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A reappraisal of the vital effect in cultured benthic foraminifer *Bulimina marginata* on Mg/Ca values: assessing temperature uncertainty relationships

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Abstract. The reconstruction of past temperatures is often achieved through measuring the Mg/Ca value of foraminiferal test carbonate. The diversity in foraminiferal Mg/Ca–temperature calibrations suggests that there is also a biological control on this proxy. This study presents a new Mg/Ca–temperature calibration for the benthic foraminifer *Bulimina marginata*, based on cultures under a range of temperatures (4–14 °C). Measured Mg/Ca values for *B. marginata* correlate with temperature ($\text{Mg/Ca} = (1.10 \pm 0.10) e^{(0.045 \pm 0.009)T}$, $R^2 = 0.28$ $p < 0.01$). The inter-individual variability is, however, also significant (standard deviation is 10–35 % of the average). Before applying this or any calibration, the effect of the inter-individual variability on the accuracy of the Mg/Ca–temperature calibration has to be evaluated. The inter-individual variability is quantified and split into three components, namely (1) an analytical error, (2) an environmental effect and (3) a vital effect. The effect of inter-individual variability on the accuracy of Mg/Ca–temperature calibrations depends on the sensitivity of the calibration used and the number of individuals measured (temperature uncertainty = $(0.33 \cdot N^{-0.50})/\text{sensitivity}$). The less sensitive a calibration, the greater is the impact of inter-individual variability, which can partly be circumvented by measuring more individuals. This study shows the link between inter-individual variability and sensitivity and quantifies their influence on the accuracy of Mg/Ca–temperature calibrations. Differences in the sensitivity of the Mg/Ca–temperature calibration of foraminifera may depend

on the environmental conditions in which foraminifera live and their concurring ecological strategies.

1 Introduction

The ratio of magnesium to calcium in the calcite of benthic foraminifera (i.e. test Mg/Ca) is an important tool to reconstruct past bottom water temperatures. From basic thermodynamic principles it follows that the rate of substitution of Mg ions for Ca in the CaCO_3 lattice increases with temperature. The incorporation of Mg into foraminiferal calcite is thus expected to primarily depend on changes in environmental temperature. However, incorporation of Mg is also affected by other environmental parameters, including salinity, carbonate ion concentration (CO_3^{2-}) and seawater Mg/Ca (Mg/Ca_{sw}) (Nürnberg et al., 1996; Elderfield et al., 2006; Wit et al., 2012). Moreover, most foraminiferal species produce calcite with a Mg/Ca value approximately an order of magnitude lower than those from inorganic precipitation experiments (Bentov and Erez, 2006; Morse et al., 2007). This shows that, besides an environmental control, there is also a strong biological control on Mg incorporation. The difference in element (and isotope) composition between biologically and inorganically precipitated calcium carbonate is often abbreviated as the vital effect (Urey et al., 1951; Weiner and Dove, 2003) and is caused by biological impacts on the calcification process (Erez, 2003; Bentov and Erez,

2006; De Nooijer et al., 2009a). These include modifications of the internal pH, thereby affecting the carbonate ion concentration of the calcification environment, potentially altering the Mg/Ca of the calcite precipitated (Elderfield et al., 2006; Bentov and Erez, 2006; De Nooijer et al., 2009b). Active discrimination against magnesium during production of a privileged space in which high concentrations of Ca^{2+} are actively maintained is another example of how these vital effects impact foraminiferal Mg/Ca values (Erez, 2003; Bentov and Erez, 2006; De Nooijer et al., 2009a). The vital effect is responsible for the difference in Mg/Ca values between species, indicated by large inter-species differences in Mg incorporation at the same temperature (Lear et al., 2002; Anand et al., 2003; Rathmann et al., 2004; Elderfield et al., 2006; Rosenthal et al., 2011; Toyofuku et al., 2011; Wit et al., 2012). Variability in Mg/Ca between individual tests of the same species, furthermore, suggests that the biologically-induced offset might not be constant within one species. Part of such variability may be caused by changes in the micro-environment in which foraminifera calcify. Infaunal benthic species, for example, experience rapidly changing chemical gradients in the sediment that can affect Mg incorporation and introduce intra- and inter-individual variability in Mg/Ca. The inter-individual variability as a result of vital effects is significantly affecting temperature reconstructions based on foraminiferal Mg/Ca values (Sadekov et al., 2008; Hathorne et al., 2009). The ability to quantify and recognize the amplitude, and changes therein, of the vital effect is thus of vital importance in improving the accuracy of the Mg/Ca-thermometer.

Despite differences between species-specific Mg/Ca-temperature calibrations, most calibrations found are described by an exponential function linking Mg/Ca and temperature (Eq. 1):

$$\text{Mg/Ca} = a \cdot e^{(b \cdot T)}, \quad (1)$$

where T is the temperature in degrees Celsius and a and b are empirically derived species-specific constants. The pre-exponential constant a equals the (theoretical) Mg/Ca at 0°C and the exponential constant b describes the steepness of the slope with increasing temperature and is often referred to as the sensitivity of the Mg/Ca-temperature calibration.

Here, a new Mg/Ca-temperature calibration based on cultured specimens of the benthic foraminifer *Bulimina marginata* is presented. Within the culture setup, maintained at a range of set temperatures, all other parameters influencing foraminiferal Mg/Ca values (salinity, carbonate ion concentration, seawater Mg/Ca) were kept constant in a controlled environment. Such a culturing approach in which environmental parameters are rigorously constant for all individuals is vital for the assessment of intra-individual variability in foraminiferal Mg/Ca due to biological factors, as benthic foraminifera, especially infaunal living species such as *B. marginata*, calcify in a wide range of biogeochemically different micro-environments. This study thus al-

lows accurate quantification of inter- and intra-individual variability as a result of biologically controlled changes in the foraminiferal calcification process, as all other parameters are kept constant within the experiment. This calibration study thus provides insight into the environmental and biological factors potentially offsetting Mg/Ca-temperature calibrations and the effect on the accuracy of this paleothermometer.

2 Methods

Living specimens of the benthic, symbiont-barren foraminifer *Bulimina marginata* were collected from two stations in the Bay of Biscay (450 m and 600 m deep). Isolated specimens were placed in culture set-ups between 4 and 14°C (natural range for *B. marginata* in the Bay of Biscay) at Utrecht University and the University of Angers (8 experiments, Table 1). Growth was monitored through incorporation of the fluorescent marker Calcein, after which the foraminifera were introduced to the experimental set-up. This compound is a suitable marker for recognizing newly formed calcite (Bernhard et al., 2004), and does not affect the incorporation of Mg and Sr in foraminiferal calcite (Dissard et al., 2009).

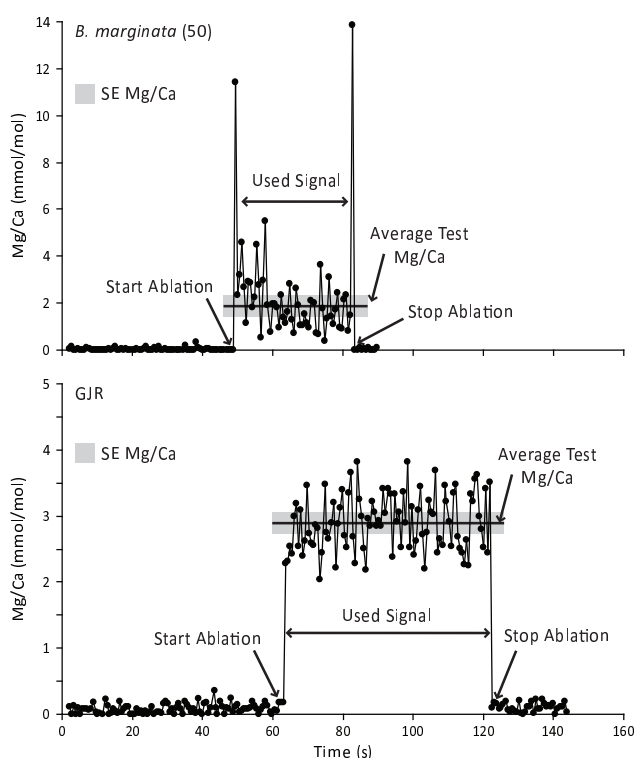
Two different culture setups were used for this Mg/Ca- T calibration: (1) an open system using 250 ml water, of which the seawater was replaced weekly to bi-weekly, and (2) a closed system with seawater circulation from a large reservoir (25 l) towards the different experiments (Barras et al., 2010). Temperature was controlled in climatic controlled incubators, which were set at the preferred temperatures. Seawater from both setups was sampled weekly to monitor salinity, total alkalinity, and pH or dissolved inorganic carbon (DIC) of the media. Total alkalinity and DIC or pH were used to calculate the carbonate ion concentration ($[\text{CO}_3^{2-}]$) using the CO2SYS software (Lewis and Wallace, 1998) (Table 1).

Experiments ran for 2–3 months to maximize the chance of sufficient calcite addition. Specimens were harvested by sieving over a $63\ \mu\text{m}$ mesh with de-ionized water. After terminating each experiment, specimens were cleaned for 20 min in 5 % NaClO to dissolve organic matter attached to the surfaces of the foraminiferal shells. Afterwards, individual foraminifera were rinsed 3–6 times with MilliQ and 2 times with methanol (Utrecht samples) to prepare the samples for trace metal analysis (Barker et al., 2003; Wit et al., 2010; Rosenthal et al., 2011).

Elements were measured on newly calcified chambers of adult foraminifera as a ratio to calcium with laser ablation inductively coupled mass spectrometry (LA-ICP-MS), using a deep ultraviolet wave length laser (193 nm) with a Lambda Physik excimer laser system with Geolas 200Q optics and a quadrupole ICP-MS instrument (Micromass Platform) (Reichert et al., 2003). Laser ablation spot size was $80\ \mu\text{m}$ and foraminiferal chambers were ablated through the whole outer

Table 1. Average and standard deviation of the main seawater parameters for all temperature experiments. Experiments contain samples from cultures at (1) Utrecht University, (2) University of Angers or (3) combined samples.

Experiment	Temperature (°C)	Salinity (psu)	Alkalinity ($\mu\text{mol l}^{-1}$)	pH	DIC ($\mu\text{mol l}^{-1}$)	CO_3^{2-} ($\mu\text{mol l}^{-1}$)
1 ²	4.1 ± 1.1	35.8 ± 0.1	2528 ± 13	7.80 ± 0.07	2492 ± 23	60 ± 8
2 ²	6.0 ± 0.5	35.8 ± 0.1	2524 ± 12	7.80 ± 0.08	2480 ± 25	64 ± 10
3 ³	7.9 ± 0.1	35.8 ± 0.1	2452 ± 30	7.93 ± 0.05	2357 ± 24	87 ± 7
4 ²	9.3 ± 0.7	35.8 ± 0.1	2524 ± 13	7.78 ± 0.09	2473 ± 29	69 ± 12
5 ²	10.2 ± 0.1	35.8 ± 0.1	2454 ± 32	7.94 ± 0.05	2344 ± 41	96 ± 10
6 ¹	11.3 ± 0.3	34.7 ± 0.2	2470 ± 73	8.14 ± 0.22	2215 ± 18	187 ± 54
7 ²	12.7 ± 0.1	35.9 ± 0.1	2473 ± 34	7.98 ± 0.04	2334 ± 32	114 ± 8
8 ¹	14.0 ± 0.2	35.0 ± 0.2	2500 ± 77	8.16 ± 0.03	2206 ± 6	214 ± 48
Average	9.7	35.6	2494	7.9	2373	107
σ	3.2	0.4	32.4	0.1	110.7	55.7

**Fig. 1.** Laser ablation profiles for Mg/Ca measured on benthic foraminifer *B. marginata* (upper panel) and the in-house GJR (Reichart et al., 2003) standard (lower panel). Parts of the profiles with elevated magnesium at the surface of the chamber walls are removed before calculating the average Mg/Ca. The absence of peak values for Mg/Ca in the GJR standard at the start and end of the ablation rule out any instrumental cause for the spikes observed in *B. marginata*.

test wall. Measured elements included ^{24}Mg , ^{26}Mg , ^{27}Al , ^{42}Ca , ^{43}Ca , ^{44}Ca , ^{55}Mn , ^{88}Sr and their relative natural abundances. Mg/Ca ratios were determined using obtained ^{24}Mg concentration and assuming 40 wt% ^{44}Ca in CaCO_3 . Counts

for ^{26}Mg were used to check for consistency of the ^{24}Mg concentrations. Element/Ca ratios were calibrated against the NIST 610 and an in-house calcite standard, verifying that differences in ablation energy do not affect measured elemental concentrations (Hathorne et al., 2008; Wit et al., 2010). Of all measured data, about 22% was discarded because ablation profiles were too short (less than 20–30 pulses at 6 Hz), contamination values for Al were too high (>20 ppm), or the standard deviation of the measurement was too high (>70 ppm for Mg). High standard deviations in individual measurements are indicative for a heterogeneous distribution of Mg through the foraminiferal chamber wall. Elemental ratios with respect to Ca were based on the average of each ablation profile (Fig. 1). Individual foraminiferal Mg/Ca values were based on the average of 1–4 measured test-chambers. Foraminifera were measured for size, in order to assess any ontogenetic effect within the Mg/Ca–temperature calibration, using an ocular with a built-in scale bar, which was scaled on a 1 mm slide. Size was determined by measuring the height of each individual *B. marginata*. The very small size of the first chambers makes it impossible to count the chamber number in this species, hampering comparison with previously reported ontogenetic trends (or absence thereof) in element/Ca ratios based on chamber number (Dueñas-Bohórquez et al., 2011a).

3 Results

All culture experiments were monitored for stability of temperature, salinity, alkalinity and pH (University of Angers) or DIC (Utrecht University) (Table 1). Individuals of *Bulimina marginata* calcified 1–4 new chambers in every experiment (Barras et al., 2010). The Mg/Ca of the newly formed calcite was measured by laser ablation ICP-MS. Recognition of enriched trace element concentrations at the inner and outer surface of the test wall enables removal of contaminations before calculation of the average foraminiferal Mg/Ca (Fig. 1).

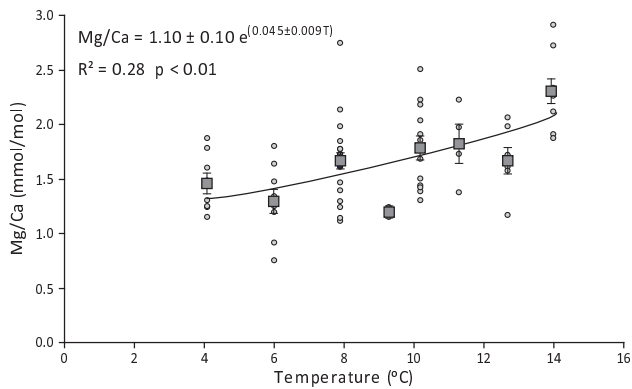


Fig. 2. Mg/Ca versus temperatures for all experiments with *B. marginata*. The error bars are based on the standard error of the mean (σ/\sqrt{n}).

Values for Mg/Ca of individual specimens range from 0.75 to 2.9 mmol mol (Table 2). Inter-individual variability is calculated as a standard deviation expressed as a percentage of the average and varies between 5 and 25 %. Combining the results from individuals cultured in the same conditions (Fig. 2) shows that Mg/Ca in *Bulimina marginata* increases exponentially with temperature (R^2 of the regression is 0.28, $p < 0.01$) and is described by Eq. (2).

$$\text{Mg/Ca} = (1.10 \pm 0.10) e^{(0.045 \pm 0.009)T} \quad (2)$$

The obtained Mg/Ca are not correlated with test size ($R^2 = 0.03$, $p > 0.10$, 300–600 μm , Fig. 3), excluding the possibility that differences in maximum test diameter between conditions caused differences in Mg/Ca between specimens grown at different temperatures.

4 Discussion

4.1 Mg/Ca–temperature calibration for *Bulimina marginata*

The Mg/Ca–temperature calibration indicates a relatively low sensitivity of Mg/Ca in the calcite of *B. marginata* to changes in temperature, as expressed by the low exponential constant (0.045 ± 0.009) (Eq. 2). Values for Mg/Ca are relatively low ($\sim 1\text{--}3$ mmol mol⁻¹) and similar to values for other calcitic hyaline foraminifera (Lear et al., 2002; Anand et al., 2003; Rathmann et al., 2004; Elderfield et al., 2006; Rosenthal et al., 2011). Analyses by Filipsson et al. (2010) suggested higher Mg/Ca values for *B. marginata*. Their results, however, were based on laser ablation rastering of the test surface. Since the outermost layer of calcite is commonly enriched in Mg (Fig. 1 and Hathorne et al., 2009), their results may not be representative for the average chamber wall Mg/Ca. Despite the different analytical procedures and much higher absolute Mg/Ca values, the obtained Mg/Ca–

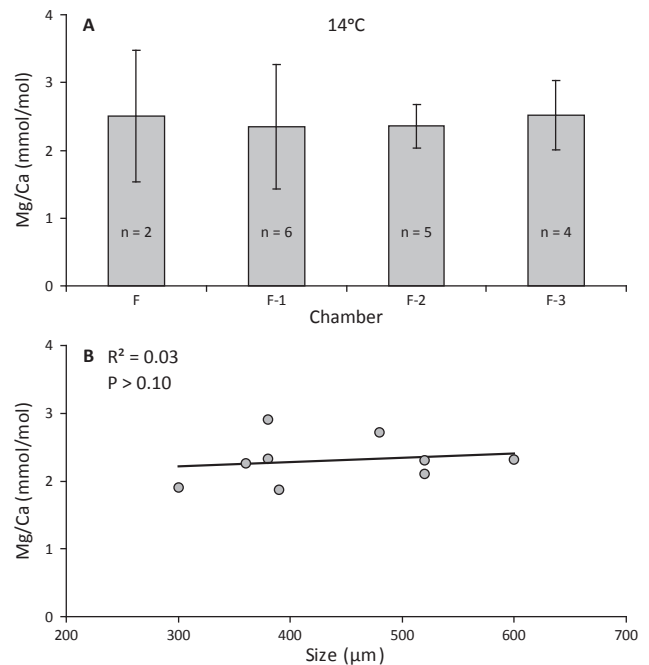


Fig. 3. Mg/Ca versus size for experiment 8 (14 °C). The upper panel depicts the average Mg/Ca value per measured chamber and the number of individual chambers analyzed (n). The final chamber is indicated by F and counted down in the whorl afterwards (F-1, F-2, etc.). Measured Mg/Ca values are statistically not different from one another. The lower panel displays the average Mg/Ca values of individual *B. marginata* born in the experiment versus their size. No trend can be observed between size and Mg/Ca.

temperature calibration of Filipsson et al. (2010) does have a similar sensitivity as the one presented here.

4.2 Ontogeny

Since the response of Mg/Ca to temperature is relatively low, additional impacts (e.g. size effects) may have a relatively large impact on the Mg/Ca–temperature calibration presented here. An effect of ontogeny on planktonic foraminiferal Mg/Ca has been stipulated (Nürnberg et al., 1996; Wit et al., 2010; Dueñas-Bohórquez et al., 2011a). Ontogenetic effects for benthic foraminiferal Mg/Ca values are generally less well known, although Hintz et al. (2006) reported elevated Mg/Ca values for the mid-life stage of *Bulimina aculeata* by measuring Mg/Ca on both the whole foraminifer and on micro-dissected chambers. However, the Mg/Ca values reported by Hintz et al. (2006) were exceptionally high (up to 84 mmol mol⁻¹), suggesting that a phase with elevated Mg concentrations biased their results. An ontogenetic trend observed in the results of the micro-dissection method should be directly comparable to laser ablation Mg/Ca measurements of individual chambers. The mid-life stage from Hintz et al. (2006) corresponds to the chamber two positions from the final chamber (F-2) in this

Table 2. Sample number with single specimen Mg/Ca value for *B. marginata*. Mg/Ca values for individual foraminifers are based on 1–4 laser ablation profiles. The error in averaged Mg/Ca values per temperature experiment is based on the standard error of the average (σ/\sqrt{n}).

Sample no.	Temperature (°C)	Mg/Ca (mmol mol ⁻¹)	Average Mg/Ca (mmol mol ⁻¹)	Sample no.	Temperature (°C)	Mg/Ca (mmol mol ⁻¹)	Average Mg/Ca (mmol mol ⁻¹)
1	4.1	1.30		37	10.2	1.38	
2	4.1	1.78		38	10.2	1.30	
3	4.1	1.87		39	10.2	1.44	
4	4.1	1.60		40	10.2	2.22	
5	4.1	1.48		41	10.2	1.85	
6	4.1	1.24		42	10.2	2.50	
7	4.1	1.25		43	10.2	1.91	
8	4.1	1.15	1.46 ± 0.09	44	10.2	2.18	
9	6.0	1.80		45	10.2	1.50	
10	6.0	1.64		46	10.2	1.42	
11	6.0	0.91		47	10.2	1.68	
12	6.0	1.30		48	10.2	2.03	1.78 ± 0.11
13	6.0	0.75		49	11.3	2.22	
14	6.0	1.47		50	11.3	1.97	
15	6.0	1.25		51	11.3	1.73	
16	6.0	1.34		52	11.3	1.37	1.82 ± 0.18
17	6.0	1.19	1.30 ± 0.11	53	12.7	1.63	
18	7.9	1.73		54	12.7	1.61	
19	7.9	1.77		55	12.7	1.98	
20	7.9	1.39		56	12.7	2.06	
21	7.9	1.77		57	12.7	1.65	
22	7.9	1.72		58	12.7	1.17	
23	7.9	1.61		59	12.7	1.71	
24	7.9	1.98		60	12.7	1.72	
25	7.9	1.24		61	12.7	1.57	1.68 ± 0.09
26	7.9	1.11		62	14.0	2.31	
27	7.9	1.14		63	14.0	2.33	
28	7.9	1.29		64	14.0	1.91	
29	7.9	1.46		65	14.0	2.11	
30	7.9	1.65		66	14.0	1.87	
31	7.9	1.70		67	14.0	2.72	
32	7.9	1.84		68	14.0	2.26	
33	7.9	2.13		69	14.0	2.32	
34	7.9	2.77	1.67 ± 0.10	70	14.0	2.91	2.31 ± 0.11
35	9.3	1.15					
36	9.3	1.24	1.19 ± 0.04				

study. Intra-test variability for the experiment at 14 °C was, therefore, tested by using an analysis of variance (ANOVA) because the experiment contained enough data for this analysis. The ANOVA was designed to test whether Mg/Ca values for F-2 were significantly elevated compared to the F, F-1 and F-3 chambers.

In our dataset, Mg/Ca for F-2 is not significantly different ($F(3, 13) = 0.071$, $p > 0.10$), nor is there a systematic difference in Mg/Ca with size (200–580 µm, $R^2 = 0.03$, $p > 0.10$), indicating that there is no significant size-related impact on the Mg/Ca of *B. marginata* (Fig. 3). A positive and significant correlation between oxygen isotope values and size for *B. marginata*, possibly related to changes in growth rates, has been reported (Barras et al., 2010; Filipsson et al.,

2010). The absence of an ontogenetic effect in Mg/Ca while a significant effect on oxygen isotopes is recognized (Barras et al., 2010) fits the hypothesis that divalent cations (Ca and Mg) are transported to the site of calcification by a different mechanism than DIC (Erez, 2003; De Nooijer et al., 2009a; Dueñas-Bohórquez et al., 2011b).

4.3 Inter-individual Mg/Ca variability, low sensitivity and temperature uncertainty relations

Measured inter-individual variability in foraminiferal test carbonate Mg/Ca of cultured foraminifera is larger than for other elements (Dissard et al., 2010; Dueñas-Bohórquez et al., 2011a, b). The standard deviation in Mg/Ca between

Table 3. Mg/Ca standard deviation (σ , as percentage of the average) based on the measured standard deviation of each parameter during the experiments. Standard deviations from Table 1 are used and converted to Mg/Ca values using the same Mg/Ca parameter relations as (a) Dueñas-Bohórquez et al. (2009) ($0.11 \cdot \text{Salinity} + 1.00$), (b) Wit et al. (2012) ($\text{Mg/Ca} = a \cdot R \cdot e^{(b \cdot T)}$), and (c) Dueñas-Bohórquez et al. (2011b) ($0.0012 \cdot [\text{CO}_3^{2-}] + 1.50$). Not all experiments had Mg/Ca_{sw} data, experiments without Mg/Ca_{sw} measurements were assumed to have variability according to the average variability of the measured experiments.

Experiment	σ %		Mg/Ca _{sw} ^b	Carbonate ion ^c	Measured
	Temperature	Salinity ^a			
1	5.4	0.7	2.9	1.4	18.4
2	2.5	0.6	2.9	1.3	25.4
3	0.5	0.6	2.9	1.2	24.3
4	3.4	0.5	2.9	1.5	5.2
5	0.5	0.5	2.9	2.7	21.8
6	1.2	0.9	2.3	3.7	20.0
7	0.5	0.4	2.9	1.3	15.2
8	0.8	0.8	4.3	2.8	14.7

individuals is an order of magnitude larger than what can be explained on the basis of the analytical uncertainty (on average 11 % of the mean, Fig. 1). Besides the relatively small analytical errors, variability in Mg/Ca is caused by a combination of (1) variability in culture conditions (e.g. temperature, salinity, seawater Mg/Ca (Mg/Ca_{sw}) and carbonate ion concentration) and (2) inherent biological effects (i.e. the vital effect).

For our results, the first cause of variability in foraminiferal Mg/Ca can be quantified using the measured variability in seawater temperature, carbonate ion concentration, Mg/Ca and salinity (Table 1). For instance, the temperature for the experiment at 6 °C varied with a standard deviation of 0.5 °C over the course of the experiment (Table 1). Using Eq. (2), this temperature variability can be translated to a range in foraminiferal Mg/Ca and expressed as a percentage of the Mg/Ca based on the average of the recorded temperature. For the experiment conducted at 6 °C, an uncertainty of 0.5 °C in temperature thus introduces an uncertainty in the average Mg/Ca value of 2.5 % (Table 3). This uncertainty is the maximum offset caused by variability in temperature for this experiment. A similar procedure can be applied to all other experiments and for the uncertainties in salinity, Mg/Ca_{sw} and carbonate ion concentration using the data from Table 1 and the sensitivities from the concurring Mg/Ca parameter calibrations (Dueñas-Bohórquez et al., 2009, 2011b; Wit et al., 2012) (Table 3). From this table it can be concluded that in our culture experiment variability in Mg/Ca_{sw} and temperature explain most of the variability in Mg/Ca, whereas variability in the culture medium's salinity and [CO₃²⁻] play only a minor role.

Variability in environmental parameters affecting Mg/Ca other than temperature causes an uncertainty in Mg/Ca-based temperature reconstructions. This uncertainty depends on the sensitivity of the Mg/Ca–*T* calibration and therefore varies between species. The impact of changes in salinity, Mg/Ca_{sw} and carbonate ion concentration on the uncertainty

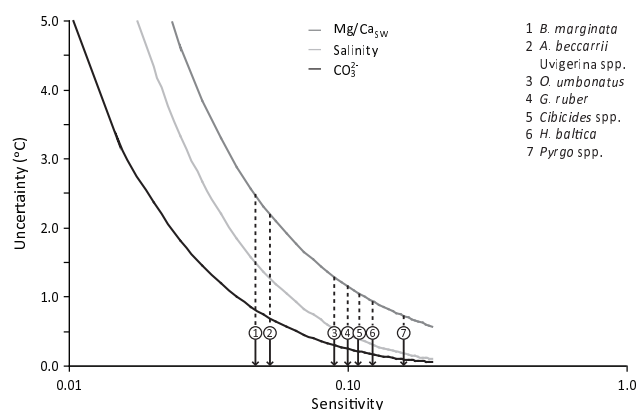


Fig. 4. Temperature uncertainty caused by variability in salinity (1), Mg/Ca_{sw} (0.6 mol mol⁻¹) and carbonate ion concentration (50 μmol kg⁻¹). Temperature uncertainties are calculated at 8 °C using the Mg/Ca–temperature calibration for *B. marginata* with a changing temperature sensitivity (exponential constant). Temperature sensitivities used for the different species are from Table 4. Mg/Ca parameter relations from a number of studies were used to calculate the uncertainty in temperature. Mg/Ca_{sw}: Wit et al. (2012). Salinity: Dueñas-Bohórquez et al. (2009). Carbonate ion concentration: Dueñas-Bohórquez et al. (2011b).

in reconstructed temperatures was calculated using different Mg/Ca parameter calibrations (Dueñas-Bohórquez et al., 2009, 2011b; Wit et al., 2012). Using the calibration for *B. marginata* (Eq. 2) with varying sensitivities (exponential constant), the impact on temperature uncertainties of changes in salinity (1), Mg/Ca_{sw} (0.6 mol mol⁻¹) and carbonate ion concentration (50 μmol kg⁻¹) at any given temperature can be calculated as a function of the sensitivity of the calibration (Fig. 4). It follows that at a low sensitivity this uncertainty in Mg/Ca translates into a larger temperature uncertainty, while at higher sensitivities the uncertainty is much smaller (Fig. 4).

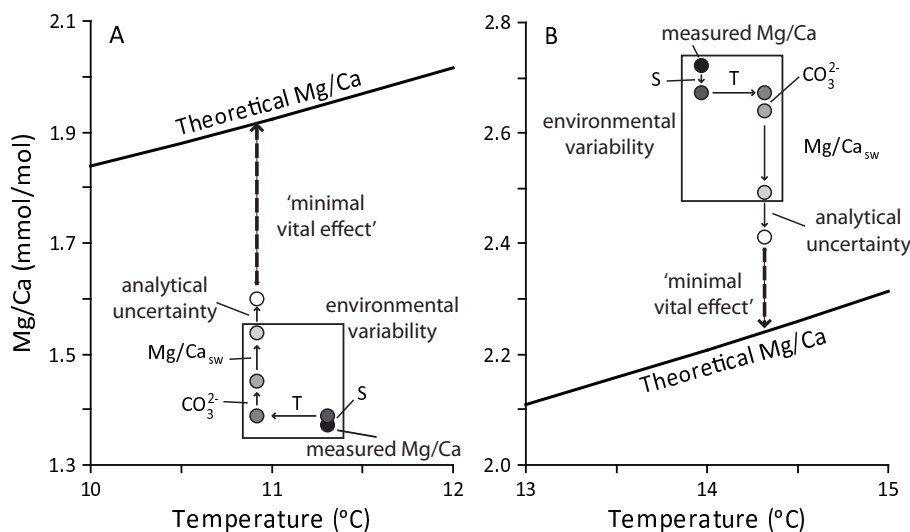


Fig. 5. Maximum correction for variability in culture parameters for measured Mg/Ca values of *B. marginata* no. 52 (A) and no. 67 (B) (numbers corresponding to Table 2). Corrections are based on the maximum variability of each experiment (Table 3). Variability was expressed as a correction in foraminiferal Mg/Ca using the same relations as for Fig. 4.

Table 4. The uncertainty in temperature (°C) as a temperature range ($T_{\max} - T_{\min}$) based on the averaged standard deviation (16.3 %) of the culture experiments. $T_{\max/\min}$ is based on the Mg/Ca value at a temperature plus or minus the uncertainty (σ/\sqrt{n}). Temperature values are calculated using the species-specific calibrations available for each species of foraminifera. (1) This study, (2) Toyofuku et al. (2011), (3) Elderfield et al. (2006), (4) Rathmann et al. (2004), (5) Anand et al. (2003), (6) Lear et al. (2002), (7) Rosenthal et al. (2011), (8) Wit et al. (2012).

Species	Sensitivity	N			
		10	20	30	40
<i>B. marginata</i> ¹	0.045	2.29	1.62	1.32	1.14
<i>A. beccarii</i> ²	0.053	1.95	1.38	1.12	0.97
<i>Uvigerina</i> spp. ³	0.053	1.95	1.38	1.12	0.97
<i>O. umbonatus</i> ⁴	0.090	1.15	0.81	0.66	0.57
<i>G. ruber</i> ⁵	0.100	1.03	0.73	0.60	0.52
<i>Cibicides</i> spp. ⁶	0.109	0.95	0.67	0.55	0.47
<i>H. baltica</i> ⁷	0.123	0.84	0.59	0.48	0.42
<i>Pyrgo</i> spp. ⁸	0.160	0.64	0.46	0.37	0.32

The second source for the large inter-individual variability is the vital effect, caused by variability in the efficiency and rate of various cell physiological processes that constitute the calcification pathway (Erez, 2003; Bentov and Erez, 2006; De Nooijer et al., 2009a). The impact of these processes can be estimated by correcting the observed Mg/Ca values for the maximum analytical error and the environmentally induced offsets calculated above. If the vital effect and the error of calibration equation would be zero, every measured foraminiferal Mg/Ca value would fit the calibrated regression

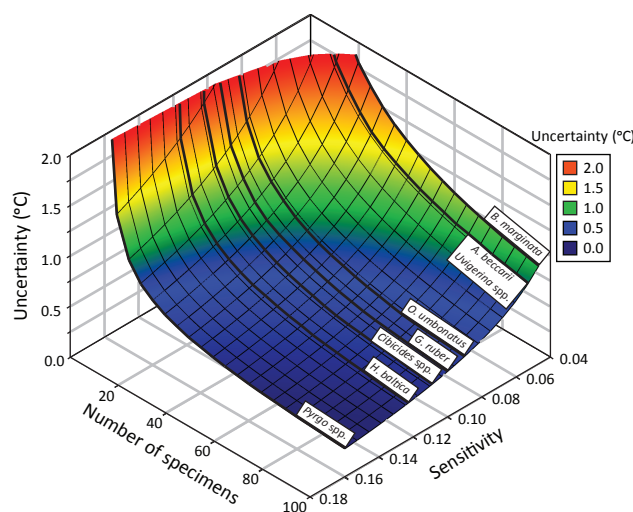


Fig. 6. Relation between sensitivity of a temperature calibration, the number of specimens analyzed and uncertainty in temperature based on an average standard deviation in a population of foraminifera of 16.3 % of the average.

line (Fig. 5). Although impact of the vital effect cannot be determined directly, we can estimate its magnitude. The two examples in Fig. 5 show how the three types of variability in foraminiferal test Mg/Ca are related to the measured Mg/Ca values. The total range in test carbonate Mg/Ca caused by uncertainties in the four culture parameters over this experiment explains part of the observed inter-individual variability (Fig. 2, Table 3). The remaining component, expressed as the distance of the corrected Mg/Ca to the calibration curve, reflects the offset caused by the vital effect (Fig. 5, Table 3).

The estimated vital effect may be larger than plotted, since we assume that analytical and environment-induced offsets are all lower than the measured variability in foraminiferal Mg/Ca, i.e. they all work in the same “direction” (Fig. 5).

The impact of inter-individual variability on the accuracy of paleo-temperature reconstructions can be calculated by assuming the standard deviation in the Mg/Ca values (measure of variability) from this culture study is applicable to other foraminiferal species as well. The average variability (standard deviation) within one temperature experiment for a population of *B. marginata* is 16.3 % (Table 2), which is similar to percentages found in other foraminiferal species (Sadokov et al., 2008; Dissard et al., 2010; Wit et al., 2010; Dueñas-Bohórquez et al., 2011a). This percentage can be used to calculate a standard error (σ/\sqrt{n}) of the average Mg/Ca value at any given temperature for a number of foraminiferal Mg/Ca–temperature calibrations. This results in a temperature uncertainty (range of $(\text{Mg/Ca} + \sigma/\sqrt{n}) - (\text{Mg/Ca} - \sigma/\sqrt{n})$ and thus expressed as a relative % of measured Mg/Ca), which is thus independent of the absolute temperature due to the exponential relation between Mg/Ca and temperature but is dependent on the number of foraminiferal specimens analyzed (N) (Table 4). This can be done for a number of foraminiferal species for which the Mg/Ca–temperature calibration is known. The relation between temperature uncertainty and sensitivity can now be calculated for each number of specimens analyzed (N) based on Table 4 (Eq. 3).

$$\text{Temperature uncertainty} = c/\text{sensitivity} \quad (3)$$

The constant c , subsequently, varies with the number of individuals analyzed (N) for each temperature uncertainty and can be numerically expressed (Eq. 4).

$$c = 0.33 \cdot N^{-0.50} \quad (4)$$

Combining Eqs. (3) and (4) results in:

$$\text{Temperature uncertainty} = (0.33 \cdot N^{-0.50})/\text{sensitivity}. \quad (5)$$

With this equation, the number of specimens that need to be measured for a certain temperature uncertainty as a function of the sensitivity (exponential constant) of the used Mg/Ca–temperature calibration (Fig. 6) can be determined. The value of 0.33 is in fact a doubling of the determined relative standard deviation used to calculate the temperature uncertainties. For species with a relatively low temperature sensitivity, more specimens need to be analyzed to obtain the same temperature uncertainty (Table 5). For example, 93 individuals of *B. marginata* need to be analyzed to obtain an uncertainty in temperature of 0.75 °C (Table 5), which is often impractical due to foraminiferal scarcity in geological samples and time needed for elemental analyses. Alternatively, the minimum sensitivity needed to for a certain accuracy in reconstructed temperature can also be expressed as a function of the number of individuals available for analyses by

using Eq. (5) (Table 6). If, for instance, an accuracy of 1 °C is desirable and there are 20 individuals available for analyses, the sensitivity of the calibration should not be below 0.0738 (Eq. 5, Table 6). This means that a reconstruction based on species such as *B. marginata*, *A. beccarii* and *Uvigerina* spp. will not provide the required precision when 20 or less specimens are analyzed.

4.4 Controls on sensitivity

The sensitivity of a calibrated Mg/Ca–temperature relationship is crucial for the accuracy of reconstructed paleotemperatures. Increasing the number of specimens can compensate for the large uncertainty when using low sensitivity species, although practicality limits this approach (Eq. 5, Fig. 6). The accuracy will ultimately depend on the combination of analytical errors, the vital effect and absolute calcitic Mg concentration, as an offset in Mg/Ca will have a relatively large impact on foraminifera with low Mg concentrations. Species that have a similar sensitivity have calibration curves with a comparable steepness (Fig. 7), but not necessarily the same Y-axis intercept. There appear to be three distinct sensitivities in the Mg/Ca response to temperature (Fig. 7). The first group includes only the calibration for the miliolid benthic foraminifer *Pyrgo* spp. with a sensitivity of 0.16. The sensitivity of the second group varies between 0.09–0.13 and contains the foraminifera *Oridorsalis umbonatus*, *Cibicides* spp., *Globigerinoides ruber* (and most other planktonic species) and *Hyalinea balthica*. The third group entails *B. marginata*, *Uvigerina* spp. and *Ammonia beccarii*, which all have Mg/Ca– T sensitivities ranging from 0.04–0.06.

The miliolid benthic foraminifer *Pyrgo* spp. is the only species studied so far that belongs to the group with high sensitivity in Mg incorporation with respect to increasing temperature. Miliolid foraminifera calcify using a different calcification mechanism than that adopted by hyaline species (low and intermediate group) (Erez, 2003; de Nooijer et al., 2009a). Although the exact influence of this difference in calcification mechanisms on the sensitivity is unknown, it is likely that their different calcification pathways cause the difference in sensitivity between hyaline and porcelaneous foraminifera.

The mechanisms responsible for the distinction between low and intermediate groups are unknown, but may be related to their evolutionary history or ecological strategies. Discrimination against Mg during calcification seems taxonomically related at least at a high level, since all known miliolid species produce calcite with high Mg/Ca ($>50 \text{ mmol mol}^{-1}$), while only some hyaline species are producing high Mg calcite (Toyofuku et al., 2000). For hyaline species, three different clades were recognized based on 26 SSU (small subunit) sequence analyses (Schweizer et al., 2008). Foraminifera with the lowest temperature sensitivity have representatives from all three clades, indicating that the Mg/Ca– T sensitivity

Table 5. Number of individuals needed to obtain a given uncertainty in temperature, based on the sensitivity of a Mg/Ca–temperature calibration and the averaged standard deviation of 16.3 %. Uncertainty is expressed as a range (max–min) around the average reconstructed temperature. (1) This study, (2) Toyofuku et al. (2011), (3) Elderfield et al. (2006), (4) Rathmann et al. (2004), (5) Anand et al. (2003), (6) Lear et al. (2002), (7) Rosenthal et al. (2011), (8) Wit et al. (2012).

Species	Sensitivity	Uncertainty (°C)					
		2.0	1.5	1.0	0.75	0.50	0.25
<i>B. marginata</i> ¹	0.045	13	23	52	93	210	837
<i>A. beccarii</i> ²	0.053	9	17	38	67	151	604
<i>Uvigerina</i> spp. ³	0.053	9	17	38	67	151	604
<i>O. umbonatus</i> ⁴	0.090	3	6	13	23	52	210
<i>G. ruber</i> ⁵	0.100	3	5	11	19	42	170
<i>Cibicidoides</i> spp. ⁶	0.109	2	4	9	16	36	143
<i>H. balthica</i> ⁷	0.123	2	3	7	12	28	112
<i>Pyrgo</i> spp. ⁸	0.160	1	2	4	7	17	66

Table 6. Sensitivity (b in Eq. 1) as a function of a given uncertainty in reconstructed temperature and number of specimens (N) used for Mg/Ca analyses. Uncertainty is expressed as a range (max–min) around the average reconstructed temperature.

N	Uncertainty (°C)					
	2.0	1.5	1.0	0.75	0.50	0.25
10	0.0522	0.0696	0.104	0.139	0.209	0.417
20	0.0369	0.0492	0.0738	0.0984	0.148	0.295
30	0.0301	0.0402	0.0602	0.0803	0.121	0.241
40	0.0261	0.0348	0.0522	0.0696	0.104	0.209

may not be (fully) related to taxonomic relationships within foraminifera.

Alternatively, differences in ecological strategies might provide an explanation on the species-specific Mg sensitivity to temperature. Foraminifera inhabit environments with contrasting food regimes. The shallow to deep infaunal species *B. marginata* is mainly found at locations relatively rich in organic matter (Jorissen, 1987; Jorissen et al., 1992). The benthic cosmopolitan *Ammonia beccarii*/*A. tepida* (Hayward et al., 2004) inhabits shallow marine to brackish environments, often very rich in organic matter (Murray, 1968). The third species with a low Mg– T sensitivity, *Uvigerina* spp., is commonly found in mesotrophic environments, often characterized by fine-grained sediments with elevated organic content (Van der Zwaan et al., 1986), and lives in shallow infaunal depth habitats (Van der Zwaan et al., 1986; Fontanier et al., 2002; Schweizer et al., 2005).

The group of species with intermediate sensitivity of Mg incorporation to temperature change contains the benthic species *Cibicidoides* spp., *O. umbonatus* and *H. balthica* and the planktonic species *G. ruber*. Most species within the genus *Cibicidoides* are epifaunal to shallow infaunal, living close to or at the sediment–water interface, commonly in

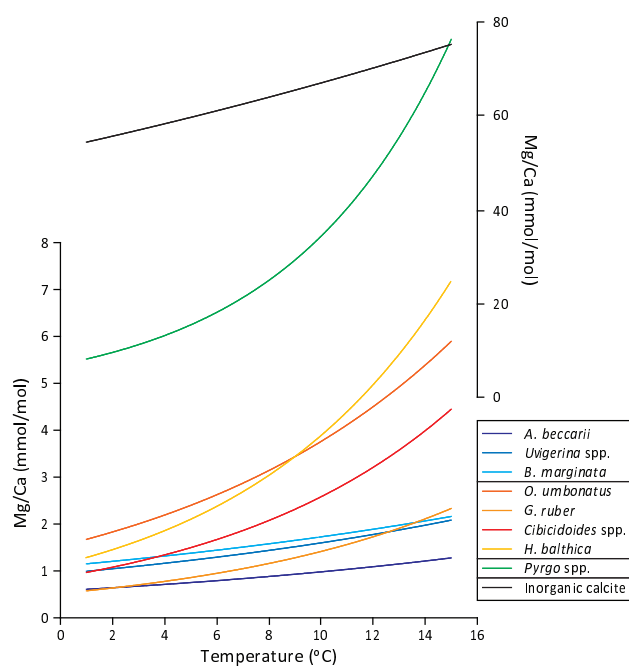


Fig. 7. Different Mg/Ca–temperature calibrations for a number of foraminiferal species (Table 5) and inorganic calcite (black line). Calibrations with a similar Mg sensitivity to temperature have a comparable steepness of the calibration slope. Note that the calibration for *Pyrgo* spp. and inorganic calcite are plotted on a secondary y-axis. Mg/Ca values for these two calibrations are a magnitude of order larger compared to the other calibrations.

mesotrophic to oligotrophic well oxygenated environments with relatively stable physio-chemical parameters (Jorissen et al., 1998; Gooday, 2003). The benthic foraminifer *O. umbonatus* has an epifaunal to shallow infaunal depth habitat and is mainly found in oligotrophic deep-sea environments (Jorissen et al., 1998; Rathmann et al., 2004). *Hyalinea balthica* is a shallow infaunal living benthic foraminifer, typical

for upper bathyal environments with mesotrophic conditions, although in some studies an opportunistic behavior has been described (Hess and Jorissen, 2009; Rosenthal et al., 2011). The planktonic foraminifer *G. ruber* is a shallow dwelling (living in the upper 50 m of the water column), symbiont-bearing species, living preferentially in oligotrophic surface waters (Hemleben et al., 1989). In summary, all species of this group are typical for oligotrophic to mesotrophic environments.

All species of the low sensitivity group show some characteristics typical of an opportunistic lifestyle. *B. marginata* may reach very high densities in eutrophic settings (e.g. Jorissen, 1987; Jorissen et al., 1992), and is one of the few deep-sea species which reproduces in laboratory conditions (Barras et al., 2010). *Ammonia* spp. contain dominant taxa in a wide range of coastal ecosystems, where they tolerate large salinity and temperature variations. *U. peregrina* and *U. mediterranea* show a reproductive and growth response to phytoplankton bloom events in the Bay of Biscay (Fontanier et al., 2003, 2006). In the literature, all these taxa are generally considered as opportunists.

However, also for some species of the intermediate sensitivity group, an opportunistic behavior is suspected. This is clearly the case for *Hyalinea balthica*, which has been described with very high densities in eutrophic submarine canyon environments (Hess and Jorissen, 2009). But also *Cibicides* species sometimes occur in high densities, and dominate the foraminiferal fauna (e.g. Koho et al., 2008). Conversely, both *G. ruber* and *O. umbonatus* are always considered as oligotrophic taxa, without any opportunistic tendency. Summarizing, there is indeed a tendency for the low sensitivity taxa to be more opportunistic than the intermediate sensitivity taxa, but the separation between the two groups is not as clear as we would hope. A better knowledge about the ecological strategies of these species is necessary to confirm that the lower temperature sensitivity is indeed the result of a more opportunistic lifestyle.

5 Conclusions

LA-ICP-MS-measured Mg/Ca in cultured *B. marginata* correlates with temperature, although the sensitivity of Mg incorporation to temperature is low. The calibration is not hindered by any ontogenetic effects. The inter-individual variability within this calibration is too large to be caused by variations in culture parameters over the course of the experiment, but is tied to an intrinsic “vital effect” within the calcification process.

This inter-individual variability influences the practicality of the Mg/Ca-thermometer, especially impacting calibrations with a low sensitivity. Foraminifera with this low sensitivity are, therefore, not ideal for reconstructing paleotemperatures due to associated large uncertainties or large

sample sizes needed for an accurate reconstruction of temperature.

Although the biochemical mechanism responsible for the low sensitivity is yet unknown, it appears that foraminiferal species with this low sensitivity (*B. marginata*, *A. beccarii* and *Uvigerina* spp.) are living in more eutrophic environments. Foraminifera mainly living in oligotrophic to mesotrophic environments should, therefore, be used when reconstructing temperatures with the help of the Mg/Ca temperature proxy. Examples of such taxa are *Cibicides* spp., *O. umbonatus*, and *G. ruber* but especially *H. balthica* and *Pyrgo* spp.

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