidence intervals were calculated for each individual laser measurement. This was done by using the software package Glitter (Macquarie Research Limited, 1999–2000).

From each treatment and from each replicate or triplicate group one or two foraminiferal tests were selected and ablated 4–6 times. These ablations were performed on different chambers, with each chamber being ablated for a maximum time span of 30 s or until the inside of the test wall was reached. A study by De Nooijer et al. (2014b) showed no significant difference between Mg/Ca_{CC} and Sr/Ca_{CC} between single chambers within one test and also no significant difference between

Table 1
Parameters of the different culture experiments.

	Experiment 1 (constant Ca ²⁺), Mewes et al. (2014a)						Experiment 2 (constant Mg ²⁺), Mewes et al. (2014b)					
	Ammonia aomoriensis			Amphistegina lessonii			Ammonia aomoriensis			Amphistegina lessonii		
	Treat. 1	Treat. 2	Treat. 3	Treat. 1	Treat. 2	Treat. 3	Treat. 1	Treat. 2	Treat. 3	Treat. 4	Treat. 5	Treat. 6
SW Mg ²⁺ [mM] ± 0.5	9.83	50.28	91.13	13.90	48.01	91.86	51.64	52.56	52.75	52.66	52.05	52.40
SW Ca ²⁺ [mM] ± 0.2	8.88	9.93	9.95	9.14	9.08	9.06	34.19	17.86	9.22	6.63	4.77	3.18
SW Sr ²⁺ [mM] ± 0.5 × 10 ⁻³	0.09	0.09	0.10	0.08	0.09	0.09	0.11	0.11	0.11	0.11	0.10	0.10
Mg/Ca _{SW} [mol/mol]	1.11	5.07	9.16	1.52	5.29	10.14	1.51	2.94	5.72	7.95	10.91	16.47
Sr/Ca _{SW} [mol/mol]	1.01 × 10 ⁻²	0.91 × 10 ⁻²	1.01 × 10 ⁻²	0.88 × 10 ⁻²	0.99 × 10 ⁻²	0.99 × 10 ⁻²	0.32 × 10 ⁻²	0.60 × 10 ⁻²	1.14 × 10 ⁻²	1.59 × 10 ⁻²	2.18 × 10 ⁻²	3.27 × 10 ⁻²
Mg/Ca _{CC} [mmol/mol] ± st. error	1.60 ± 0.10	3.61 ± 0.21	5.90 ± 0.34	12.28 ± 0.37	35.45 ± 0.90	59.89 ± 2.17	22.95 ± 0.81	40.79 ± 1.38	52.08 ± 1.72	67.50 ± 2.37	83.35 ± 1.96	-
Sr/Ca _{CC} [mmol/mol] ± st. error	1.79 ± 0.04	1.83 ± 0.03	1.94 ± 0.03	1.45 ± 0.03	1.84 ± 0.02	2.16 ± 0.04	0.70 ± 0.02	1.50 ± 0.03	3.02 ± 0.04	4.75 ± 0.11	7.58 ± 0.16	-
D _{Sr}	0.19	0.19	0.20	0.16	0.19	0.22	0.22	0.21	0.26	0.29	0.35	-
± St. error	± 3.68 × 10 ⁻³	± 3.37 × 10 ⁻³	± 3.24 × 10 ⁻³	± 2.95 × 10 ⁻³	± 2.21 × 10 ⁻³	± 3.69 × 10 ⁻³	± 4.71 × 10 ⁻³	± 5.26 × 10 ⁻³	± 3.47 × 10 ⁻³	± 6.69 × 10 ⁻³	± 7.24 × 10 ⁻³	-
T [°C] ± 0.5	25	25	25	25	25	25	25	25	25	25	25	25
S ‰ ± 0.5	32.8	32.4	32.5	32.9	32.5	32.4	32.4	32.4	32.4	32.4	32.4	32.4
pH (NBS) ± 0.04	8.2	8.1	8.1	8.1	8.1	8.1	8.1	8.1	8.1	8.1	8.1	8.1
TA [μmol/kg] ± 5 μmol/kg	2530	2489	2663	2254	2297	2509	2615	2545	2504	2504	2492	2479
Ω (calcite)	4.82	4.52	5.06	4.80	4.50	5.08	16.75	8.74	4.49	3.24	2.33	1.55
DiC [μmol/kg] ± 7 μmol/kg	2215	2192	2236	2105	2060	2168	2302	2298	2286	2295	2294	2290

ablated chambers from different juveniles grown under the same cultural conditions. Also in our study the inter-chamber reproducibility of laser spot measurements was 95% and the inter-individual reproducibility was 92% for *A. lessonii*. For *A. aomoriensis* the inter-chamber reproducibility of laser spot measurements was 93% and the inter-individual reproducibility was 90%. We therefore exclude a potential influence of systematic patterns in inter-chamber and inter-individual differences in our data. We therefore do not further consider a potential influence of systematic patterns in inter-chamber and inter-individual differences in our data.

Obtained seawater and foraminiferal Mg/Ca and Sr/Ca were used to calculate partition coefficients (D). The D for an element is a measure of how strongly foraminifers fractionate against or remove a certain element while precipitating the calcium carbonate to build their tests. A value of 1 indicates that the element is incorporated into the calcium carbonate at the same ratio as it occurs to calcium in seawater. Values <1 indicate that this element is fractionated against, while at values >1 relatively more of this element is incorporated in comparison to its relative abundance with respect to seawater $[Ca^{2+}]$. Accordingly, the partition coefficient (D_{Sr}), as a measure to determine fractionation against Sr, was determined by dividing calcite Sr/Ca by the seawater Sr/Ca: $D_{Sr} = (Sr/Ca_{CC}) / (Sr/Ca_{SW})$.

3. Results

3.1. Effect of different seawater Mg^{2+}

Sr/Ca_{CC} increases linearly with increasing Mg/Ca_{SW} and thus also with increasing Mg/Ca_{CC} (Figs. 1a+c and 2a+c). This relationship is obvious for *A. lessonii*, while the relationship in *A. aomoriensis* is less sensitive,

showing only little relationship between Sr/Ca_{CC} and Mg/Ca_{SW} or Mg/Ca_{CC} respectively. However, the data for *A. aomoriensis* show the same positive trend as for *A. lessonii*. Sr/Ca_{CC} is similar for both species (Table 1). Also the partition coefficient, D_{Sr} , increases linearly with increasing Mg/Ca_{SW} and increasing Mg/Ca_{CC} for both, *A. aomoriensis* (Fig. 1b+d) and *A. lessonii* (Fig. 2b+d). It is also incorporated at similar concentrations in both species (Table 1). When Sr/Ca_{CC} is plotted against Mg/Ca_{SW} (Fig. 1a+2a) the slope of the regression is steeper in the intermediate-Mg calcite species, *A. lessonii* (slope = 0.08 ± 0.004), compared to the low-Mg calcite species, *A. aomoriensis* (slope = 0.02 ± 0.005). When Sr/Ca_{CC} is however plotted against Mg/Ca_{CC} (Fig. 1c+2c), the slope of the regression is steeper in the low-Mg calcite species, *A. aomoriensis* (slope = 0.03 ± 0.007), compared to the intermediate-Mg calcite species, *A. lessonii* (slope = 0.01 ± 0.001). The same is observed for D_{Sr} when plotted versus Mg/Ca_{SW} and Mg/Ca_{CC} , respectively (Figs. 1b+2b and 1d+2d).

We tested the significance of all correlations using a t-test to verify whether the slope is unequal to 0. For all potential regressions the t-test revealed a significant difference of the slope from 0 at a 99% confidence interval ($p < 0.01$). The correlation coefficient (r^2) was much higher for the data derived from *A. lessonii*, which is probably related to the larger variability in Sr/Ca_{CC} in the dataset of *A. aomoriensis*. The somewhat higher variability is most likely due to shorter ablation profiles and hence more limited data acquisition, which is due to thinner test walls of *A. aomoriensis*. In addition, the chambers of *A. aomoriensis* are smaller, necessitating a smaller laser spot size, which result in lower yields of calcite for analyses. The variability was highest in the control treatment, but never exceeded 1.4 mmol/mol. This is in line with a previous study by De Nooijer et al. (2014a, 2014b), which detected an inter-individual Sr/Ca variability range of 1.4–1.7 mmol/mol.

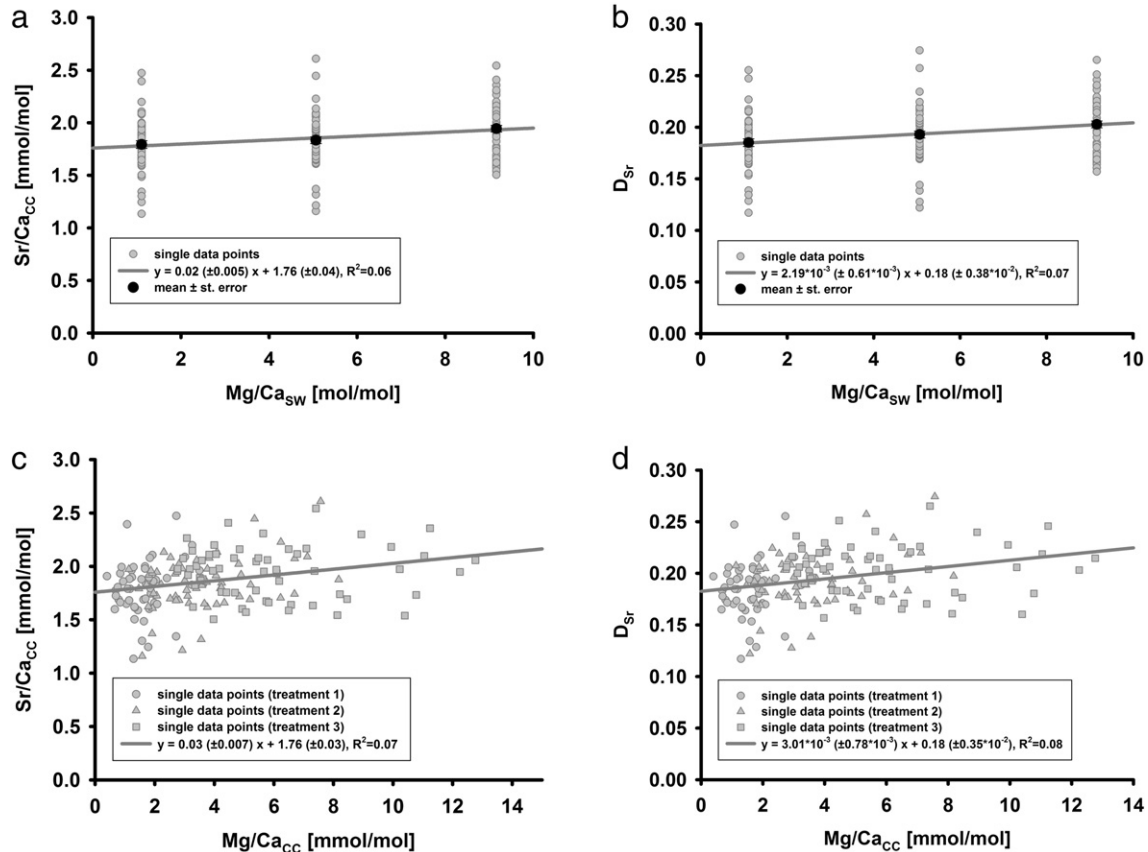


Fig. 1. Results for *Ammonia aomoriensis* when Mg/Ca was varied via Mg^{2+} : Sr/Ca_{CC} and D_{Sr} increase with increasing Mg/Ca_{SW} ($n = 51$ –60) (a + b) and with increasing Mg/Ca_{CC} (c + d). Single data points represent single laser ablation measurement spot analyses.

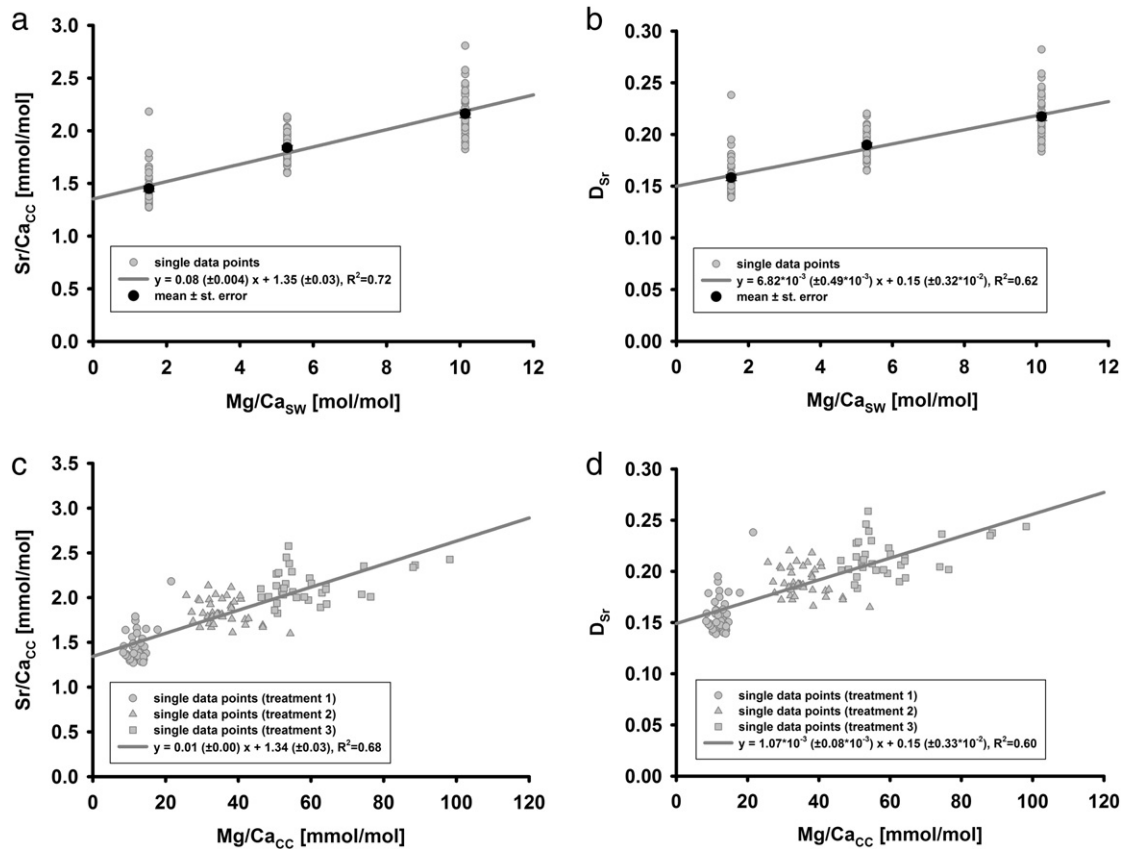


Fig. 2. Results for *Amphistegina lessonii* when Mg/Ca was varied via Mg^{2+} : Sr/Ca_{CC} and D_{Sr} increase with increasing Mg/Ca_{SW} ($n = 34\text{--}42$) (a + b) and with increasing Mg/Ca_{CC} (c + d). Single data points represent single laser ablation measurement spot analyses.

3.2. Effect of different seawater Ca^{2+}

Our results also demonstrate a linear increase in Sr/Ca_{CC} and D_{Sr} with both Mg/Ca_{SW} and Mg/Ca_{CC} when Mg/Ca_{SW} is varied via Ca^{2+} (Fig. 3). However, slopes of all regressions are higher when Mg/Ca_{SW} was varied via Ca^{2+} compared to varying via Mg^{2+} (compare Figs. 3 and 2). Absolute calcitic and seawater Mg, Ca and Sr concentrations are summarized in Table 1. Our regression analyses with a t-test showed again a significant deviation of the slope from 0 and thus a significant correlation at a 99% confidence interval ($p < 0.01$).

With varying seawater Mg/Ca, which is manipulated via Ca^{2+} , Sr/Ca_{SW} also changed. The increasing Sr/Ca_{SW} values in our experiment had a significant ($p < 0.01$) effect on Sr/Ca_{CC} and thus also on the Sr partitioning in *A. lessonii* (Fig. 4).

4. Discussion

4.1. Biological control on Sr incorporation during foraminiferal calcification

Foraminiferal Sr/Ca_{CC} increased with increasing Mg/Ca_{CC} and Mg/Ca_{SW} , which does at first sight contradict a recently developed biomineralization model by Nehrke et al. (2013), predicting a constant Sr/Ca_{CC} for different Mg/Ca_{SW} . This model suggests that foraminifers calcify mainly via selective transmembrane transport of Ca^{2+} . Other ions than Ca^{2+} , e.g. Mg^{2+} and Sr^{2+} , may enter the cell mainly via passive transport, either by leakage into the “privileged space” for calcification or via seawater vacuolization. As Sr^{2+} and Mg^{2+} enter in proportion to their seawater concentrations, this model predicts a constant Sr/Ca_{CC} offset between foraminiferal species, but also a constant Sr/Ca_{CC} at varying Mg/Ca_{SW} , when Sr/Ca_{SW} remains constant. This model assumes that

only a small but constant amount of Sr^{2+} reaches the calcification site, equivalent to the percentage of passive transport (Nehrke et al., 2013). [Sr^{2+}] in the culture media was constant in all treatments, in both experiments, and therefore a constant Sr/Ca_{CC} was expected. However, we observed increasing Sr/Ca_{CC} with increasing Mg/Ca_{CC} and Mg/Ca_{SW} values. Hence, we need to clarify whether the increase in Sr partitioning is caused by increasing Mg/Ca_{SW} as such or rather an artifact caused by increasing Mg/Ca_{CC} , similar to what is observed in inorganic precipitation experiments (Mucci and Morse, 1983). Therefore, we will discuss our data in comparison with inorganic calcite data (Mucci and Morse, 1983) and with data from coccolithophores (Müller et al., 2011) (Fig. 5).

When plotting D_{Sr} versus Mg/Ca_{SW} (Fig. 5a), there is no, or at best, a negative correlation with a very shallow slope for coccolithophores (Müller et al., 2011). Also for *A. aomoriensis* only a very weak positive correlation can be detected, indicated by the shallow sensitivity of the D_{Sr} – Mg/Ca_{SW} relationship. In contrast, when plotting D_{Sr} versus the Mg/Ca_{CC} (Fig. 5b), strong positive correlations are observed, with much steeper slopes. This suggests that D_{Sr} depends on Mg/Ca_{CC} rather than on Mg/Ca_{SW} . Admittedly, the correlation and slope observed for coccolithophores are inconclusive, due to the small range of Mg/Ca_{CC} studied (Müller et al., 2011), but do, nevertheless, not exclude a positive correlation between D_{Sr} and Mg/Ca_{CC} . Because different species, different organisms and even inorganically precipitated calcite all show the same pattern, it may well be that there is a common mechanism for the dependency of D_{Sr} on Mg/Ca_{CC} . This is not taken into account by the biomineralization model of Nehrke et al. (2013), and therefore an additional “inorganic process” during crystal formation should be taken into account. Based on an inorganic precipitation study, Mucci and Morse (1983) suggested that the incorporation of Mg^{2+} ions causes stress in the calcite crystal lattice, which can partially be compensated by inclusion of Sr^{2+} . Therefore, Sr^{2+} is more easily incorporated at

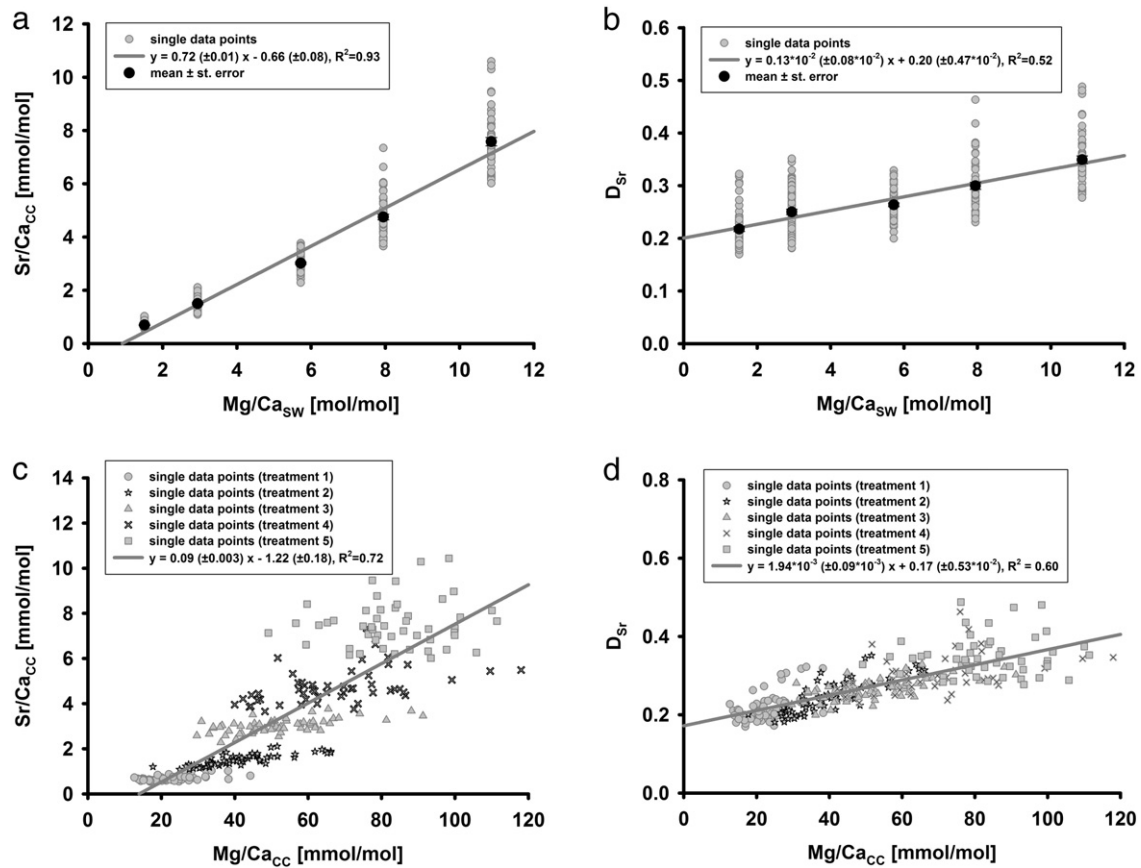


Fig. 3. Results for *Amphistegina lessonii* when Mg/Ca was varied via Ca^{2+} : $\text{Sr}/\text{Ca}_{\text{CC}}$ and D_{Sr} increase with increasing $\text{Mg}/\text{Ca}_{\text{SW}}$ ($n = 50\text{--}65$) (a + b) and with increasing $\text{Mg}/\text{Ca}_{\text{CC}}$ (c + d). Single data points represent single laser ablation measurement spot analyses.

high $\text{Mg}/\text{Ca}_{\text{CC}}$. Hence, the observed correlation between D_{Sr} and $\text{Mg}/\text{Ca}_{\text{SW}}$ in our data is primarily explained by the fact that with increasing $\text{Mg}/\text{Ca}_{\text{SW}}$ $\text{Mg}/\text{Ca}_{\text{CC}}$ also increases (compare Table 1).

Higher Sr incorporation at higher $\text{Mg}/\text{Ca}_{\text{CC}}$, due to stress compensation, is also consistent with the steeper slope observed in *A. aomoriensis* (slope: 3.01 ± 0.78 , Fig. 1d) compared to *A. lessonii* (slope: 1.07 ± 0.08 , Fig. 2d). *A. aomoriensis* has a 10-times lower Mg concentration in its test than *A. lessonii*. At higher seawater Mg concentrations, the incorporation of more Mg^{2+} immediately adds stress to the calcite crystal lattice. The slope of D_{Sr} as a function of Mg incorporated is steeper compared to *A. lessonii* because additional Mg incorporated into tests of *A. lessonii* would add relatively less to the overall crystal lattice stress.

If incorporation of Sr^{2+} into the crystal as stress compensation is the only control, it can be expected that the $\text{Sr}/\text{Ca}_{\text{CC}}$ and D_{Sr} are similar at any given $\text{Mg}/\text{Ca}_{\text{CC}}$. However, different organisms (coccolithophores in comparison to foraminifers) and different species (*A. aomoriensis* compared to *A. lessonii*) display different D_{Sr} at the same $\text{Mg}/\text{Ca}_{\text{CC}}$ (Fig. 5b). This is plausible when considering that, besides processes inherent to inorganic precipitation, cell physiological processes such as binding of ions to polysaccharides and transmembrane transport of ions also influence Sr partitioning. These physiological processes depend on the particular type of e.g. polysaccharide or ion channels and therefore probably differs between species. Conceptual calcification models, including physiological processes and their effects on minor element partitioning, exist for coccolithophores (Langer et al., 2006) and foraminifera (Mewes et al., 2014b).

4.2. Reliability of $\text{Sr}/\text{Ca}_{\text{CC}}$ as a possible $\text{Sr}/\text{Ca}_{\text{SW}}$ proxy

Different studies suggested that the $\text{Sr}/\text{Ca}_{\text{CC}}$ of foraminiferal calcite is a proxy for past seawater Sr/Ca (e.g. Stoll et al., 1999; Raitzsch et al.,

2010). This assumption mainly builds on the independence of $\text{Sr}/\text{Ca}_{\text{CC}}$ from other environmental parameters, such as e.g. temperature, pH and salinity.

Our data, however, show $\text{Sr}/\text{Ca}_{\text{CC}}$ to increase with increasing $\text{Mg}/\text{Ca}_{\text{CC}}$. Although we infer a causal relationship between $\text{Sr}/\text{Ca}_{\text{CC}}$ and $\text{Mg}/\text{Ca}_{\text{CC}}$ rather than between $\text{Sr}/\text{Ca}_{\text{CC}}$ and $\text{Mg}/\text{Ca}_{\text{SW}}$, it is obvious that differences in $\text{Mg}/\text{Ca}_{\text{CC}}$ are, in addition to temperature, caused by different $\text{Mg}/\text{Ca}_{\text{SW}}$ (Mewes et al., 2014a, 2014b). Hence, seawater Mg/Ca needs to be accounted for when using $\text{Sr}/\text{Ca}_{\text{CC}}$ as a $\text{Sr}/\text{Ca}_{\text{SW}}$ proxy. Furthermore, our experiments, in which $\text{Mg}/\text{Ca}_{\text{SW}}$ was modified via Ca^{2+} , are also characterized by a variation in $\text{Sr}/\text{Ca}_{\text{SW}}$ (Fig. 4). Many studies have shown that increasing $\text{Sr}/\text{Ca}_{\text{SW}}$ increase calcite $\text{Sr}/\text{Ca}_{\text{CC}}$ (e.g. Langer et al., 2006; Raitzsch et al., 2010). This was confirmed in our study (Fig. 4a) and may explain observed steeper regressions in the experiment where Ca was varied (Fig. 3a+b) compared to the experiment with varying seawater [Mg^{2+}] (Fig. 2a+b). In contrast, the relationships between $\text{Sr}/\text{Ca}_{\text{CC}}$ and D_{Sr} , with $\text{Mg}/\text{Ca}_{\text{CC}}$ show similar slopes for both experiments with *A. lessonii* (compare Figs. 2c+d and 3c+d), irrespective of whether $\text{Mg}/\text{Ca}_{\text{SW}}$ was varied via Mg^{2+} or Ca^{2+} . This similarity supports our conclusion that Sr partitioning rather correlates with $\text{Mg}/\text{Ca}_{\text{CC}}$ than with $\text{Mg}/\text{Ca}_{\text{SW}}$ (compare Section 4.1).

From the linear relationship between $\text{Sr}/\text{Ca}_{\text{CC}}$ and $\text{Sr}/\text{Ca}_{\text{SW}}$, that almost intersects with the origin, we expect a constant D_{Sr} with increasing $\text{Sr}/\text{Ca}_{\text{SW}}$ (Fig. 4a). The increasing D_{Sr} (Fig. 4b) can be explained by the $\text{Sr}/\text{Ca}_{\text{SW}}$ variation via Ca, which in turn, increases $\text{Mg}/\text{Ca}_{\text{SW}}$ and hence $\text{Mg}/\text{Ca}_{\text{CC}}$.

Based on these observations we infer that $\text{Sr}/\text{Ca}_{\text{CC}}$ cannot be used as a direct proxy for $\text{Sr}/\text{Ca}_{\text{SW}}$ to determine past seawater [Sr], because $\text{Sr}/\text{Ca}_{\text{CC}}$ is also influenced by $\text{Mg}/\text{Ca}_{\text{CC}}$, which depends on $\text{Mg}/\text{Ca}_{\text{SW}}$ and second, it is further influenced by varying seawater Ca^{2+} that also changes $\text{Sr}/\text{Ca}_{\text{SW}}$. This holds true for the species investigated in this

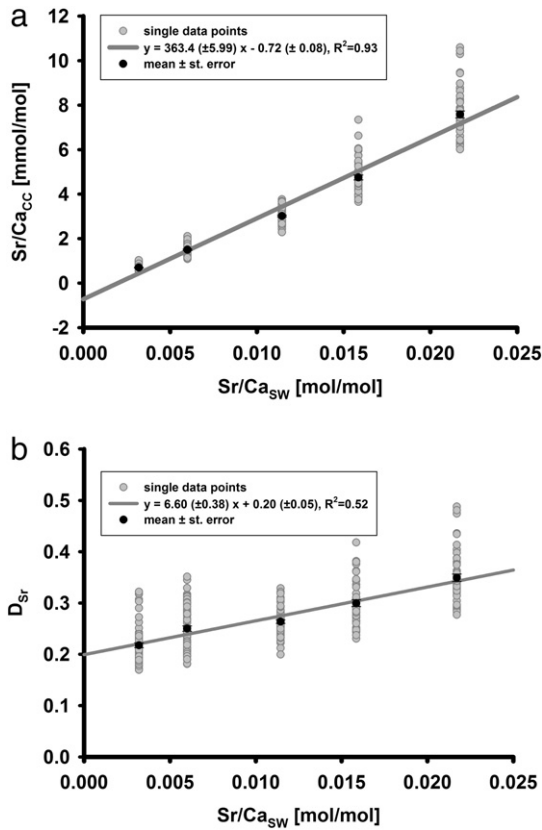


Fig. 4. a) When Mg/Ca was varied via Ca^{2+} also $\text{Sr}/\text{Ca}_{\text{SW}}$ is manipulated, resulting in increasing $\text{Sr}/\text{Ca}_{\text{CC}}$. b) Increasing D_{Sr} with $\text{Sr}/\text{Ca}_{\text{SW}}$, due to impact of $\text{Mg}/\text{Ca}_{\text{CC}}$. Single data points represent single laser ablation measurement spot analyses.

study. However, neither *A. lessonii* nor *A. aomoriensis* are commonly used for paleo-reconstructions. It is thus a matter of further investigations to reveal how the results presented here can be transferred to other benthic and planktonic foraminiferal species, which are commonly used for paleo-reconstructions.

5. Conclusion

By analyzing Sr/Ca in foraminiferal calcites that were grown under different seawater Mg/Ca, we showed that Sr partition increases with increasing $\text{Mg}/\text{Ca}_{\text{SW}}$ and $\text{Mg}/\text{Ca}_{\text{CC}}$. We infer a causal relationship between D_{Sr} and $\text{Mg}/\text{Ca}_{\text{CC}}$, because high $\text{Mg}/\text{Ca}_{\text{CC}}$ cause stress in calcite crystal lattices that can be compensated by higher Sr^{2+} incorporation. This relationship is not taken into account by a recent biomineralization model and since it is observed in biogenic calcite as well as inorganic calcite, this relationship is most likely based on “inorganic processes” during formation of the crystal lattice. Different physiological processes among different organisms and different species cause the observed different slopes within this relationship. From our data we furthermore conclude that $\text{Sr}/\text{Ca}_{\text{CC}}$ as a proxy for $\text{Sr}/\text{Ca}_{\text{SW}}$ has to be used with care for time periods in which the Mg/Ca of seawater differed from the conditions under which the proxy relationship has been calibrated. In fact, it is indispensable that paleoceanographers consider the respective $\text{Mg}/\text{Ca}_{\text{SW}}$, because this ratio influences $\text{Mg}/\text{Ca}_{\text{CC}}$ in foraminiferal tests, which in turn have an impact on Sr partitioning. This study illustrates the complex relation between seawater parameters and how important it is in paleo-oceanographic studies to consider the potential of elements to affect each other's incorporation into foraminiferal calcium carbonate.

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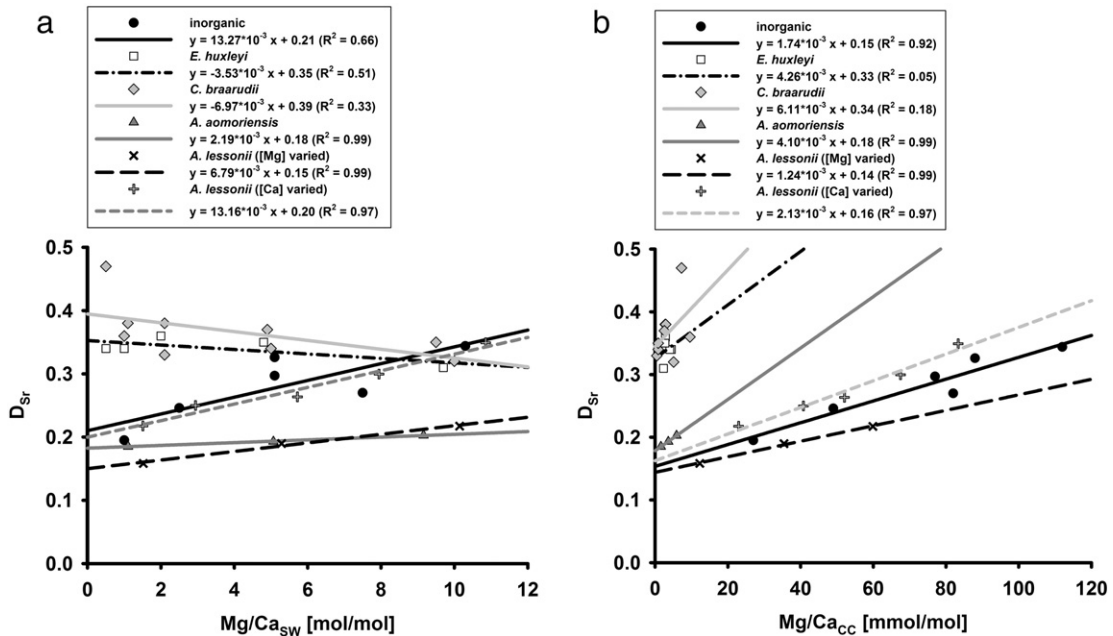


Fig. 5. a) $\text{Mg}/\text{Ca}_{\text{SW}}$ and b) $\text{Mg}/\text{Ca}_{\text{CC}}$ versus mean partition coefficient D_{Sr} for inorganic precipitated calcite (Mucci and Morse, 1983), two species of coccolithophores (Müller et al., 2011) and two species of foraminifers (this study).

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