



RESEARCH ARTICLE

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The Impacts of Seawater Mg/Ca and Temperature on Element Incorporation in Benthic Foraminiferal Calcite

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Key Points:

- Two foraminiferal species were cultured at a range of temperatures and seawater Mg/Ca
- These parameters appeared to influence element incorporation independently
- General differences between these two species are caused by differences in their biomineralization pathways

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Abstract On geological timescales, oceanic [Mg²⁺] and [Ca²⁺] vary with changing rates of weathering, seafloor spreading and dolomite formation. Accurate reconstruction of the ratio between [Mg²⁺] and [Ca²⁺] in seawater (Mg/Ca_{sw}), may potentially be reconstructed using foraminiferal Mg/Ca ratios. Since both temperature and seawater Mg/Ca impact foraminiferal Mg/Ca, successful reconstruction of Mg/Ca_{sw} requires quantification of both these parameters independently on foraminiferal Mg/Ca, as well as their combined effect on Mg-incorporation. Here we present the combined and isolated impacts of temperature and Mg/Ca_{sw} on Mg incorporation in two model species, the benthic hyaline (i.e., perforate) foraminifer *Elphidium crispum* and porcelaneous (i.e., miliolid) foraminifer *Quinqueloculina* sp. using controlled growth experiments. Specimens of these two species were kept at four different temperatures (ranging from 10 to 27°C) and three Mg/Ca_{sw}'s (3.4, 6.4 and 8.5 mol/mol), resulting in 12 experimental conditions. Newly grown calcite was analyzed for a number of elements (Na, Mg and Sr) by laser ablation-ICP-MS. Results show that although the Mg/Ca varied by more than an order of magnitude between species, the sensitivity of Mg incorporation with respect to temperature appeared not to be influenced by Mg/Ca_{sw}. By extension, these results may also help improving accuracy in the reconstruction of past Mg/Ca_{sw} based on foraminifera with contrasting Mg/Ca.

1. Introduction

Foraminiferal calcite element concentrations are popular tools to reconstruct past seawater conditions and thereby serve as the basis of many paleoclimate reconstructions. Incorporation of magnesium (Mg) into the tests (i.e., shells) of planktonic (Anand et al., 2003; Elderfield & Ganssen, 2000; Nürnberg et al., 1996) and benthic (e.g., Billups and Schrag, 2002; Elderfield et al., 2006; Lear et al., 2000; Martin et al., 2002) foraminifera is a function of ambient temperature and can hence be used in fossil specimens to derive past sea surface (e.g., Hastings et al., 1998) and bottom water (e.g., Lear et al., 2000) temperatures. Salinity and carbonate ion concentration additionally impact benthic and planktonic foraminiferal Mg/Ca (Dueñas-Bohórquez, da Rocha, et al., 2011; Dueñas-Bohórquez et al., 2009; Hertzberg and Schmidt, 2013; Hönisch et al., 2013; Nürnberg et al., 1996; Rosenthal et al., 1997; Yu & Elderfield, 2008), but in many environmental settings, these influences are relatively small or can be accounted for using other proxies, e.g., B/Ca for saturation state (Yu & Elderfield, 2007) and Na/Ca for salinity (Allen et al., 2016; Wit et al., 2013).

The ratio of [Mg²⁺] over [Ca²⁺] in seawater (seawater Mg/Ca or Mg/Ca_{sw}) has a significant effect on benthic foraminiferal Mg/Ca (Mewes et al., 2014; Segev & Erez, 2006) and thus needs to be corrected for when reconstructing seawater temperature from periods with a different Mg/Ca_{sw} than that of today (Billups & Schrag, 2002). Due to changes in the balance between rates of weathering, seafloor spreading and dolomite formation, Mg/Ca_{sw} changes over geological timescales (Bernier, 2004; Farkaš et al., 2007; Gothmann et al., 2015; Hardie, 1996; Holland & Zimmermann, 2000; Steuber & Veizer, 2002). Due to the relatively long residence times of Ca²⁺ and Mg²⁺ (~1 and ~13 Ma, respectively; Broecker et al., 1982), changes in this ratio are notable over timescales >1 Ma. For example, Mg/Ca_{sw} during the early Cretaceous was close to 1 (Farkaš et al., 2007; Hardie, 1996) and application of uncorrected Mg/Ca-T calibrations would thus greatly underestimate seawater temperatures at that time (e.g., Billups & Schrag, 2002; Evans & Müller, 2012; Hasiuk & Lohmann, 2010).

Table 1
Element Composition and Inorganic Carbon Chemistry of the Prepared Culture Media (Artificial Seawater or ASW)

Element	ASW1	ASW2	ASW3
Ca	9.31 (± 0.09)	8.88 (± 0.23)	9.39 (± 0.14)
Mg	31.9 (± 0.3)	56.7 (± 1.3)	80.1 (± 1.1)
Na	533 (± 4)	481 (± 12)	452 (± 6)
Sr	0.159 (± 0.001)	0.152 (± 0.003)	0.161 (± 0.003)
Mg/Ca (mol/mol)	3.43 (± 0.01)	6.40 (± 0.02)	8.55 (± 0.05)
Na/Ca (mol/mol)	57.3 (± 0.2)	54.2 (± 0.1)	48.1 (± 0.3)
Sr/Ca (mmol/mol)	17.1 (± 0.1)	17.1 (± 0.1)	17.1 (± 0.1)
Total Alkalinity	2170 (± 75)	2209 (± 76)	2122 (± 93)
pH	7.75 (± 0.051)	7.77 (± 0.090)	7.70 (± 0.054)

Note. All element concentrations are in mmol/kg seawater, standard deviations in parentheses ($n = 9$ for the element concentrations, $n = 4$ for the total alkalinity).

When applying Mg/Ca as a temperature proxy to foraminifera older than ~ 1 Ma, a correction factor based on reconstructed Mg/Ca_{sw} is often applied (e.g., Evans et al., 2015; Lear et al., 2000; Tripathi et al., 2005). This approach assumes that the sensitivity of the relation between foraminiferal Mg/Ca and seawater temperature is independent of seawater Mg/Ca, and thus remains constant. Although several studies have quantified the sensitivity of foraminiferal Mg/Ca as a function of both temperature (Lea et al., 1999; Nürnberg et al., 1996; Toyofuku et al., 2000) and Mg/Ca_{sw} (Raitzsch et al., 2010; Segev & Erez, 2006), the synergistic effects of those parameters remains to be investigated in benthic foraminifera. As for foraminiferal Mg/Ca, the isolated impact of both seawater Mg/Ca and temperature on incorporation of other elements (e.g., Na and Sr) have been identified (Dissard et al., 2010; Dueñas-Bohórquez, da Rocha, et al., 2011; Elderfield et al., 2000; Mewes, Langer, Reichart, et al., 2015; Raitzsch et al., 2010; Russell et al., 2004), their combined effects have not been quantified.

Here we present results from a culturing study using two benthic species with contrasting calcification mechanism: the hyaline (i.e., perforate) *Elphidium crispum*, precipitating calcite with a low Mg content (~ 5 mmol/mol; Allison et al., 2010, 2011) and the porcelaneous (i.e., miliolid) *Quinqueloculina* sp. (Mg/Ca = ~ 140 mmol/mol; Toyofuku et al., 2000). In planktonic and some benthic low-Mg species, Mg incorporation increases exponentially with temperature (e.g., Nürnberg, 2015; Nürnberg et al., 1996), whereas it increases linearly with temperature in porcelaneous foraminifera (Toyofuku et al., 2000; Wit et al., 2012). The difference in absolute Mg content between members of these two groups is a consequence of the different biomineralization strategies between hyaline and porcelaneous foraminifera (Bentov & Erez, 2006; Debenay et al., 1998; Erez, 2003; De Nooijer et al., 2009; De Nooijer, Spero, et al., 2014). In our culturing experiment, seawater temperature and Mg/Ca_{sw} were varied independently to quantify the effect of these two parameters combined as well as decoupled. Newly formed calcite was also analyzed for Na/Ca and Sr/Ca to quantify the impact of both temperature and Mg/Ca_{sw} on incorporation of these elements.

2. Methods

2.1. Culture Set-Up and Media Preparation

Culturing experiments were conducted at the Japan Agency for Marine-Earth Sciences and Technology (JAMSTEC), Japan. Different species of shallow benthic foraminifera were collected from Morito-kaigan rocky shore (35.2660° N, 139.5708° E), Hayama, Miura peninsula, Kanagawa, Japan in October 2012. Upon return in the laboratory, specimens of *Elphidium crispum* and *Quinqueloculina* sp. were isolated from sieved sediment ($> 125 \mu\text{m}$). To monitor chamber addition, single specimens were photographed at 50x magnification using a Zeiss Stemi 2000-C microscope with an Axiocam ERc 5s camera (Zeiss, Germany). After photographing, 10 single specimens per condition were placed in 20 ml vials with screw caps to avoid evaporation and minimize changes in salinity and carbonate chemistry. Vials were filled with either one of three different media (Table 1) and placed for 100 days in incubators at four different temperatures (10, 17, 22 and 27°C, measured hourly with a maximum SD of 0.3°C). This resulted in specimens cultured at twelve different conditions. Media were replaced every two weeks, after which the foraminifera were fed with the green algae *Chlorella*, cultured in natural seawater (NSW). To avoid contamination of seawater with NSW Mg/Ca ratio

(~5.2 mol/mol) when adding the algae cells to the culture vials, the *Chlorella* cells were centrifuged for 5 minutes at 3000 rpm and dissolved in the three culture media (Table 1) at 17°C. The incubated foraminifera were subjected to a 12h:12h day-night cycle with an average photon flux of 15 $\mu\text{mol}/\text{m}^2/\text{s}$. At four moments, evenly spaced during the experimental period, samples were collected from the reservoirs for determining inorganic carbon chemistry (Table 1). Assuming that each foraminifer produces 20 μg CaCO_3 during the experiment, it can be calculated that between moments when the culture media were replaced, the concentration of dissolved inorganic carbon (DIC) of the culture media could not have decreased by more than 1% due to calcification by the 10 incubated specimens. The effect of a 1% decrease in [DIC] is a <0.1% change in pH and $[\text{CO}_3^{2-}]$, of which the impact on Na-, Mg- and Sr-incorporation in foraminifera is insignificant (e.g., Van Dijk et al., 2017).

After termination of the culturing experiment on day 100, the foraminifera were photographed again. Specimens were then rinsed three times with ultrapure water (18.2 M Ω), once with 5% NaOCl for 15 minutes and again three times with ultrapure water to remove any remaining salts and organic matter at the shell surface. Prior to geochemical analysis, specimens were dried overnight at 45°C.

Artificial seawater (ASW) was prepared by mixing salts (KANTO Chemicals Co. Inc., Japan) according to Kester et al. (1967) corresponding to the average chemical composition of seawater. Gravimetric salts and volumetric salts (excluding $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) were dissolved in 2.00 and 1.00 kg, respectively, of ultrapure water before combining with the other salts to avoid precipitation of CaCO_3 , CaSO_4 , SrCO_3 or SrSO_4 . Seawater Mg/Ca was altered by changing the amount of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, resulting in ASW with different $[\text{Mg}^{2+}]$. The reduction in [Cl] was compensated by addition of NaCl. Undiluted seawater element composition was determined by ICP-MS (X-series, Thermo Fisher). Analytical precision was 0.4% for Mg/Ca and Na/Ca and 0.5% for Sr/Ca. Seawater Mg/Ca ratios produced were 3.43, 6.40 and 8.55 (± 0.05) mol/mol (Table 1), of which the middle treatment was slightly higher than intended (which was supposed to be 5.2 mol/mol). Salinities of the culture media were determined using a VWR CO310 salinometer at the beginning and end of the experiments and ranged from 35.0 to 35.3.

2.2. Calcite Element Analyses

Element composition of the newly formed calcite (expressed as $\text{Na}/\text{Ca}_{\text{cc}}$, $\text{Mg}/\text{Ca}_{\text{cc}}$ and $\text{Sr}/\text{Ca}_{\text{cc}}$) was determined by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) at Utrecht University (Reichert et al., 2003). This system consists of a Lambda Physik Excimer laser system with GeoLas 200Q optics. Ablation was performed in a helium atmosphere at a pulse repetition of 6 Hz, energy density of ~ 1 J/cm^2 and a spot diameter of 40 (for *E. crispum*) or 60 μm (for *Quinqueloculina* sp.) until the shell wall was completely penetrated, usually lasting 30–50 seconds. Ablated particles were measured using a sector field ICP-MS (Element2, Thermo Fisher). Scanned masses included ^{23}Na , ^{24}Mg , ^{26}Mg , ^{27}Al , ^{43}Ca , ^{44}Ca , ^{55}Mn and ^{88}Sr . Calibration and standardization was done using a NIST SRM 610 glass (values from Jochum et al., 2012) that was ablated using a higher laser fluency of ~ 5 J/cm^2 . Using a different energy density between foraminiferal calcite and glass standard has been shown to not affect the analyses (Dueñas-Bohórquez et al., 2009). An in-house calcite standard (Raitzsch et al., 2010) and the glass standard NIST SRM 612 were used to correct for drift by applying a linear fit through all analyzed glass standards. Analytical precision (relative standard deviation, or RSD, of measurements on an in-house calcite standard) was 3% for Na, 5% for ^{24}Mg and 2% for ^{88}Sr , which are similar to those reported previously using this procedure (Dueñas-Bohórquez, da Rocha, et al., 2011; Dueñas-Bohórquez et al., 2009; Dueñas-Bohórquez, Raitzsch, et al., 2011; Mewes, Langer, Reichart, et al., 2015; Raitzsch et al., 2010). The obtained time resolved counts were blank subtracted, internally standardized to ^{43}Ca and calibrated using data reduction software (GLITTER) to obtain depth profiles and calculate the single chamber $\text{Na}/\text{Ca}_{\text{cc}}$, $\text{Mg}/\text{Ca}_{\text{cc}}$ and $\text{Sr}/\text{Ca}_{\text{cc}}$.

In total 84 chambers were analyzed, 37 for *Quinqueloculina* sp., divided over 20 specimens, and 47 for *E. crispum*, distributed over 36 specimens. Half of the *Quinqueloculina* specimens were ablated once; the other ten specimens were ablated twice ($n = 6$), three times ($n = 3$) or four times ($n = 1$). Ten specimens of *E. crispum* were ablated twice, the other 26 were ablated once. In total, 2 measurements for *Quinqueloculina* sp. were discarded due to short ablation profiles and consequently, elevated element concentrations. The remaining 82 single laser spot measurements used for calculating average element concentrations were relatively evenly dispersed over the 12 experimental conditions (Supplementary Information, Tables 1 and 3). We calculated the standard deviation (SD) and relative standard deviation (RSD) per condition. The

Table 2
Total Number of Chambers Added During the Culturing Period (100 days) by the Two Species Across the 12 Experimental Conditions

	Mg/Ca _{sw} = 3.5 mol/mol	Mg/Ca _{sw} = 6.4 mol/mol	Mg/Ca _{sw} = 8.5 mol/mol	Total
<i>Quinqueloculina</i> sp.				
T=10 °C	1 (2): # spec (# chambers)	3 (6)	1 (1)	5 (9)
T=17 °C	3 (8)	2 (5)	1 (2)	6 (15)
T=22 °C	2 (4)	1 (1)	1 (1)	4 (6)
T=27 °C	1 (2)	2 (2)	2 (3)	5 (7)
Total	7 (16)	8 (14)	5 (7)	20 (37)
<i>Elphidium crispum</i>				
T=10 °C	1 (1)	2 (3)	0	3 (4)
T=17 °C	7 (8)	3 (4)	6 (7)	16 (19)
T=22 °C	4 (7)	8 (9)	4 (6)	16 (22)
T=27 °C	1 (2)	0	0	1 (2)
Total	13 (18)	13 (16)	10 (13)	36 (47)

partitioning coefficient (D) of an element (E) between seawater and foraminiferal calcite is expressed as $D_E = (E/Ca_{cc})/(E/Ca_{sw})$.

3. Results

3.1. Chamber Addition

For the porcelaneous species, growth was highest at the seawater with the lowest [Mg²⁺] and decreased with increasing Mg/Ca_{sw} (Table 2). At lowest Mg/Ca_{sw}, 16 new chambers were produced during 100 days. At intermediate and high Mg/Ca_{sw}, 14 and 7 new chambers were produced, respectively. Temperature did not have a clear impact on chamber addition rates: at 10 °C, 9 new chambers were formed, which was similar to the number of chambers formed at 27 °C (7; Table 2). For *E. crispum*, chamber addition decreased slightly with increasing Mg/Ca_{sw}. During the experiment, 18 new chambers were produced at lowest Mg/Ca_{sw}, whereas at intermediate and high Mg/Ca_{sw}, 16 and 13 new chambers were formed during 100 days of incubation, respectively (Table 2).

3.2. Foraminiferal Mg/Ca

Obtained Mg/Ca_{cc} increased with temperature and Mg/Ca_{sw} in both species (Table 3). In *Quinqueloculina* sp., Mg/Ca_{cc} increased linearly with temperature and was approximately 30 times higher than in *E. crispum*, for which the Mg/Ca_{cc} increases exponentially with temperature. Combining all Mg/Ca_{cc} from one

Table 3
Average Element to Calcium Ratio and Partition Coefficient per Condition of *Quinqueloculina* sp. and *E. crispum*

ASW	T (°C)	n	Mg/Ca mmol/mol	D _{Mg} (*10 ⁻³)	Na/Ca mmol/mol	D _{Na} (*10 ⁻³)	Sr/Ca mmol/mol	D _{Sr}
<i>Quinqueloculina</i> sp. (n=35)								
1	10	2	120.1 ± 2.1	35.0 ± 0.6	3.8 ± 2.9	0.03 ± 0.05	3.4 ± 1.0	0.16 ± 0.06
1	17	8	130.5 ± 4.1	38.3 ± 1.3	4.8 ± 0.5	0.08 ± 0.01	2.9 ± 0.1	0.17 ± 0.01
1	22	4	133.9 ± 7.1	39.3 ± 2.3	4.8 ± 0.9	0.08 ± 0.02	3.3 ± 0.6	0.19 ± 0.04
1	27	2	142.5 ± 1.1	41.9 ± 0.4	5.5 ± 0.2	0.10 ± 0.00	3.0 ± 0.2	0.18 ± 0.01
2	10	6	132.0 ± 4.1	20.6 ± 0.6	6.5 ± 2.0	0.12 ± 0.04	3.0 ± 0.1	0.17 ± 0.01
2	17	5	138.3 ± 3.1	21.6 ± 0.5	3.8 ± 0.9	0.07 ± 0.02	3.3 ± 0.8	0.19 ± 0.05
2	22	1	139.8	21.80	5.3	0.10	3.5	0.21
2	27	2	147.2 ± 1.1	23.0 ± 0.2	5.6 ± 0.04	0.10 ± 0.01	3.1 ± 0.1	0.18 ± 0.005
3	10	1	138.4	16.30	6.4	0.13	3.7	0.22
3	17	2	142.8 ± 0.1	16.8 ± 0.1	6.4 ± 0.4	0.14 ± 0.01	3.8 ± 0.9	0.22 ± 0.05
3	22	1	153.3	18.00	5.1	0.11	3.0	0.17
3	27	3	154.4 ± 3.1	18.2 ± 0.4	4.9 ± 1.7	0.10 ± 0.03	3.1 ± 0.4	0.18 ± 0.02
<i>Elphidium crispum</i> (n=47)								
1	10	1	2.19	0.64	4.3	0.08	2.30	0.13
1	17	8	3.03 ± 0.86	0.89 ± 0.25	6.9 ± 1.7	0.12 ± 0.03	2.6 ± 0.2	0.15 ± 0.01
1	22	7	4.06 ± 0.63	1.19 ± 0.19	7.8 ± 1.6	0.14 ± 0.03	2.0 ± 0.4	0.12 ± 0.02
1	27	2	4.81 ± 0.05	1.42 ± 0.01	8.4 ± 0.2	0.15 ± 0.00	2.3 ± 0.7	0.14 ± 0.04
2	10	3	3.28 ± 1.16	0.51 ± 0.18	7.9 ± 0.8	0.15 ± 0.01	1.5 ± 0.1	0.08 ± 0.01
2	17	4	4.71 ± 0.87	0.74 ± 0.14	8.8 ± 1.8	0.16 ± 0.03	2.7 ± 0.5	0.16 ± 0.03
2	22	9	6.21 ± 1.30	0.97 ± 0.20	6.7 ± 1.8	0.12 ± 0.03	2.6 ± 0.5	0.15 ± 0.03
2	27	0	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
3	10	0	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
3	17	7	8.29 ± 1.59	0.97 ± 0.19	6.1 ± 1.4	0.13 ± 0.03	2.4 ± 0.4	0.14 ± 0.02
3	22	6	9.27 ± 2.38	1.09 ± 0.28	8.0 ± 2.2	0.17 ± 0.05	2.5 ± 0.3	0.15 ± 0.02
3	27	0	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.

Note. Standard deviations in parentheses, n.m. = not measured. All single-chamber element/Ca ratios are listed in the supporting information Tables S1 and S2.

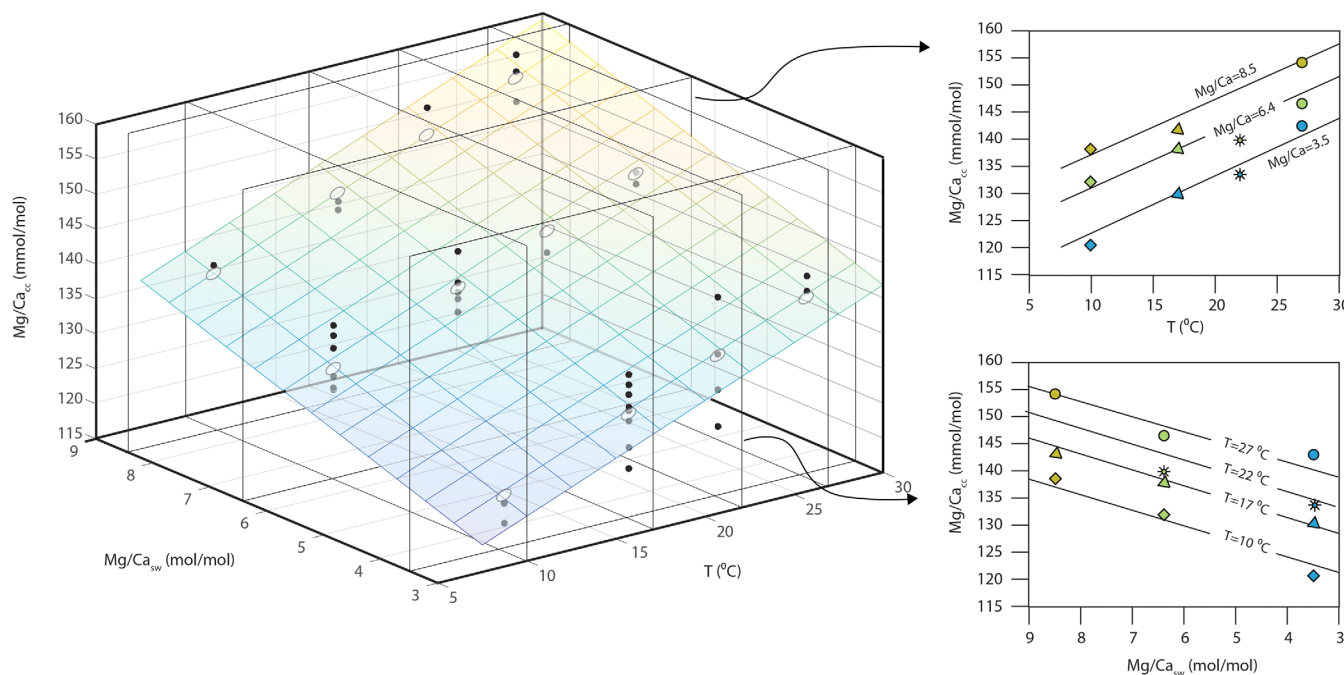


Figure 1. Measured $\text{Mg}/\text{Ca}_{\text{cc}}$ (mmol/mol) for *Quinqueloculina* sp. as a function of $\text{Mg}/\text{Ca}_{\text{sw}}$ (mol/mol) and temperature ($^{\circ}\text{C}$). The 3-D regression plane is described by equation (1), with two vertical planes (at $\text{Mg}/\text{Ca}_{\text{sw}} = 6$ mol/mol and temperature = 17.5 $^{\circ}\text{C}$) showing the response of $\text{Mg}/\text{Ca}_{\text{cc}}$ as a sole function of temperature (upper right panel) and $\text{Mg}/\text{Ca}_{\text{sw}}$ (lower right panel). Symbols in right panels represent the different temperatures: 10 $^{\circ}\text{C}$ (\diamond), 17 $^{\circ}\text{C}$ (Δ), 22 $^{\circ}\text{C}$ ($*$) and 27 $^{\circ}\text{C}$ (\circ).

condition, the average relative standard deviations are 20.5 and 2.40% for *E. crispum* and *Quinqueloculina* sp., respectively.

A multiple linear regression analysis for the $\text{Mg}/\text{Ca}_{\text{cc}}$ of *Quinqueloculina* sp. as a function of both temperature and $\text{Mg}/\text{Ca}_{\text{sw}}$ (Figure 1) shows that the $\text{Mg}/\text{Ca}_{\text{cc}}$ of this species is best described by:

$$\text{Mg}/\text{Ca}_{\text{Quinqueloculina}} = 1.02(\pm 0.11) * T + 2.87(\pm 0.34) * \text{Mg}/\text{Ca}_{\text{sw}} + 102.6(\pm 2.8) \quad (1)$$

The reported uncertainties associated with this multiple regression (equation (1)) represent Standard Errors (SE), which are calculated using the least sum of squares. R^2 value for this regression analysis is 0.82, $p < 0.001$ ($n = 37$). A linear regression model is chosen since this provides the highest correlation coefficient when relating $\text{Mg}/\text{Ca}_{\text{cc}}$ to $\text{Mg}/\text{Ca}_{\text{sw}}$.

For *E. crispum*, the multiple regression (Figure 2) results in the equation:

$$\text{Mg}/\text{Ca}_{\text{Elphidium}} = 10^{(0.0729 (\pm 0.054) * T - 1.54(\pm 1.41))} + 0.831(\pm 0.98) * \text{Mg}/\text{Ca}_{\text{sw}} \quad (2)$$

The reported uncertainties associated with this multiple regression (equation (2)) represent the SE for the three constants of equation (2), which are based on the least sum of squares. R^2 value for this regression analysis is 0.67, $p < 0.001$ ($n = 47$). Contrary to the regression model for *Quinqueloculina* sp. (Figure 1), an exponential regression was chosen for the $\text{Mg}/\text{Ca}_{\text{cc}}$ in *E. crispum* as a function of temperature since this describes the relation between these two parameters best for low-Mg, hyaline species (e.g., Anand et al., 2003; Toyofuku et al., 2011). The relation between $\text{Mg}/\text{Ca}_{\text{cc}}$ of low-Mg foraminiferal calcite and $\text{Mg}/\text{Ca}_{\text{sw}}$ is assumed to be linear, as this explains the increase in $\text{Mg}/\text{Ca}_{\text{cc}}$ similarly as does a power function in low- and intermediate benthic species (Mewes et al., 2014; Raitzsch et al., 2010).

3.3. Foraminiferal Na/Ca and Sr/Ca

For *E. crispum*, average $\text{Na}/\text{Ca}_{\text{cc}}$ was 7.3 mmol/mol (± 1.8 SD) and 5.9 mmol/mol (± 3.7 SD) for *Quinqueloculina* sp. For both investigated species, these values did not vary significantly with $\text{Mg}/\text{Ca}_{\text{sw}}$ and were not correlated to temperature (Figure 3). Since $[\text{Na}^+]$ varied between conditions due to the addition of NaCl (Table 1; from 57 to 48 mol Na/mol Ca), the foraminiferal sodium content is expressed as the partition coefficient (D_{Na}), equaling $(\text{Na}/\text{Ca}_{\text{cc}})/(\text{Na}/\text{Ca}_{\text{sw}})$.

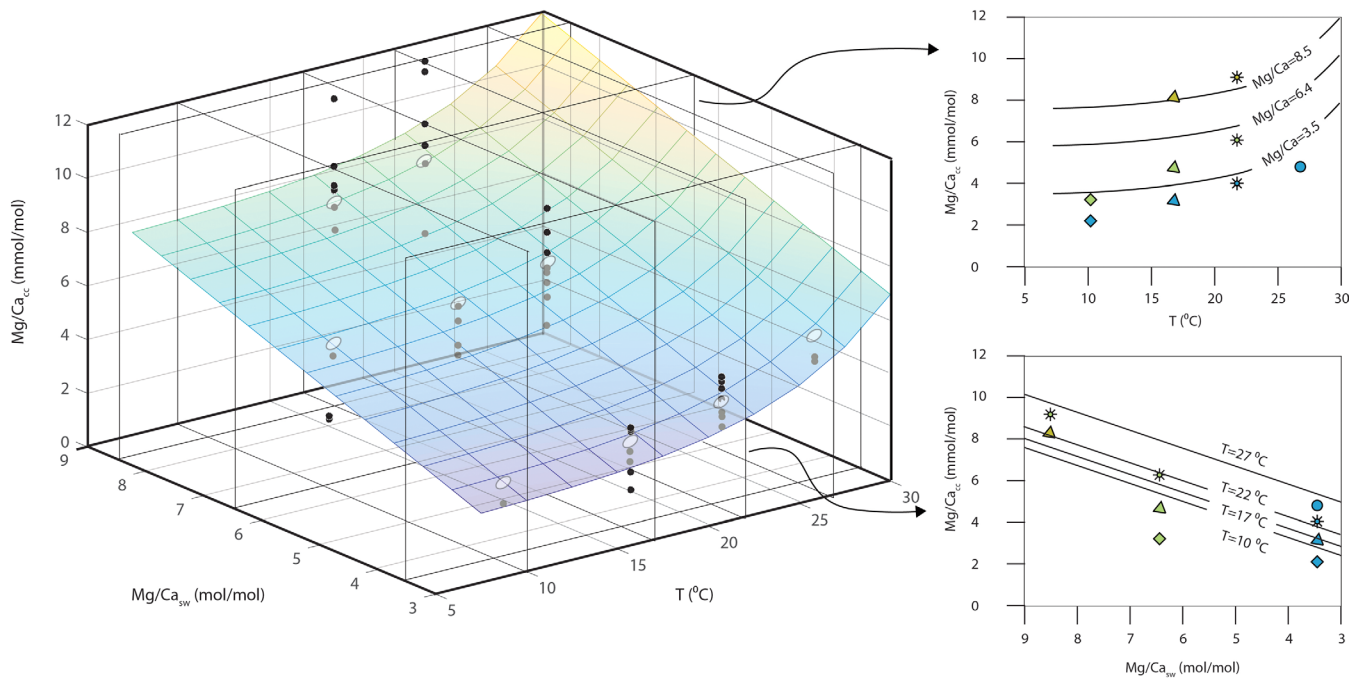


Figure 2. Measured Mg/Ca_{cc} (mmol/mol) for *E. crispum* as a function of Mg/Ca_{sw} (mol/mol) and temperature (°C). The 3-D regression plane is described by equation (2), with two vertical planes (at Mg/Ca_{sw} = 6 mol/mol and temperature = 17.5 °C) showing the response of Mg/Ca_{cc} as a sole function of temperature (top right) and Mg/Ca_{sw} (bottom right). Symbols in right panels represent the different temperatures: 10 °C (◇), 17 °C (△), 22 °C (*) and 27 °C (○).

Sr/Ca_{cc} were slightly higher in *Quinqueloculina* sp., 3.4 mmol/mol (±1.6 SD), than in *E. crispum*, 2.4 mmol/mol (±0.46 SD) and these values did not vary significantly with temperature or Mg/Ca_{sw} for either species (Figure 4). This is contrasting with findings of Mewes, Langer, Thoms, et al. (2015), who reported a linear increase in Sr/Ca_{cc} with increasing Mg/Ca_{cc}. In *Quinqueloculina* sp., incorporation of Sr was approximately 1.5 times higher than in *E. crispum*.

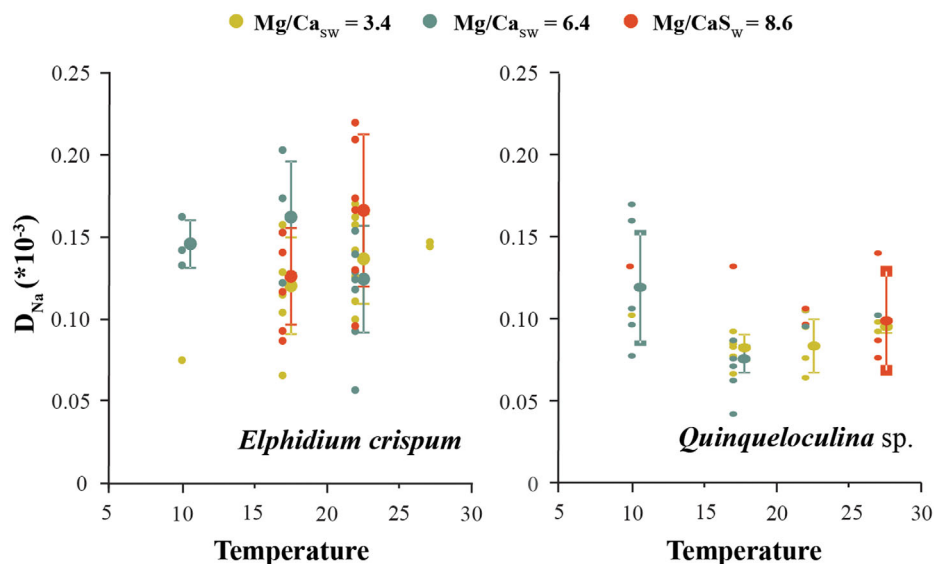


Figure 3. Partition coefficient of Na (D_{Na}) in *E. crispum* (left) and *Quinqueloculina* sp. (right) versus seawater temperature. Different seawater Mg/Ca are indicated by different colors. Small spots indicate single laser ablation measurements upon which averages and standard deviations (only calculated for $n > 2$) are superimposed. These averages and their standard deviations are slightly offset to the right for clarification.

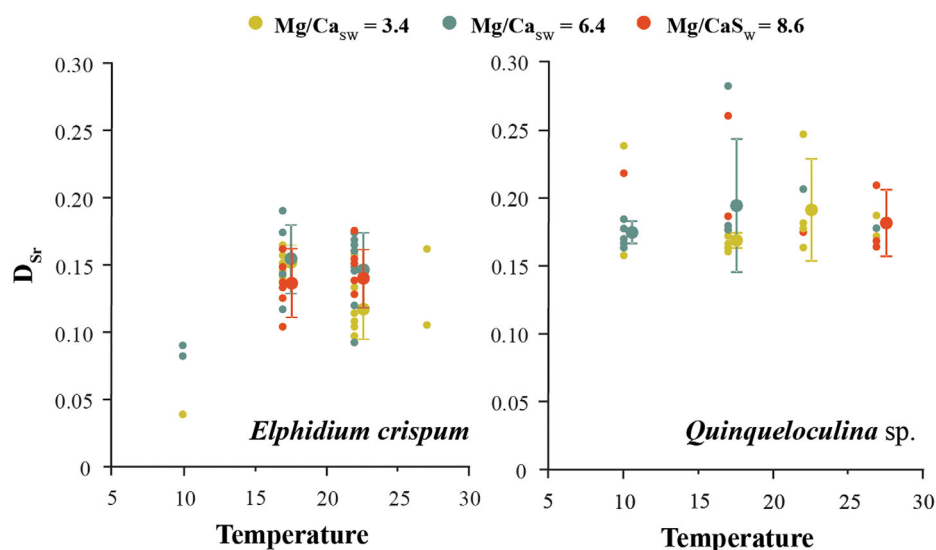


Figure 4. Partition coefficient of Sr (D_{Sr}) in *E. crispum* (left) and *Quinqueloculina* sp. (right) versus seawater temperature. Different seawater Mg/Ca are indicated by different colors. Small spots indicate single laser ablation measurements upon which averages and standard deviations (only calculated for $n > 2$) are superimposed. These averages and their standard deviations are slightly offset to the right for clarification.

4. Discussion

4.1. Chamber Addition

Chamber addition rates in *Quinqueloculina* sp. were highest at lowest Mg/Ca and vice versa. In *E. crispum*, this relation was less pronounced. Production of new calcite as a function of Mg/Ca_{sw} was also reported to increase at lower ratios in *Amphistegina lessonii* and *A. lobifera* by Segev and Erez (2006). Under experimental conditions, *Operculina ammonoides*, however, produced a variable amount of new chambers as a function of Mg/Ca_{sw}, with highest chamber addition rates at modern-day Mg/Ca_{sw} (Evans et al., 2015). Temperature did not have a clear impact on the total number of chamber added in our experiment, which may be contrary to Evans et al. (2015), reporting higher growth rates at higher temperatures. Differences between these experimental results may be caused by species-specific responses to temperature (e.g., Anand et al., 2003; Wit et al., 2012) or to the difference between field- and experimental conditions and the subsequent foraminiferal response to this transition at the start of the experimental incubation. Another difference is the presence of photosynthetic symbionts in *Operculina ammonoides* (Evans et al., 2015), whose activity may change with temperature and therefore influence calcification as a function of temperature.

Any differences in chamber addition between conditions did not affect the relation between Mg/Ca_{cc} and their sensitivity to either temperature or seawater Mg/Ca. The variability in Mg/Ca within specimens was only marginally higher than that between specimens that were grown under identical conditions. This is in line with an overall variability in benthic foraminiferal element composition that is not related to ontogeny or differences between specimens (De Nooijer, Hathorne, et al., 2014; Sadekov et al., 2008, 2009).

4.2. Magnesium in Foraminifera as a Function of Temperature and Seawater Mg/Ca

In our experiments, seawater Mg/Ca was altered by changing the $[Mg^{2+}]$. When comparing foraminiferal Mg/Ca from previous studies manipulating $[Mg^{2+}]$ and $[Ca^{2+}]$, it appears as if Mg incorporation depends primarily on the seawater Mg/Ca, rather than the concentration of any of the two ions (Segev & Erez, 2006; Mewes et al., 2014; Mewes, Langer, Thoms, et al., 2015, for species within the intermediate-Mg/Ca precipitating genus *Amphistegina*). In this discussion we assume that a similar dependence applies to the genera *Quinqueloculina* and *Elphidium*, although this will require future testing. This is particularly necessary for the former species, since porcelaneous species have their own biomineralization pathway (Debenay et al., 1996; De Nooijer et al., 2009; Hemleben et al., 1986) and the general difference in Mg/Ca between porcelaneous and hyaline foraminifera (Bentov & Erez, 2006) may be the result of differences in the mechanism by which

these groups take up Ca^{2+} from seawater into the site of calcification (De Nooijer, Spero, et al., 2014; Van Dijk et al., 2017).

The relation between Mg/Ca_{cc} of low-Mg foraminifera and seawater temperature is generally described by an exponential function (e.g., Anand et al., 2003; Lea et al., 1999; Nürnberg et al., 1996; Toyofuku et al., 2011; Wit et al., 2012). The sensitivity (exponential constant) for the calibrations of most of these published calibrations vary between 0.05 and 0.10. The sensitivity for the specimens of *E. crispum* grown at Mg/Ca_{sw} of 3.4 – 8.5 falls within this range (0.073; equation (2)). The relatively high R^2 value for this regression suggests that the linear relation between Mg/Ca_{cc} and Mg/Ca_{sw} in this species is independent of the temperature, although the relatively large scatter in the data indicates that additional experiments will have to constrain the here-presented sensitivities. Partition coefficients (D_{Mg}) calculated from the calcite Mg/Ca and seawater Mg/Ca , i.e., $(Mg/Ca_{cc})/(Mg/Ca_{sw})$, in *E. crispum* are between $0.51 \cdot 10^{-3}$ and $1.42 \cdot 10^{-3}$ (Table 3). The partition coefficient ($0.74 \cdot 10^{-3}$) from our experimental condition closest to published D_{Mg} ($T = 17^\circ C$ and $Mg/Ca_{sw} = 6.4$; Table 1) is slightly higher than those reported for *E. williamsoni* ($0.28-0.46 \cdot 10^{-3}$; Allison et al., 2010, 2011), but this may be related to species-specific offsets or differences in culturing conditions. The range of partition coefficients found here is similar to those found for other benthic, symbiont-barren intertidal foraminiferal species (e.g., $0.29 \cdot 10^{-3}$ for *Ammonia beccarii*; Toyofuku et al., 2011; $0.6-1.2 \cdot 10^{-3}$ for *Ammonia tepida*; De Nooijer, Hathorne, et al., 2014; $0.4-1.5 \cdot 10^{-3}$ for *Ammonia aomoriensis*; Mewes et al., 2014).

The Mg/Ca_{cc} in *E. crispum* may change linearly (rather than exponentially) to changes in temperature over the range studied here. When assuming a linear response in both dependencies (i.e., $Mg/Ca_{cc} = a \cdot T + b + c \cdot Mg/Ca_{sw}$; same as for the reported *Quinqueloculina* regression; equation (1)), the resulting R^2 values are similar (0.73, p-value <0.05; Table 4). The associated standard errors for the linear equation are also similar as those of the exponential regression (equation (2)). Testing the power of different regression models in explaining the observed variability in both the Mg/Ca_{sw} as temperature dimension (Table 4), shows that the evident regression models all fit the data relatively well. Assuming an exponential response of Mg/Ca_{cc} in *E. crispum* results in slightly better fit of the regression model to the data, whereas a linear versus exponential response to changes in temperature result in a similar fit (Table 4). The linear response model, however, predicts a significant incorporation of Mg at a Mg/Ca_{sw} of 0, whereas the exponential model predicts an Mg/Ca_{cc} close to 0 at a Mg/Ca_{sw} of 0. This means that either the exponential response (equation (2)) approximates Mg-incorporation in *E. crispum* relatively well over the Mg/Ca_{sw} interval from 0 to 8.5 or that Mg/Ca_{cc} increases linearly for this species over the Mg/Ca_{sw} interval studied here and that it responds differently at lower Mg/Ca_{sw} . Evans et al. (2016) suggested that the combined effects of temperature and seawater Mg/Ca on Mg-incorporation in cultured *Globigerinoides ruber* is best described by: $Mg/Ca_{cc} = (a \cdot (Mg/Ca_{sw})^2 + b \cdot Mg/Ca_{sw} + c) \cdot 10^{(d \cdot (Mg/Ca_{sw})^2 + e \cdot Mg/Ca_{sw}) \cdot T}$. Using this regression model to explain our data, the obtained fit (R^2) is slightly higher (0.77) than those of the other regression models. However, with the similarity in fits

Table 4
Estimate of the Constants in Four Regression Models for Mg/Ca_{cc} of Elphidium and Quinqueloculina as a Function of Mg/Ca_{sw} and Temperature

Regression model ($Mg/Ca_{cc} =$)	Estimated values for the constants (SE in parentheses)				R^2	F	p
	a	b	c	d			
<i>Elphidium</i>							
$aT + b + cMg/Ca_{sw}$	0.226 (0.051)	-4.45 (1.2)	0.978 (0.097)		0.73	59	<0.05
$10^{(aT + b)} + cMg/Ca_{sw}$	0.073 (0.054)	-1.54 (1.4)	0.830 (0.097)		0.67	241	<0.05
$aT + b + 10^{(cMg/Ca_{sw} + d)}$	0.211 (0.048)	-1.60 (1.5)	0.154 (0.058)	-0.510 (0.56)	0.77	48	<0.05
$10^{(aT + b)} + 10^{(cMg/Ca_{sw} + d)}$	0.032 (0.013)	-0.193 (0.38)	0.177 (0.059)	-0.723 (0.55)	0.76	252	<0.05
$(aMg/Ca_{sw})^2 + bMg/Ca_{sw} + cT + d$	0.424 (0.076)	-1.11 (0.75)	0.211 (0.048)	1.12 (2.3)	0.77	48	<0.05
<i>Quinqueloculina</i>							
$aT + b + cMg/Ca_{sw}$	1.02 (0.11)	102 (2.80)	2.87 (0.34)		0.82	79	<0.05
$10^{(aT + b)} + cMg/Ca_{sw}$	0.0037(0.0004)	2.02 (0.011)	2.85 (0.34)		0.82	<<	<0.05
$aT + b + 10^{(cMg/Ca_{sw} + d)}$	1.01 (0.12)	59 (212)	0.021 (0.073)	1.66 (1.9)	0.82	51	<0.05
$10^{(aT + b)} + 10^{(cMg/Ca_{sw} + d)}$	0.0065 (0.014)	1.71 (1.2)	0.0176(0.039)	1.74 (1.2)	0.82	<<	<0.05
$(aMg/Ca_{sw})^2 + bMg/Ca_{sw} + cT + d$	0.264 (0.47)	2.08 (2.9)	1.01 (0.12)	105 (8.3)	0.82	51	<0.05

between the applied regression models, it is unlikely that there is a strong interaction between seawater Mg/Ca and temperature on Mg/Ca_{cc} of *E. crispum*, at least not over the ranges studied here.

4.3. Partition Coefficients for Mg

Calculated partition coefficients for Mg in *Quinqueloculina* sp. are in the range of 0.015 and 0.045, increasing significantly with decreasing Mg/Ca_{sw}. These coefficients are similar to those of previously analyzed porcelaneous foraminifera (Maeda et al., 2017; Raja et al., 2005; Sadekov et al., 2014; Toyofuku et al., 2000). In species in which magnesium is incorporated at high concentrations (>100 mmol/mol Ca), Mg/Ca_{cc} increases linearly with temperature with a sensitivity of 1.6–2.9 mmol/mol Mg/Ca increase for every degree of temperature increase (Maeda et al., 2017; Toyofuku et al., 2000; Toyofuku & Kitazato, 2005). This is slightly higher than the sensitivity obtained here (~1.0 mmol/mol increase in Mg/Ca for every degree of temperature increase; equation (1)), which may be explained by species-specific biomineralization differences or offsets in culturing conditions (i.e., as a result of the combined impacts of differences in irradiance, seawater Mg/Ca, carbonate chemistry etc.). The difference between studies may also be caused by different methods employed to determine the Mg/Ca. Whereas dissolution of multiple tests involves cleaning of the calcium carbonate (Barker et al., 2003), our study determined Mg/Ca by laser ablation-ICP-MS. The former may affect the Mg/Ca in case part of the Mg in foraminiferal shell walls is associated to the organic matrix (and thus removed during cleaning), while the latter method commonly focusses on removal of Mg (and other elements) associated to surface contamination.

A number of previous culture studies suggested that both temperature (see above) and Mg/Ca_{sw} (e.g., Maeda et al., 2017; Mewes et al., 2014; Mewes, Langer, Thoms, et al., 2015) have a linear impact on Mg/Ca_{cc} in high-Mg precipitating foraminifera. However, studies by Segev and Erez (2006) and Evans et al. (2015, 2016) suggested that the impact of Mg/Ca_{sw} on Mg-incorporation is not linear. This may be related to the differences in biomineralization strategies and contrasting absolute Mg/Ca between hyaline and porcelaneous species. Secondly, absence (our study) and presence (Evans et al., 2015; Segev & Erez, 2006) may also explain (part of) the observed difference in sensitivity of Mg incorporation as a function of temperature and Mg/Ca_{sw}. As for the multiple regression analyses using the Mg/Ca of *E. crispum*, the fit of the regression model does not improve for *Quinqueloculina* sp. when forcing an exponential or cubic fit along the Mg/Ca_{cc}-T axis (Table 4). Based on the fit (i.e., least sum of squares) of the applied regression models, the exponential constant for the temperature sensitivity on Mg-incorporation does not contribute considerably in improving the multiple linear regression (equation (1)). For any of the investigated response models (Table 4), the regression does not pass through Mg/Ca_{cc} = 0 at Mg/Ca_{sw} = 0. This indicates that the regressions reported here are only applicable to the ranges of seawater Mg/Ca studied here: at Mg/Ca_{sw} lower than 3.4, Mg/Ca_{cc} of *Quinqueloculina* sp. may well decrease exponentially toward 0 (see Mewes, Langer, Thoms, et al., 2015, for a similar discussion on Mg-incorporation at low Mg/Ca_{sw} in *Heterostegina depressa*).

4.4. Inter-Species Differences in Mg-Incorporation

Across the temperature range studied here, the increase in Mg/Ca_{cc} for every 1 mol/mol increase in Mg/Ca_{sw} is 0.83 and 2.9 mmol/mol for *E. crispum* and *Quinqueloculina* sp., respectively (Figures 1 and 2; equations (1) and (2)). These sensitivities are comparable to the relative increase in Mg/Ca_{cc} with changing Mg/Ca_{sw} in *Amphistegina lobifera* and *A. lessonii* (Segev & Erez, 2006) and *Heterostegina depressa* (Raitzsch et al., 2010). The difference in absolute Mg/Ca between the two species studied here is likely related to the difference in calcification strategy between these groups (De Nooijer et al., 2009; Hemleben et al., 1986) and more specifically, the way these groups concentrate Ca²⁺ and the co-transport of other ions (Nehrke et al., 2013).

Partitioning of magnesium during calcification in porcelaneous species is similar to inorganic CaCO₃ precipitation from seawater (resulting in ~100 mmol Mg/mol Ca; Mucci & Morse, 1983; Mucci, 1987; Morse et al., 2007). In addition, partition coefficients for *Quinqueloculina* sp. increase at lower Mg/Ca_{sw} similarly as they do in inorganically precipitated calcites (Mucci & Morse, 1983). The actual biomineralization involves vacuolization of seawater and subsequent precipitation of calcite within vesicles without (major) compositional modification (Ter Kuile et al., 1989). In some porcelaneous species, the Mg/Ca is described to surpass the inorganic partitioning (e.g., Evans et al., 2015), which challenges the 'inorganic-like' precipitation mode for these foraminifera. Calcite precipitation in porcelaneous species may differ from that in many inorganic precipitation experiments by involvement of an amorphous pre-cursor (e.g., Weiner et al., 2003) and hence a

different element partitioning than in the step-wise crystal growth generally characterizing inorganic calcite precipitation (Davis et al., 2004; De Yoreo et al., 2015). Coccolithophores also precipitate their calcite within vesicles (e.g., Young & Henriksen, 2003), but are thought to transport calcium- and carbonate-ions to these vesicles by transmembrane transport (e.g., Brownlee et al., 2015), resulting in relatively pure calcite. Low-Mg calcite producing (planktonic) foraminifera are hypothesized to produce their calcite by a mixture of these two processes (Nehrke et al., 2013). This mixture of processes (involvement of seawater and transmembrane Ca-transport) may be responsible for 1) the general intermediate Mg/Ca of many foraminiferal species, 2) the alternation of high- and low-Mg bands in many foraminifera and 3) the differences in the sensitivity of Mg-incorporation as a function of Mg/Ca_{sw} (Figures 1 and 2).

4.5. Sr and Na Incorporation in Hyaline and Porcelaneous Foraminifera

The obtained D_{Na}'s are similar for both species and are not related to temperature, nor to Mg/Ca_{sw} (Figure 4). The ratios are in the same range as those reported for cultured specimens of the benthic *Ammonia tepida* (Wit et al., 2013), the planktonic *G. ruber*, *G. sacculifer* and *O. universa* cultured at a similar salinity (Allen et al., 2016; Delaney et al., 1985) and *G. ruber* and *G. sacculifer* collected from the Red Sea (Mezger et al., 2016). The relatively high variability in Na/Ca_{cc} (RSD's of 25% for *E. crispum* and 63% for *Quinqueloculina* sp.; Figure 3) may be caused by cleaning the specimens with NaOCl, even though specimens were thoroughly rinsed with ultrapure water after the organic removal step. Previous studies reported considerable inter- and intra-specimen variability (expressed as relative standard deviation) in Na/Ca_{cc}: 5–11% for *A. tepida* (Wit et al., 2013), 8–17% and 4–14% for Red Sea *G. ruber* and *G. sacculifer*, respectively (Mezger et al., 2016) and 6% and 7% for cultured *G. ruber* and *G. sacculifer* (Allen et al., 2016). As shown for foraminiferal Mg/Ca and Sr/Ca (e.g., De Nooijer, Hathorne, et al., 2014), part of the variability in Na/Ca_{cc} may not be attributable to variability in the (culturing) conditions, but may well be caused by (a yet unidentified) process during biomineralization (De Nooijer, Spero, et al., 2014). For application as a salinity reconstruction tool, this variability needs to be accounted for by determining Na/Ca_{cc} on a sufficient number of specimens (e.g., Sadekov et al., 2008).

Previously reported Sr/Ca for most foraminiferal species are lower than those reported here, ranging from 1.3 to 1.5 in field collected planktonic species (e.g., Friedrich et al., 2012) and from 0.80 to 1.0 in core-top derived specimens of the benthic *Oridorsalis umbonatus* (Dawber & Tripathi, 2012). These differences can be explained by the relatively high [Sr²⁺] in our culture media. When expressing the Sr/Ca as partition coefficient (D_{Sr}), the incorporated Sr is relatively similar across species (Figure 4). Similar D_{Sr} were also found in cultured specimens of *Elphidium williamsoni* (0.13–0.16; Allison et al., 2011), *Ammonia* spp. (0.17; Dueñas-Bohórquez, da Rocha, et al., 2011; Diz et al., 2012; De Nooijer, Hathorne, et al., 2014) and the planktonic *Globigerinoides sacculifer* (0.15; Dueñas-Bohórquez et al., 2009; Dueñas-Bohórquez, da Rocha, et al., 2011). Comparable to the D_{Sr} reported here for *Quinqueloculina* sp. (0.19), Sr partitioning in the high-Mg secreting porcelaneous species *Marginopora vertebralis* and *Amphisorus hemprichii* cultured at similar conditions 0.14–0.21 (Raja et al., 2005).

The impact of Mg/Ca_{sw} on incorporation of elements other than Mg in the species studied here is negligible (Figures 3 and 4). This means that past changes in Mg/Ca_{sw} do not necessarily affect calibrations for other elements (e.g., Na/Ca_{cc} as a function of salinity; Wit et al., 2013 or Sr/Ca_{cc} as a function of Sr/Ca_{sw}; Elderfield et al., 2000; Raitzsch et al., 2010; Dueñas-Bohórquez, da Rocha, et al., 2011). Part of the apparent absence of this impact may also be due to the relatively large variability in single-chamber element/Ca composition (Figures 1 and 2; De Nooijer et al., Hathorne, et al., 2014). The apparent absence of an impact of Mg/Ca_{sw} on incorporation of elements other than Mg only holds true, of course, if past changes in Mg/Ca_{sw} are caused by changes in past [Mg²⁺]_{sw}. Seawater temperature has no significant impact on Na- and Sr-incorporation over the ranges studied here, which is in line with previous studies on Sr incorporation in foraminiferal calcite (e.g., Dissard et al., 2010; Russell et al., 2004). In inorganically grown calcium carbonates, the incorporation of Sr²⁺ is found to be positively influenced by Mg²⁺-incorporation (Mucci and Morse, 1983), which may help explaining the inter-species differences in Sr/Ca (Van Dijk et al., 2017).

4.6. Paleooceanographic Implications

When using foraminiferal calcite for paleooceanographic reconstructions past ~1 Myr ago, deviations in Mg/Ca_{sw} from current day ratios need to be accounted for. Existing models and paleoreconstructions for past changes in Mg/Ca_{sw} show that in the Miocene, for example, ratios were 3–4 mol/mol (Coggon et al., 2010;

Farkaš et al., 2007; Hardie, 1996; Horita et al., 2002; Stanley & Hardie, 1998) and could have been as low as 1–2 mol/mol in the Paleocene (Berner, 2004; Stanley & Hardie, 1998). Using fossil foraminiferal Mg/Ca_{cc} for paleotemperature estimates from these periods thus requires application of a correction factor. Using two species with contrasting Mg/Ca_{cc} may provide the opportunity to circumvent the use of a correction factor based on modeled Mg/Ca_{sw} using their respective calibrated correlations to both temperature and Mg/Ca_{sw} (Wit et al., 2017). It is assumed in this approach, however, that the sensitivities of Mg/Ca_{cc} remain constant over the range of Mg/Ca_{sw} studied. In other words, this would indicate that the partition exponent H (Hasiuk & Lohmann, 2010) is close to 1, producing reasonable reconstructed temperatures and seawater Mg/Ca for the last ~10 Ma (Wit et al., 2017). Our results suggest that this may indeed be the case and that combining Mg/Ca_{cc} of the species studied here could therefore be used to reconstruct past seawater temperature and Mg/Ca_{sw}.

Previous studies have found that culturing foraminifera at much lower Mg/Ca_{sw} (e.g., 1 mol/mol) than that of current day, their growth rates decrease (e.g., Mewes et al., 2014), although this response may be species-specific (e.g., Segev & Erez, 2006). This may be due to the adaptation/evolution of the calcification process to current-day seawater Mg/Ca and experimentally-induced stress when placing them in Mg/Ca_{sw} of 1. Conversely, it is known that foraminiferal morphology can change as a function of seawater chemistry (Thomas, 2003), which may indicate that shell chemistry may be indirectly responding to changes in seawater chemistry. When using a modeled past seawater Mg/Ca_{sw} to correct for Mg/Ca_{cc}-based seawater temperatures (e.g., when only hyaline foraminifera are available), it has been argued that a power, instead of a linear function should be applied to correct fossil Mg/Ca_{cc} (Evans & Müller, 2012; Hasiuk & Lohmann, 2010). The reason for this is the non-constant relation between D_{Mg} and Mg/Ca_{sw} previously found (e.g., Delaney et al., 1985; Evans et al., 2015; Raitzsch et al., 2010; Segev & Erez, 2006). The choice for an exponential, rather than a linear response of Mg/Ca_{cc} to changes in Mg/Ca_{sw}, only marginally increases the fit of the regression models (Table 4) to the data presented here for *E. crispum* and *Quinqueloculina* sp.

On short timescales (i.e., <1 Ma), salinity and carbonate chemistry are the environmental parameters most likely biasing Mg/Ca-based temperature reconstructions. Although the genera *Elphidium* and *Quinqueloculina* are rarely used in paleoceanographic reconstructions, their responses to changes in either Mg/Ca_{sw} or temperature are comparable to previously published calibrations. Therefore, it may be that Mg-incorporation in other species show a similar combined response to Mg/Ca_{sw} and temperature as found here (Figures 1 and 2; Table 4).

5. Conclusions

Incorporation of Mg in the benthic hyaline foraminifer *Elphidium crispum* and the porcelaneous *Quinqueloculina* sp. increases as a function of both temperature and seawater Mg/Ca. The sensitivity of this increase with temperature was not found to change as a function of seawater Mg/Ca in the experiment conducted here. The overall differences in calcite Mg/Ca and the sensitivity of their increase with temperature between the two species results from the difference in biomineralization strategies between hyaline and porcelaneous species, possibly by a difference in the balance between transmembrane ion transport- and seawater-derived Mg²⁺. The combined seawater Mg/Ca-temperature calibration suggests that the cumulative impacts of these two parameters on foraminiferal Mg/Ca are similar to the individual impacts of temperature and Mg/Ca_{sw} on Mg-incorporation. These findings may be important for reliable reconstructions of past Mg/Ca_{sw} and temperature when using foraminiferal species with contrasting Mg/Ca.

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References

- Allen, K. A., Hönisch, B., Eggins, S. M., Haynes, L. L., Rosenthal, Y., & Yu, J. (2016). Trace element proxies for surface ocean conditions: A synthesis of culture calibrations with planktic foraminifera. *Geochimica et Cosmochimica Acta*, 193, 197–221.
- Allison, N., Austin, H., Austin, W., & Paterson, D. M. (2011). Effects of seawater pH and calcification rate on test Mg/Ca and Sr/Ca in cultured individuals of the benthic, calcitic foraminifera *Elphidium williamsoni*. *Chemical Geology*, 289, 171–178.
- Allison, N., Austin, W., Paterson, D., & Austin, H. (2010). Culture studies of the benthic foraminifera *Elphidium williamsoni*: Evaluating pH, Δ[CO₃²⁻] and inter-individual effects on test Mg/Ca. *Chemical Geology*, 274, 87–93.
- Anand, P., Elderfield, H., & Conte, M. H. (2003). Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series. *Paleoceanography*, 18(2), 1050. <https://doi.org/10.1029/2002PA000846>
- Barker, S., Greaves, M., & Elderfield, H. (2003). A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. *Geochemistry, Geophysics, Geophysics*, 4(9), 8407. <https://doi.org/10.1029/2003GC000559>

- Bentov, S., & Erez, J. (2006). Impact of biomineralization processes on the Mg content of foraminiferal shells: A biological perspective. *Geochemistry, Geophysics, Geophysics*, 7, Q01P08. <https://doi.org/10.1029/2005GC001015>
- Berner, R. A. (2004). A model for calcium, magnesium and sulfate in seawater over Phanerozoic time. *American Journal of Science*, 304, 438–453.
- Billups, K., & Schrag, D. (2002). Paleotemperatures and ice volume of the past 27 Myr revisited with paired Mg/Ca and 18O/16O measurements on benthic foraminifera. *Paleoceanography*, 17(1), 1003. <https://doi.org/10.1029/2006PA000567>
- Broecker, W. S., Peng, T.-H., & Beng, Z. (1982). *Tracers in the Sea*. Palisades, New York: Lamont-Doherty Geological Observatory, Columbia University.
- Brownlee, C., Wheeler, G. L., & Taylor, A. R. (2015). Coccolithophore biomineralization: New questions, new answers. *Seminars in Cell and Developmental Biology*, 46, 11–16.
- Coggon, R. M., Teagle, D. A. H., Smith-Duque, C. E., Alt, J. C., & Cooper, M. J. (2010). Reconstructing past seawater Mg/Ca and Sr/Ca from mid-ocean ridge flank calcium carbonate veins. *Science*, 327, 1114–1117.
- Davis, K. J., Dove, P. M., Wasylenki, L. E., & De Yoreo, J. J. (2004). Morphological consequences of differential Mg²⁺ incorporation at structurally distinct steps on calcite. *American Mineralogist*, 89, 714–720.
- Debenay, J. P., Guillou, J. J., & Lesourd, M. (1996). Colloidal calcite in foraminiferal tests: Crystallization and texture of the test. *Journal of Foraminiferal Research*, 26(4), 277–288.
- Delaney, M. L., Bé, A. W., & Boyle, E. A. (1985). Li, Sr, Mg, and Na in foraminiferal calcite shells from laboratory culture, sediment traps, and sediment cores. *Geochimica et Cosmochimica Acta*, 49, 1327–1341.
- De Nooijer, L. J., Hathorne, E. C., Reichart, G. J., Langer, G., & Bijma, J. (2014). Variability in calcitic Mg/Ca and Sr/Ca ratios in clones of the benthic foraminifer *Ammonia tepida*. *Marine Micropaleontology*, 107, 32–43.
- De Nooijer, L. J., Spero, H. J., Erez, J., Bijma, J., & Reichart, G. J. (2014). Biomineralization in perforate foraminifera. *Earth-Science Reviews*, 135, 48–58.
- De Nooijer, L. J., Toyofuku, T., & Kitazato, H. (2009). Foraminifera promote calcification by elevating their intracellular pH. *Proceedings of National Academy of Sciences U. S. A.*, 106(36), 15374–15378.
- De Yoreo, J. J., Gilbert, P. U. P. A., Sommerdijk, N. A. J. M., Lee Penn, R., Whitlam, S., Joester, D., . . . Dove, P. M. (2015). Crystallization by particle attachment in synthetic, biogenic, and geologic environments. *Science*, 349, 6760–1–6760–9.
- Dissard, D., Nehrke, G., Reichart, G. J., & Bijma, J. (2010). Impact of seawater pCO₂ on calcification and Mg/Ca and Sr/Ca ratios in benthic foraminifera calcite: Results from culturing experiments with *Ammonia tepida*. *Biogeosciences*, 7, 81–93.
- Diz, P., Barras, C., Geslin, E., Reichart, G. J., Metzger, E., Jorissen, F., & Bijma, J. (2012). Incorporation of Mg and Sr and oxygen and carbon stable isotope fractionation in cultured *Ammonia tepida*. *Marine Micropaleontology*, 92, 16–28.
- Dawber, C. F., & Tripathi, A. (2012). Relationships between bottom water carbonate saturation and element/Ca ratios in coretop samples of the benthic foraminifer *Oridorsalis umbonatus*. *Biogeosciences*, 9, 3029–3045.
- Dueñas-Bohórquez, A., da Rocha, R. E., Kuroyanagi, A., Bijma, J., & Reichart, G. J. (2009). Effect of salinity and seawater calcite saturation state on Mg and Sr incorporation in cultured planktonic foraminifera. *Marine Micropaleontology*, 73, 178–189.
- Dueñas-Bohórquez, A., da Rocha, R. E., Kuroyanagi, A., De Nooijer, L. J., Bijma, J., & Reichart, G. J. (2011). Interindividual variability and ontogenetic effects on Mg and Sr incorporation in the planktonic foraminifer *Globigerinoides sacculifer*. *Geochimica et Cosmochimica Acta*, 75, 520–532.
- Dueñas-Bohórquez, A., Raitzsch, M., De Nooijer, L. J., & Reichart, G. J. (2011). Independent impacts of calcium and carbonate ion concentration on Mg and Sr incorporation in cultured benthic foraminifera. *Marine Micropaleontology*, 81, 122–130.
- Elderfield, H., Anand, P., Kiefer, T., & Nyland, B. (2006). Calibrations for benthic foraminiferal Mg/Ca paleothermometry and the carbonate ion hypothesis. *Earth Planetary Science Letters*, 250, 633–649.
- Elderfield, H., Cooper, M., & Ganssen, G. (2000). Sr/Ca in multiple species of planktonic foraminifera: Implication for reconstructions of seawater Sr/Ca. *Geochemistry, Geophysics, Geosystems*, 1(11), 1017. <https://doi.org/10.1029/1999GC000031>
- Elderfield, H., & Ganssen, G. (2000). Past temperature and δ¹⁸O of surface ocean waters inferred from foraminiferal Mg/Ca ratios. *Nature*, 405, 442–445.
- Erez, J. (2003). The source of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies. *Reviews in Mineralogy and Geochemistry*, 54, 115–149.
- Evans, D., Brierly, C., Raymo, M. E., Erez, J., & Müller, W. (2016). Planktonic foraminifera shell chemistry response to seawater chemistry: Pliocene-Pleistocene seawater Mg/Ca, temperature and sea level change. *Earth Planetary Science Letters*, 438, 139–148.
- Evans, D., Erez, J., Oron, S., & Müller, W. (2015). Mg/Ca-temperature and seawater-test chemistry relationships in the shallow-dwelling large benthic foraminifera *Operculina ammonoides*. *Geochimica et Cosmochimica Acta*, 148, 325–342.
- Evans, D., & Müller, W. (2012). Deep time foraminifera Mg/Ca paleothermometry: Nonlinear correction for secular change in seawater Mg/Ca. *Paleoceanography*, 27, PA4205. <https://doi.org/10.1029/2012PA002315>
- Farkaš, J., Böhm, F., Wallmann, K., Blenkinsop, J., Eisenhauer, A., van Geldern, R., . . . Veizer, J. (2007). Calcium isotope record of Phanerozoic oceans: Implications for chemical evolution of seawater and its causative mechanisms. *Geochimica et Cosmochimica Acta*, 71, 5117–5134.
- Friedrich, O., Schiebel, R., Wilson, P. A., Weldeab, S., Beer, C. J., Cooper, M. J., & Fiebig, J. (2012). Influence of test size, water depth, and ecology on Mg/Ca, Sr/Ca, δ¹⁸O and δ¹³C in nine modern species of planktic foraminifers. *Earth Planetary Science Letters*, 319, 133–145.
- Gothmann, A. M., Stolarski, J., Adkins, J. F., Schoene, B., Dennis, K. J., Schrag, D. P., . . . Bender, M. L. (2015). Fossil corals as an archive of secular variations in seawater chemistry since the Mesozoic. *Geochimica et Cosmochimica Acta*, 160, 188–208.
- Hardie, L. A. (1996). Secular variation in seawater chemistry: An explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 my. *Geology*, 24(3), 279–283.
- Hasiuk, F. J., & Lohmann, K. C. (2010). Application of calcite Mg partitioning functions to the reconstruction of paleocean Mg/Ca. *Geochimica et Cosmochimica Acta*, 74, 6751–6763.
- Hastings, D. W., Russell, A. D., & Emerson, S. R. (1998). Foraminiferal magnesium in *Globigerinoides sacculifer* as a paleotemperature proxy. *Paleoceanography*, 13(2), 161–169.
- Hemleben, C., Erson, Berthold, O. W., & Spindler, M. (1986). Calcification and chamber formation in Foraminifera—a brief overview. In B. S. C. Leadbeater & R. Riding (Eds.), *Biomineralization in lower plants and animals* (pp. 237–249). Oxford, UK: Clarendon Press.
- Hertzberg, J. E., & Schmidt, M. W. (2013). Refining *Globigerinoides ruber* Mg/Ca paleothermometry in the Atlantic Ocean. *Earth Planetary Science Letters*, 383, 123–133.
- Holland, H. D., & Zimmermann, H. (2000). The Dolomite problem revisited. *International Geology Review*, 42(6), 481–490.

- Hönisch, B., Allen, K. A., Lea, D. W., Spero, H. J., Eggins, S. M., Arbuszewski, J., . . . Elderfield, H. (2013). The influence of salinity on Mg/Ca in planktic foraminifers—Evidence from cultures, core-top sediments and complementary $\delta^{18}\text{O}$. *Geochimica et Cosmochimica Acta*, *121*, 196–213.
- Horita, J., Zimmerman, H., & Holland, H. D. (2002). Chemical evolution of seawater during the Phanerozoic: Implications from the record of marine evaporites. *Geochimica et Cosmochimica Acta*, *66*, 3733–3756.
- Jochum, K. P., Scholz, D., Stoll, B., Weis, U., Wilson, S. A., Yang, Q., . . . Andreae, M. O. (2012). Accurate trace element analysis of speleothems and biogenic calcium carbonates by LA-ICP-MS. *Chemical Geology*, *318–319*, 31–44.
- Kester, D. R., Duedall, I. W., Connors, D. N., & Pytkowicz, R. M. (1967). Preparation of artificial seawater. *Limnology and Oceanography*, *12*, 176–179.
- Lea, D. W., Mashiotta, T. A., & Spero, H. J. (1999). Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing. *Geochimica et Cosmochimica Acta*, *63*, 2369–2379.
- Lear, C. H., Elderfield, H., & Wilson, P. A. (2000). Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite. *Science*, *287*, 269–272.
- Maeda, A., Fujita, K., Horikawa, K., Suzuki, A., Yoshimura, T., Tamenori, Y., & Kawahata, H. (2017). Evaluation of oxygen isotope and Mg/Ca ratios in high-magnesium calcite from benthic foraminifera as a proxy for water temperature. *Journal of Geophysical Research: Biogeosciences*, *122*, 185–199. <https://doi.org/10.1002/2016JG003587>
- Martin, P. A., Lea, D. W., Rosenthal, Y., Shackleton, N. J., Sarnthein, N., & Papenfuss, T. (2002). Quarternary deep sea temperature histories derived from benthic foraminiferal Mg/Ca. *Earth Planetary Science Letters*, *198*, 193–209.
- Mewes, A., Langer, G., de Nooijer, L. J., Bijma, J., & Reichart, G. J. (2014). Effect of different seawater Mg^{2+} concentrations on calcification in two benthic foraminifers. *Marine Micropaleontology*, *113*, 56–64.
- Mewes, A., Langer, G., Reichart, G. J., de Nooijer, L. J., Nehrke, G., & Bijma, J. (2015). The impact of Mg contents on Sr partitioning in benthic foraminifers. *Chemical Geology*, *412*, 92–98.
- Mewes, A., Langer, G., Thoms, S., Nehrke, G., Reichart, G. J., de Nooijer, L. J., & Bijma, J. (2015). Impact of seawater $[\text{Ca}^{2+}]$ on the calcification and calcite Mg/Ca of *Amphistegina lessonii*. *Biogeosciences*, *12*, 2153–2162.
- Mezger, E. M., de Nooijer, L. J., Boer, W., Brummer, G. J. A., & Reichart, G. J. (2016). Salinity controls on Na incorporation in Red Sea planktonic foraminifera. *Paleoceanography*, *31*, 1562–1582. <https://doi.org/10.1002/2016PA003052>
- Morse, J. W., Arvidson, R. S., & Lüttge, A. (2007). Calcium carbonate formation and dissolution. *Chemical Reviews*, *107*, 342–381.
- Mucci, A. (1987). Influence of temperature on the composition of magnesian calcite overgrowths precipitated from seawater. *Geochimica et Cosmochimica Acta*, *51*, 1977–1984.
- Mucci, A., & Morse, J. W. (1983). The incorporation of Mg^{2+} and Sr^{2+} into calcite overgrowths: Influences on growth rate and solution composition. *Geochimica et Cosmochimica Acta*, *47*, 217–233.
- Nehrke, G., Keul, N., Langer, G., de Nooijer, L. J., Bijma, J., & Meibom, A. (2013). A new model for biomineralization and trace-element signatures of Foraminifera tests. *Biogeosciences*, *10*, 6759–6767.
- Nürnberg, D. (2015). Mg/Ca paleothermometry. In J. Harff, M. Meschede, S. Petersen, & J. Thiede (Eds.), *Encyclopedia of marine geosciences* (pp. 1–3). Netherlands: Springer Netherlands.
- Nürnberg, D., Bijma, J., & Hemleben, C. (1996). Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures. *Geochimica et Cosmochimica Acta*, *60*, 803–814.
- Raitzsch, M., Dueñas-Bohórquez, A., Reichart, G. J., de Nooijer, L. J., & Bickert, T. (2010). Incorporation of Mg and Sr in calcite of cultured benthic foraminifera: Impact of calcium concentration and associated calcite saturation state. *Biogeosciences*, *7*, 869–881.
- Raja, R., Saraswati, P. K., Rogers, K., & Iwao, K. (2005). Magnesium and strontium compositions of recent symbiont-bearing benthic foraminifera. *Marine Micropaleontology*, *58*, 31–44.
- Reichart, G. J., Jorissen, F., Anschutz, P., & Mason, P. R. (2003). Single foraminiferal test chemistry records the marine environment. *Geology*, *31*, 355–358.
- Rosenthal, Y., Boyle, E. A., & Slowey, N. (1997). Temperature control on the incorporation of magnesium, strontium, fluorine, and cadmium into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline paleoceanography. *Geochimica et Cosmochimica Acta*, *61*, 3633–3643.
- Russell, A. D., Hönisch, B., Spero, H. J., & Lea, D. W. (2004). Effects of seawater carbonate ion concentration and temperature on shell U, Mg, and Sr in cultured planktonic foraminifera. *Geochimica et Cosmochimica Acta*, *68*, 4347–4361.
- Sadekov, A., Bush, F., Kerr, J., Ganeshram, R., & Elderfield, H. (2014). Mg/Ca composition of benthic foraminifera Miliolacea as a new tool of paleoceanography. *Paleoceanography*, *29*, 990–1001. <https://doi.org/10.1002/2014PA002654>
- Sadekov, A., Eggins, S. M., de Deckker, P., & Kroon, H. (2008). Uncertainties in seawater thermometry deriving from intratest and intertest Mg/Ca variability in *Globigerinoides ruber*. *Paleoceanography*, *23*, PA1215. <https://doi.org/10.1029/2007PA001452>
- Sadekov, A., Eggins, S. M., de Deckker, P., Ninnemann, U., Kuhnt, W., & Bassinot, F. (2009). Surface and subsurface seawater temperature reconstruction using Mg/Ca microanalysis of planktonic foraminifera *Globigerinoides ruber*, *Globigerinoides sacculifer*, and *Pulleniatina obliquiloculata*. *Paleoceanography*, *24*, PA3201. <https://doi.org/10.1029/2008PA001664>
- Segev, E., & Erez, J. (2006). Effect of Mg/Ca ratio in seawater on shell composition in shallow benthic foraminifera. *Geochemistry, Geophysics, Geophysics*, *7*, Q02P09. <https://doi.org/10.1029/2005GC000969>
- Stanley, S. M., & Hardie, L. A. (1998). Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry. *Palaeogeography Palaeoclimatology Palaeoecology*, *144*, 3–19.
- Steuber, T., & Veizer, J. (2002). Phanerozoic record of plate tectonic control of seawater chemistry and carbonate sedimentation. *Geology*, *30*, 1123.
- Ter Kuile, B., Erez, J., & Padan, E. (1989). Mechanisms for the uptake of inorganic carbon by two species of symbiont-bearing foraminifera. *Marine Biology*, *103*, 241–251.
- Thomas, E. (2003). Extinction and food at the seafloor: A high-resolution benthic foraminiferal record across the Initial Eocene Thermal Maximum, Southern Ocean Site 690. *Geological Society of America*, *369*, 319–332.
- Toyofuku, T., & Kitazato, H. (2005). Micromapping of Mg/Ca values in cultured specimens of the high-magnesium benthic foraminifera. *Geochemistry, Geophysics, Geophysics*, *6*, Q11P05. <https://doi.org/10.1029/2005GC000961>
- Toyofuku, T., Kitazato, H., Kawahata, H., Tsuchiya, M., & Nohara, M. (2000). Evaluation of Mg/Ca thermometry in foraminifera: Comparison of experimental results and measurements in nature. *Paleoceanography*, *15*(4), 456–464.
- Toyofuku, T., Suzuki, M., Suga, H., Sakai, S., Suzuki, A., Ishikawa, T., . . . Kitazato, H. (2011). Mg/Ca and $\delta^{18}\text{O}$ in the brackish shallow-water benthic foraminifer *Ammonia 'beccarii*. *Marine Micropaleontology*, *78*, 113–120.

- Tripati, A., Backman, J., Elderfield, H., & Ferretti, P. (2005). Eocene bipolar glaciation associated with global carbon cycle changes. *Nature*, *436*, 341–346.
- Van Dijk, I., de Nooijer, L. J., & Reichart, G. J. (2017). Trends in element incorporation in hyaline and porcelaneous foraminifera as a function of $p\text{CO}_2$. *Biogeosciences*, *14*, 497–510.
- Weiner, S., Levi-Kalishman, Y., Raz, S., & Addadi, L. (2003). Biologically formed amorphous calcium carbonate. *Connective Tissue Research*, *44*, 214–218.
- Wit, J. C., de Nooijer, L. J., Barras, C., Jorissen, F. J., & Reichart, G. J. (2012). A reappraisal of the vital effect in cultured benthic foraminifer *Bulimina marginata* on Mg/Ca values: Assessing temperature uncertainty relationships. *Biogeosciences*, *9*, 3693–3704.
- Wit, J. C., de Nooijer, L. J., Haig, J., Jorissen, F. J., Thomas, E., & Reichart, G. J. (2017). Towards reconstructing ancient seawater Mg/Ca by combining porcelaneous and hyaline foraminiferal Mg/Ca-temperature calibrations. *Geochimica et Cosmochimica Acta*, *211*, 341–354.
- Wit, J. C., de Nooijer, L. J., Wolthers, M., & Reichart, G. J. (2013). A novel salinity proxy based on Na incorporation into foraminiferal calcite. *Biogeosciences*, *10*, 6375–6387.
- Young, J., & Henriksen, K. (2003). Biomineralization within vesicles: The calcite of coccoliths. *Reviews in Mineralogy and Geochemistry*, *54*, 189–215.
- Yu, J., & Elderfield, H. (2007). Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state. *Earth Planetary Science Letters*, *258*, 73–86.
- Yu, J., & Elderfield, H. (2008). Mg/Ca in the benthic foraminifera *Cibicides wuellerstorfi* and *Cibicides mundulus*: Temperature versus carbonate ion saturation. *Earth Planetary Science Letters*, *276*, 129–139.