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Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures

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Abstract—Though many studies on the Mg contents in the calcitic tests of foraminifers exist, the processes controlling its uptake are still a matter of debate. Laboratory cultures offer an excellent opportunity to reveal these mechanisms. The Mg concentrations within single chambers of the planktic foraminifer *Globigerinoides sacculifer* (BRADY) maintained under controlled laboratory conditions were measured (1) at variable temperatures (19.5–29.5°C) and constant salinity and (2) at variable salinity (22–45‰) and constant temperature.

The experimental results suggest that under natural conditions, temperature is the leading mechanism controlling the Mg/Ca ratio. Temperature and magnesium are related proportionally. A temperature increase of ca. 10°C gives rise to an increase of the magnesium concentrations of ca. 130%. Drastic (unnatural) salinity changes dominate the effects of temperature. A 110% change in the Mg/Ca ratio was observed when salinity was elevated or reduced by more than ca. 10‰. Specimens which underwent gametogenesis reveal significantly higher Mg concentrations than specimens that did not release gametes.

Partition coefficients for Mg in foraminiferal calcite are orders of magnitude lower than values from inorganically precipitated calcite. When comparing observed Mg/Ca ratios of foraminiferal tests with predicted Mg/Ca ratios calculated according to empirical equations, it becomes evident that foraminiferal tests are undersaturated with respect to Mg for the water temperature they have experienced. Apparently, foraminifers are capable of controlling their Mg concentration. The physiological processes presumably responsible for such depressed Mg/Ca ratios appear to be temperature-controlled as deduced from the close relationship of the observed Mg/Ca ratios and water temperature.

This study demonstrates that variations in temperature and salinity are definitely reflected in the Mg content of foraminiferal tests. Magnesium may thus serve as a paleo-proxy for past surface water temperatures, as long as postdepositional changes and salinity variations are of subordinate importance or can be excluded.

1. INTRODUCTION

Calcium in the calcitic skeletons of marine organisms can be substituted by many divalent cations such as Mg, Cd, Mn, Fe, Co, Zn, and Ni. This paper focusses on Mg in foraminiferal tests and assesses its relationship to water temperature and salinity. Magnesium is a conservative element, i.e., the Mg/Ca ratio is constant in the present-day ocean with depth and there is no ocean to ocean fractionation (e.g., Broecker and Peng, 1982). Despite many investigations on Mg in calcareous foraminiferal tests, the views on the processes controlling its uptake remain controversial. From the geographic distribution of skeletal marine magnesium-calcite, Chave (1954) recognized a covariance of the Mg content and latitude and thus, suggested a relationship between the substitution of Ca by Mg and water temperature. According to De Deckker and Corriège (1992), the incorporation of Mg in shells of benthic ostracods is temperature-related. Izuka (1988) showed that the correlation of Mg in recent benthic foraminifers with water depth parallels bottomwater temperature. Also, Puechmaille (1981, 1985) observed a temperature control on the Mg concentrations in planktic foraminifers. Cronblad and Malmgren (1981) reported downcore Mg and Sr variations in planktic foraminiferal tests, which correlate to late Quaternary climatic oscillations.

In contrast, magnesium concentrations in planktic foraminifers (*Globigerinoides ruber* (d'Orbigny), *Globorotalia inflata* (d'Orbigny), *Globorotalia truncatulinoides* (d'Orbigny)) from Central Atlantic surface sediments published by Krinsley (1960) do not correlate with environmental parameters. Savin and Douglas (1973) could not discover any correlation between isotopic temperature and salinity and the magnesium concentration within a single planktic foraminiferal species. From investigations of Mg/Ca ratios in *Globigerinoides sacculifer* (Brady) and *Orbulina universa* d'Orbigny, Delaney et al. (1985) concluded that additional environmental parameters (light, nutrient content, and growth rate) affect the calcium substitution by Mg. Recently, Rosenthal and Boyle (1993) pointed out that calcite dissolution may significantly alter the Mg concentrations within foraminiferal tests, and thus, may prevent the applicability of Mg as a tracer for water mass properties.

An important step towards the paleo-reconstruction of the world oceans on the basis of chemical elements within biogenic carbonate is to determine the relationship between element incorporation into tissue and/or hard parts and water mass properties. First, experimental determinations concerning the effects of seawater chemistry and temperature on minor element incorporation in foraminiferal tests were per-

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formed by Delaney et al. (1985). Although Delaney et al. (1985) concluded that the Mg/Ca ratio in foraminiferal tests is not solely controlled by temperature, they demonstrated a definite trend with temperature. The objective of this study is to further pursue the investigation of the incorporation of magnesium into tests of *G. sacculifer* under controlled laboratory conditions.

The high-resolution microprobe technique presented here allows the internal heterogeneity of magnesium in chamber walls and single chambers to be demonstrated. From this, distinct geochemical changes during the life cycle (e.g., influence of gametogenesis) may be traced. Further, the relationship between the foraminiferal Mg content, ecological parameters (temperature, salinity), and processes altering the chemical composition of the foraminiferal calcite after deposition (e.g., diagenesis) can be deciphered.

2. FORAMINIFERAL SPECIMENS, LABORATORY CULTURE, AND ANALYTICAL PROCEDURES

2.1. Foraminiferal Species Selected for Analyses

The planktic foraminifer *G. sacculifer* is a spinose species with symbiotic dinoflagellates inhabiting the shallow tropical and subtropical areas of the world oceans. Prevailing habitat temperatures are 20–30°C. Salinity may largely affect the occurrence of *G. sacculifer* (Hemleben et al., 1987) and its abundance is significantly depressed during low salinity times. Reproduction is linked to the lunar cycle (Bijma and Hemleben, 1994).

2.2. Culture Protocol

The experiments reported in this paper were originally carried out to study the morphological and physical response of *G. sacculifer* under controlled laboratory conditions with temperature and salinity as experimental variables (Hemleben et al., 1987; Bijma et al., 1990). Archived specimens from these experiments were used to investigate the effect of temperature and salinity on the incorporation of magnesium into the shell. At the time the experiments were carried out, we did not intent to calculate the partition coefficient for Mg uptake. Therefore, the chemical composition of the culture water was not monitored. Because the experiments were run parallel and over a time period of several years we assume that slight differences in the Mg concentration are averaged out.

The culture protocols for both sets of experiments are slightly different and were described in more detail in Hemleben et al. (1987; 1989) and Bijma et al. (1990). The first set of experiments was carried out at the Bellairs Research Institute, Barbados, West Indies, during the years 1980 through 1984 (temperature experiments: 19.5°C–29.5°C). The salinity experiments (26‰–44‰) were run in Barbados (between 1985 and 1987) and later at the Caribbean Marine Biological Institute (CARMABI), Curaçao, Netherlands Antilles, in 1988.

Globigerinoides sacculifer were collected individually in glass jars by SCUBA divers at 3–8 m depth about 2 miles off the west coast of Barbados and Curaçao. In the laboratory, their maximum test diameter was determined. Shell lengths ranged from 110 μm (the smallest size visible to divers) to approximately 500 μm. We attempted to place specimens of similar sizes into each treatment. All specimens were cultured individually in glass vials containing ca. 40 ml of culture water, which was obtained from the collection site. In the temperature experiments we used unfiltered water. In the salinity experiments the water was filtered (0.45 μm pore size Millipore filter).

Because the salinity at the collection site off the coast of Barbados ranged from 31.2‰ to 36‰, the specimens used in the temperature experiments were divided into two groups cultured in water with a salinity higher or lower than 34.5‰. The first group called the 36‰ group roughly coincides with the average salinity of the winter season and the second group (33‰) with the summer season. Temperature at the collection site varied between 26.2°C to 29.7°C during three years of observation (Hemleben et al., 1987).

The culture vessels were placed in temperature controlled water baths adjusted to 19.5°, 23.5°, 26.5° and 29.5°C. Temperature deviations were in the order of ±0.5°C. The salinity was usually constant over the course of the experiments but increased by 0.5–0.8‰ in the 29.5°C bath due to evaporation. The salinity experiments were conducted at 26.5°C. The different salinities were obtained by dilution with distilled water or by evaporation of natural seawater at 50°C. Precipitate as a result of evaporation was never observed. The foraminifers were acclimated to the target salinity by several transfers to lower or higher salinity water. The salinity difference between consecutive steps was approximately 3‰. Since more steps were generally needed to attain the final salinity, the time interval between transfers was 3 hrs. Transfers where carried out with a wide-mouth pipette.

Salinities were measured with an EIL (type M.C.5) salinometer calibrated with a dilution series of standard seawater (I.A.P.O. Standard seawater Service, Charlottenlund Slot, Denmark). The experiments were carried out under white and blue fluorescent light (Philips TL 40W-55, Osram L 40W-64, light tubes) with an intensity of 60–70 $\mu Em^{-2}sec^{-1}$ in a 12:12 light/dark cycle. These light conditions closely simulate the quality and the intensity of the underwater light west of Barbados at a depth of 20–30 meters (Hemleben and Spindler, 1983).

The foraminifers were fed a single, one day old *Artemia nauplius* (brine shrimp) every day, beginning on the day after collection. The individuals were examined daily using a Leitz inverted microscope. Information was recorded on chamber formation (Table 1), floating behaviour, spine length, or in the absence of spines on rhizopodial activity.

The cultures were terminated after undergoing gametogenesis (GAM) or death of the specimen, normally between 4–15 days after collection. Impending gametogenesis is morphologically signalled by discarding of spines and often by additional calcification (Spindler et al., 1978; Bé, 1980; Duplessy et al., 1981). Thus, we distinguished between DEAD (spines not discarded) and GAM (spines discarded) specimens. Finally, we remeasured the maximum test diameter and recorded the shape of the last chamber, differentiating between a normal chamber (NOR) defined as being larger than the previous one, a kummerform (KUM) chamber being equal to or smaller than the previous chamber, and finally a sac-like chamber (SAC). For analysis with the electron microprobe, only chambers secreted in culture were used.

2.3. Data Analysis

Selected foraminifers were rinsed with distilled water and embedded in resin. Ground and polished, relief-free sections of foraminiferal tests were then prepared to reveal fresh calcite surfaces of chamber walls.

The geochemical analyses were carried out on a wavelength-dispersive, automated four-spectrometer (with diffracting crystals LiF, TAP, and PET) Cameca electron microprobe applying an accelerating voltage of 15 kV (Institute for Mineralogy and Petrography at Kiel University). A beam current of 15 nA proved to be optimal. A counting time of 20 sec per element peak and 10 sec for the background before and after the peak measurement was chosen. Constancy of the beam current was 1% per 24 hours. After each analysis, the beam current was measured. Depending on the drift, beam stabilisation was performed every 0.5 seconds. In this study, the electron beam was focussed on a spot approximately 2–4 μm in diameter. Element concentrations in the ppm-range were detected quantitatively, calculated stoichiometrically in oxide form, and reported as ppm. Mg-Periclase (synthetic) and Ca-Wollastonite (natural) served as standards.

The aim of this study was to reveal the changing chemical composition of foraminiferal calcite during test growth. In this respect, the electron microprobe analytical technique is of great advantage, since the electron beam can be directly placed in freshly prepared calcite. Single chambers grown under controlled temperature and salinity conditions in the laboratory were measured and subsequently compared to chambers, which grew prior to laboratory experiments during natural conditions.

TABLE 1. MgO-concentrations (ppm) in tests of *G. sacculifer* maintained in laboratory culture experiments. The mean magnesium concentrations (MgO-mean) are derived from averaging single spot analyses (see number of analyses). Minimum and maximum magnesium concentrations, standard deviations, and Mg/Ca ratios are indicated. Growth rates and relative errors are added for the temperature experiments.

Data belonging to Fig. 2

T = variable, S = const.			# of chambers				# of				Mg/Ca
# of sample	Salinity (PSU)	Temp. (°C)	grown in cult.	Kind of chamber	Remarks	MgO-mean	analyses	Min. MgO	Max. MgO	STD	*10-3
Ch-F	36	23,5	3 - 5	n.d.	GAM	1531	8	1190	2090	281	n.d.
Ch-F-1	36	23,5	3 - 5	n.d.	GAM	1413	9	610	1910	484	n.d.
Ch-F-2	36	23,5	3 - 5	n.d.	GAM	1563	8	1090	2440	405	n.d.

Data belonging to Fig. 3

S = variable, T = const.			# of chambers				# of				Mg/Ca
# of sample	Salinity (PSU)	Temp. (°C)	grown in cult.	Kind of chamber		MgO-mean	analyses	Min. MgO	Max. MgO	STD	*10-3
7679	23	26,5	1	NOR	NO GAM	960	5	664	1665	406	1,43
7687	23	26,5	1	NOR	NO GAM	1068	5	827	1603	315	1,58
7689	23	26,5	1	NOR	GAM	2783	8	2226	3697	456	3,95
7912	26	26,5	1	NOR	GAM	2955	8	1287	3891	1028	4,19
7913	26	26,5	1	NOR	NO GAM	593	8	398	800	180	0,84
7914	26	26,5	1	NOR	NO GAM	559	8	245	796	208	0,79
8135	41	26,5	2	SAC, KUM	NO GAM	1255	8	786	1634	332	1,77
8137	41	26,5	3	NOR	NO GAM	1532	8	531	3146	1084	2,13
8138	41	26,5	2	NOR	NO GAM	1052	7	848	1399	195	1,49
7703	44	26,5	1	KUM	GAM	4197	8	2431	6036	1434	5,93
7704	44	26,5	1	KUM	GAM	3680	8	2696	5444	876	5,18
8301	45	26,5	1	KUM	NO GAM	1243	8	980	1460	154	1,74

Data belonging to Fig. 5

T = variable, S = const.			# of chambers				# of				Mg/Ca			Rel. error
# of sample	Salinity (PSU)	Temp. (°C)	grown in cult.	Kind of chamber	Remarks	MgO-mean	analyses	Min. MgO	Max. MgO	STD	*10-3	Growth rate	STD	*10-3
1	36	19,5	3 - 5	n.d.	36‰ group	1132	13	510	1820	382	1,55	36,9	7,8	0,15
1 parallel	36	19,5	3 - 5	n.d.	36‰ group	1036	13	410	1740	368	1,42	36,9	7,8	0,14
2	36	23,5	3 - 5	n.d.	36‰ group	1390	13	950	2770	508	1,91	48,8	10,7	0,19
3	36	26,5	3 - 4	n.d.	36‰ group	1734	13	1340	2440	358	2,40	50,4	10	0,14
4	36	29,5	3 - 4	n.d.	36‰ group	2222	13	1290	3050	512	3,08	50,5	6,9	0,20
5	33	19,5	3 - 4	n.d.	33‰ group	873	13	380	1740	410	1,20	34,5	8,7	0,16
6	33	23,5	3 - 4	n.d.	33‰ group	1274	13	760	2890	609	1,74	49,1	10,8	0,23
7	33	26,5	3	n.d.	33‰ group	2002	13	1390	2790	389	2,77	49,7	12,6	0,15
8	33	29,5	3 - 4	n.d.	33‰ group	2523	12	1560	3480	648	3,50	47,8	10,5	0,26

Data belonging to Fig. 6

S = variable, T = const.			# of chambers				# of				Mg/Ca
# of sample	Salinity (PSU)	Temp. (°C)	grown in cult.	Kind of chamber		MgO-mean	analyses	Min. MgO	Max. MgO	STD	*10-3
7913	26	26,5	1	new chamber	NO GAM	641	8	408	776	125	n.d.
7913	35	26,5	1	old chamber	NO GAM	1533	8	1001	2257	473	n.d.
7704	44	26,5	1	new chamber	GAM	2937	9	1614	4085	801	n.d.
7704	35	26,5	1	old chamber	GAM	1575	10	919	2114	428	n.d.

n.d. = no data or unknown

n.d. = no data or unknown.

The microprobe analysis reveals that element concentrations within single foraminiferal chambers are highly variable. A representative concentration is thus derived by averaging several individual measurements per chamber. Routinely, five spot analyses were carried out on the final chambers of each of three foraminiferal tests randomly picked from a sample. The average magnesium concentration of each sample, which is finally taken for interpretation, is, therefore, the result of a maximum of 15 Mg signals. From the culture experiments with variable salinities (23–45‰), only single specimens were available. In this case, as many as possible spot analyses were performed within the final chambers and compared to preceding chambers.

The range of the resulting small geochemical datasets ($n < 20$) is presented as box and whiskers plots (Tukey, 1979, Kürzl, 1988). The box reaches from quartile Q (.25) to quartile Q (.75), thus including 50% of the data. The median value is indicated as a bold line. Lengths of lines to the right and to the left of the box (whiskers) amount maximum 3 * IQR/2 (IQR = Interquartile range) and delineate maximum and minimum values. Data points outside these whiskers are defined as outliers and are excluded from the calculation of the arithmetic mean. Most important statistical values are presented in Table 1. The magnesium raw data, from which the mean concentrations were calculated, will be offered in diskette format upon request.

To investigate whether the relatively small number of spot analyses performed was sufficient to reflect the true sample concentration, we considered the following (Nürnberg, 1995): the median values derived from parallel measurements on the same tests of *N. pachyderma* sin. averaged (1) from as large a number of spot analyses as possible ($n = 49$; mean = 222 ppm; median = 220 ppm; standard error = 17 ppm) and (2) calculated from the ca. 15 measurements routinely performed on three tests ($n = 14$; mean = 214 ppm; median = 220 ppm; standard error = 20 ppm) were calculated. These independant measurements correspond quite well implying that no statistically significant difference exists on the 5% level. We conclude, therefore, that the spot analyses ($n \approx 15$) presented here should be sufficient to derive a representative and reproducible element concentration for the sample.

2.4. Reproducibility, Accuracy, and Sample Contamination

Following the statistical procedures outlined above, the reproducibility of Mg measurements is good ($r = 0.9$, Nürnberg, 1995). The precision is about 10%. Deviations from the regression line may be explained by inhomogeneously distributed elements within the calcitic matrix. The standard deviation is ca. 30 ppm at most (Fig. 1). Absolute changes in magnesium concentrations, which are ultimately considered for our interpretations, by far exceed the average deviation.

The accuracy of magnesium measurements in tests of *G. sacculifer* can not directly be assessed from the microprobe methodology. Since we did not perform wet-chemical analyses parallel to the microprobe measurements (e.g., AAS, ICP), the accuracy can only be evaluated from literature data. The range of Mg/Ca ratios from 1.2×10^{-3} to 3.5×10^{-3} derived from this study (mean = 2.17×10^{-3}, standard deviation = 0.8×10^{-3}) is somewhat lower than Mg/Ca ratios

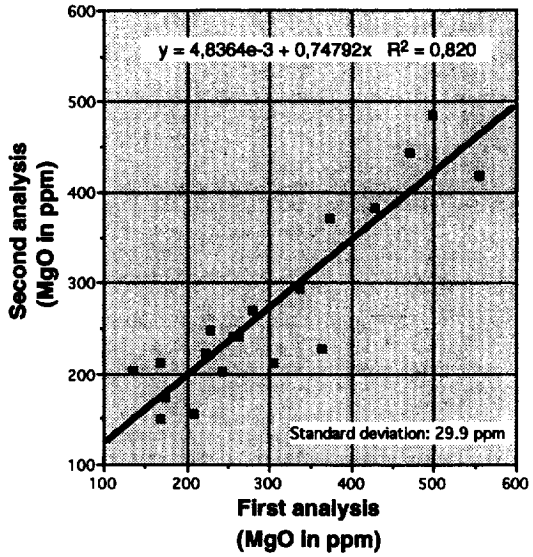

FIG. 1. The reproducibility of magnesium analyses by microprobe is tested by parallel measuring samples. Measurements were performed in the same tests of *N. pachyderma* sin., *O. umbonatus* and *C. wuellerstorfi* from sediment cores and sediment surface samples from the North Atlantic and the Norwegian-Greenland Sea. The standard deviation is ca. 30 ppm.

presented by Delaney et al. (1985) from Indian Ocean core tops (2.01×10^{-3} to 4.58×10^{-3}, mean = 3.96×10^{-3}, standard deviation = 0.83×10^{-3} at ca. 25–28°C) and sediment traps (3.23×10^{-3} to 3.56×10^{-3}, mean = 3.40×10^{-3}, standard deviation = 0.18×10^{-3} at ca. 27°C), and lower than Mg/Ca ratios presented by Rosenthal and Boyle (1993) from Sierra Leone core tops (3.41×10^{-3} to 4.38×10^{-3}, mean = 3.98×10^{-3}, standard deviation = 0.29×10^{-3} at ca. 26.5°C). However, when considering only those values cultured at >26°C, the mean value rises to 2.93×10^{-3} (standard deviation = 0.47×10^{-3}), which is at least in good accordance to the sediment trap data of Delaney et al. (1985). Still, a direct comparison of these datasets is problematic, since different analytical methods were applied, and because foraminiferal tests were taken from culture experiments vs. core tops and sediment traps.

Alumosilicate detritus, grinding powder, adsorbed hydrated iron, barium, and manganese-phases, organic material, and clay minerals can severely contaminate the samples and may, therefore, alter the trace analytical investigation (Goldberg, 1954; Emiliani, 1955; Krinsley, 1960; Lipps and Ribbe, 1967; Savin and Douglas, 1973; Turekian et al., 1973; Bender et al., 1975). Most contaminating phases adhere to the outer foraminiferal tests and are simply avoided by focussing the electron beam directly on freshly prepared calcite surfaces. This also eliminates diagenetically influenced parts like pores and edges. In addition, microprobe measurements are carried out in the interior of the solid phase rather than on the surface. Thus, the influence of contamination on the microprobe analyses is mostly eliminated (see also Nürnberg, 1995).

In order to evaluate the amount of magnesium potentially bound to organic compounds (e.g., proteins and polypeptides), which are present as a primary organic membrane (POM) on which calcification was initiated, we follow the approach of Lea and Boyle (1993). The concentrations of these proteins range between 0.02% and 0.04% of the total mass of foraminiferal tests (King and Hare, 1972; Robbins and Brew, 1990; Weiner and Erez, 1984). Since we are not aware of direct determinations of Mg in these proteins, the maximum Mg concentration of $17.8 * 10^3$ μg/g observed in oceanic particulate matter (Martin and Knauer, 1973) serves as the upper limit for the Mg occurrence in proteins. Taking 0.04% as the upper limit for the protein content of foraminiferal tests, the proteins could account for about 7 ppm Mg. This is ca. 5% of the lowest magnesium concentration we observe in *G. sacculifer* of about 150 ppm (this study). This value rises to about 10% when applying 0.08% as the upper limit for all organic matter being present in fossil foraminiferal tests (Stott, 1992). Organically bound magnesium obviously may contribute to, but by far cannot account for all Mg present in the foraminiferal tests.

TABLE 2. Statistical parameters for the magnesium distribution in individual chambers of *G. sacculifer* maintained in culture. MgO-concentrations in ppm.

	Chamber F n = 8	Chamber F-1 n = 9	Chamber F-2 n = 8
Mean MgO	1531	1413	1563
Std. Dev.	281	484	405
Variance	78784	234625	164421
Minimum	1190	610	1090
Maximum	2090	1910	2440
Range	900	1300	1350
Geo. Mean	1510	1323	1522
Har. Mean	1490	1219	1485
Kurtosis	0,09	-1,25	1,01
Skewness	0,82	-0,56	1,18

3. RESULTS

3.1. Internal Mg-Variability in *G. sacculifer*

As can be inferred from Figs. 2–6 and Table 1, the spot analyses performed by microprobe reveal a broad range of Mg concentrations within single foraminiferal tests. The mean MgO-concentration in tests of *G. sacculifer* is about 1700 ppm (n = 205) showing a standard deviation of about 1070 ppm. Minimum concentrations are around 250 ppm and maximum concentrations increase to ca. 6000 ppm.

In order to decipher possible changes in the Mg content during ontogeny, three consecutive chambers of a single specimen that were secreted in culture (T = 23.5°C, S = 36‰) were examined. Their Mg concentrations do not show significant differences (Fig. 2). The median values correspond quite well (Table 2). The boxes in Fig. 2, which comprise 50% of the spot analyses performed in each cham-

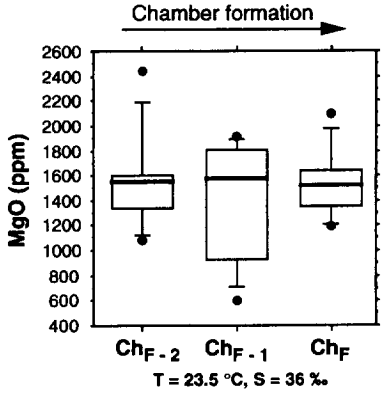

FIG. 2. Magnesium concentrations within consecutive chambers of one specimen of *G. sacculifer*. The three final chambers, the magnesium concentrations of which are presented, grew in culture at T = 23.5°C and S = 36‰. Box plots indicate the large variability of magnesium concentrations with median values (broad horizontal line), minimum and maximum concentrations (whiskers), and outliers (black dots). Ch_F = final chamber; Ch_{F-1} = last chamber but one etc. Statistical parameters see Table 2.

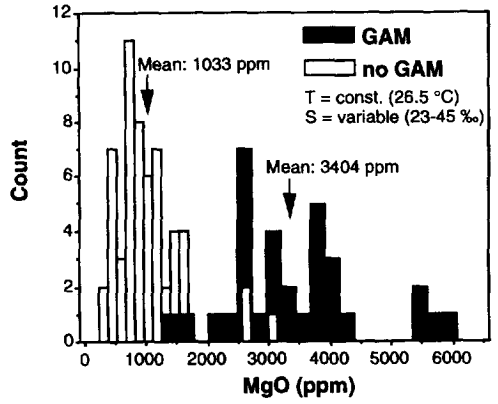

FIG. 3. The comparison of frequency distributions of magnesium concentrations in final chambers of both No GAM (white bars) and GAM foraminifers (black bars) reveals that gametogenic calcite has significantly higher magnesium concentrations.

TABLE 3. Magnesium concentrations along profiles across chamber walls. Numbers of samples correspond to Table 1. Magnesium concentrations listed to the left belong to inner (primary) calcite, whereas the concentrations to the right belong to outer (secondary) calcite.

	Inner calcite			Outer calcite
# of sample	MgO (ppm)	MgO (ppm)	MgO (ppm)	MgO (ppm)
1	1410	1590	2570	
1 parallel	1080	1410	1620	
2	1040	1330	4280	
3	1210	1460	2170	2340
4	1710	3080	4430	
6	700	700	850	1060
7	2240	3100	4060	
8	2110	2540	3030	
2	910	1330	1510	3330
2	910	990	1760	2270
2	1030	1140	1210	
2	1040	1810	3130	
2	710	1740		
2	1090	3760		

ber, overlap significantly implying that no inter-chamber variability in magnesium content occurs during constant culture conditions.

On average, the final chambers of foraminifers, which underwent gametogenesis, are apparently enriched in Mg (mean: 3404 ppm; standard deviation: 656 ppm; $n = 4$) in comparison to specimens that did not produce gametes (mean: 1033 ppm; standard deviation: 331; $n = 8$) (Fig. 3, Table 1). Note that the GAM-measurements were made on the outermost sides of the cross-sections of the final chambers. The observed increase of Mg concentrations after gametogenesis is also evident from profiles across single chamber walls within GAM specimens. Fourteen transects each consisting of up to four spot analyses were performed from the inner to the outer wall calcite. Figure 4 exhibits significantly enhanced magnesium concentrations within the outer calcite (Table 3).

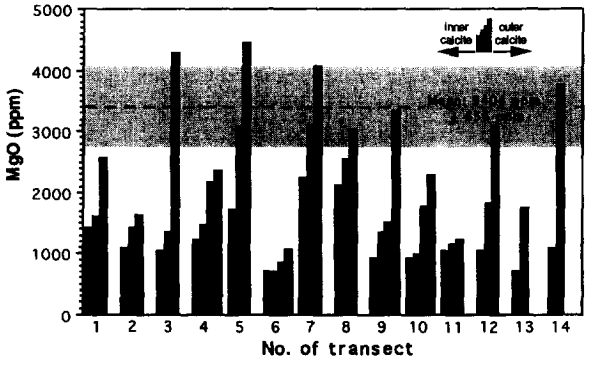

FIG. 4. 2-4 spot analyses were performed along transects crossing the final chamber walls of GAM specimens of *G. sacculifer*. Histograms show magnesium concentrations increasing from the inner (left bars) to the outer foraminiferal calcite (right bars). 50% of magnesium concentrations in outer calcite reach values typical for GAM calcite (shaded area; mean MgO: 3404 ppm; standard deviation: 656 ppm; deduced from Fig. 3) suggesting that a change in metabolic processes and/or habitat occurs during reproduction. The remaining measurements are below the concentrations of GAM calcite, most probably due to the heterogeneous distribution of GAM calcite. Statistical parameters see Table 3.

3.2. Temperature Experiment

Figure 5 presents the MgO-distributions and the corresponding average Mg/Ca ratios calculated for both 33‰ and 36‰ foraminiferal groups at various temperatures. The mean Mg/Ca ratios in foraminiferal calcite increase linearily from ca. 1.39 at 19.5°C to ca. 3.28 at 29.5°C (Table 1), thus, increasing by ca. 130%. Quantitative differences between both groups are insignificant, since one group is not consistently enriched in magnesium compared to the other. Growth rates (expressed as growth in μm/d) do not exhibit a clear relationship to the magnesium content (Fig. 5). Between 23.5°C and 29.5°C no differences in growth rates were observed. Only at 19.5°C growth rates are clearly lower.

3.3. Salinity Experiment

At constant temperature (26.5°C), the natural salinity conditions (ca. 35‰) were changed to 26‰ and 44‰, respectively (Fig. 6). The final chamber of a first foraminiferal test grown at low salinity (26‰) is depleted (mean: 641 ppm MgO, standard deviation: 125 ppm; $n = 8$) in comparison to an older chamber of the same test, which still grew under open ocean conditions (ca. 35‰) (mean: 1533 ppm MgO, standard deviation: 473 ppm; $n = 8$) (Table 1). The final chamber of a second specimen grown at high salinity (44‰), instead, is enriched with Mg (mean: 2937 ppm MgO, standard deviation: 801 ppm; $n = 9$) in comparison to an older chamber, which grew under natural conditions (mean: 1575 ppm MgO, standard deviation: 428 ppm, $n = 10$).

4. DISCUSSION

4.1. The Applicability of Magnesium as a Proxy for Water Mass Properties

To date, controversial discussions about the processes responsible for the uptake of Mg into foraminiferal calcite have precluded the establishment of Mg as a tool for paleoenvironmental reconstructions. The lack of agreement may be due to inadequate analytical techniques and/or contamination. In addition, some species may hide a clear relation

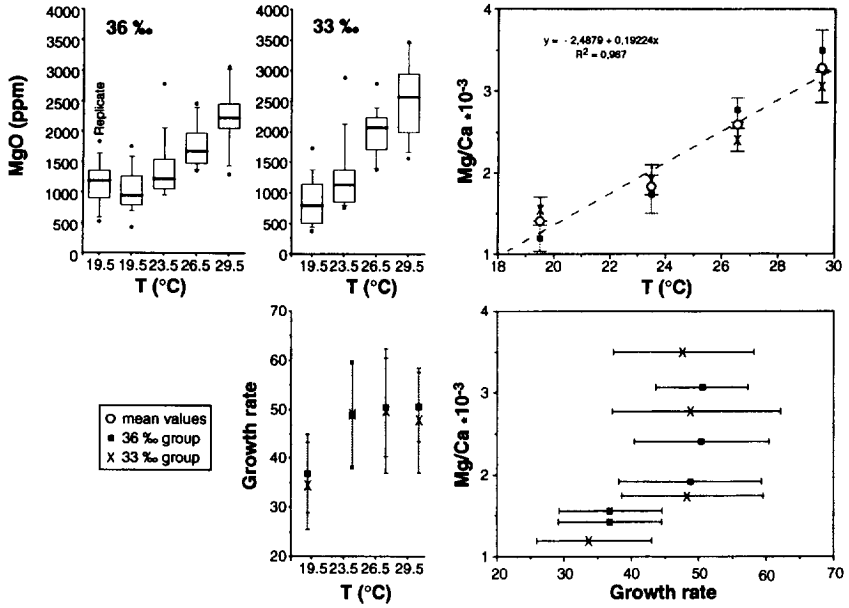

FIG. 5. Magnesium concentrations in both 33‰ and 36‰ foraminiferal groups vs. temperature and growth rates. The upper left two diagrams exhibit the range of magnesium concentrations within each sample. The upper right diagram shows the linear increase of mean Mg/Ca ratios with temperature (horizontal bars indicate the relative error). The lower diagrams indicate the relationship between both growth rates and temperature, and growth rates and magnesium content. Growth rates (growth in μm per day) are defined as the final size minus the initial size of the foraminiferal tests divided by the survival time (Hemleben et al., 1987). Statistical parameters see Table 1.

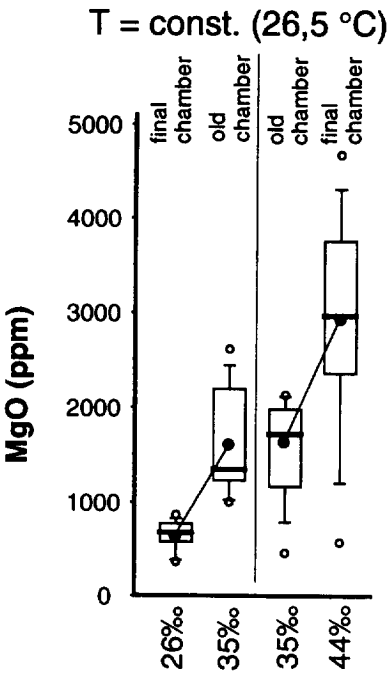

FIG. 6. The effect of salinity on the magnesium signal is proved by changing the salinity during test growth at constant temperature. The oldest chambers, grown under open ocean conditions (S = ca. 35‰, T = 26.5°C), show medium magnesium concentrations. Final chambers formed under different saline conditions in the laboratory (either 26‰ or 44‰) show significantly different magnesium concentrations. These changes are exclusively attributed to salinity changes. Black dots = mean MgO-concentrations calculated without outliers; open circles = outliers. Statistical parameters see Table 1.

between magnesium and water mass properties due to vital effects. Compared to core-top and downcore investigations, culture experiments are best suited to reveal processes controlling Mg uptake.

4.2. Intra- and Inter-Species Variability of Magnesium

The large variability of Mg in individual foraminiferal tests, as observed in this study, was also demonstrated by Lipps and Ribbe (1967), Bender et al. (1975), Puechmaille (1994), and Nürnberg (1995). The absence of any reproducible covariance between silicate and Mg, or Fe and Mg (Nürnberg, 1995), is consistent with the idea that Mg is bound in lattice sites rather than at ion-exchangeable and/or interstitial positions, since silicate and Fe are supposedly contaminant phases adhered to the surface of calcite crystals. Further evidence for lattice-bound magnesium comes from Angus et al. (1979), who found that coprecipitated magnesium-in contrast to barium-perturbs the electron spin resonance signal from manganese-doped calcites due to the local displacement of CO_3-ligants in the calcite structure. The wide range of concentrations, therefore, must be related to a heterogenous distribution of Mg within the calcite lattice when substituting for Ca. The Mg concentration in central parts along a single chamber wall of *G. sacculifer*, for example, may vary by a factor of 3.

In comparison to mean MgO-concentrations of ca. 365 ppm in tests of *Neogloboquadrina pachyderma* sin. from high latitudes (Nürnberg, 1995), Mg is significantly enriched in tests of *G. sacculifer* (mean MgO = 1700 ppm) from lower latitudes. Generally, benthic foraminifers (*Oridorsalis umbonatus, Cibicidoides wuellerstorfi, Uvigerina spp.*) also have higher mean Mg concentrations (ca. 400–

600 ppm MgO) than *N. pachyderma* sin. from corresponding sampling sites (Nürnberg, 1991). These quantitative differences imply (1) that different species may differentially incorporate magnesium, (2) that a covariance of the magnesium content and latitude and thus, a relationship between magnesium and water temperature may exist as already proposed by Chave (1954).

4.3. Salinity Effect

Debate continues concerning the impact of salinity on the Mg concentrations in foraminiferal tests. Chave (1954) estimated that the influence of salinity is of minor importance. Accordingly, Savin and Douglas (1973) did not observe a relationship between salinity and the magnesium concentration in planktic foraminiferal tests (*Globigerinoides spp., Globorotalia spp.*) under normal oceanic conditions. In contrast, the effect of salinity apparently becomes dominant over temperature under changing euhaline to hyperhaline environments (Yusuf, 1980). The Mg and Sr concentrations from foraminiferal tests (*Globigerinoides ruber*) derived from Red Sea glacial and interglacial sediments are positively correlated with paleosalinity estimations (30–40‰). Unfortunately, results from culture experiments performed with *Globigerinoides sacculifer* and *Orbulina universa* by Delaney et al. (1985) show no clear pattern with regard to a correspondance between the Mg/Ca ratio in foraminiferal tests and the Mg/Ca ratio in culture solution.

Our experiments clearly reveal that pronounced salinity changes (>10‰) at constant temperature significantly affect the Mg concentrations (Fig. 6). For a 10‰ salinity change, Mg changes by about 110%. Minor changes (<3‰) apparently have no systematic impact (Fig. 5). According to Hemleben et al. (1987), the general vitality of foraminifers increases with increasing salinity. In the 36‰ group significantly more chambers are formed in comparison to the 33‰ group. Moreover, the acceptance of food increases towards higher salinities independant of temperature. From these observations we speculate that the drastically enhanced Mg uptake at high salinity conditions is a direct consequence of increased metabolic activity.

4.4. Temperature Effect

The investigations of Delaney et al. (1985) on sediment trap material and sediment cores demonstrated a positive correlation between Mg/Ca ratios in both *G. sacculifer* and *O. universa* and the temperature of the overlying watermass. Although the Mg increase was not consistent, they showed an increase between 40% and 130% for a 10°C temperature increase. This is consistent with our culture experiments, which also reveal a magnesium increase of ca. 130% for such a temperature increase (Fig. 5). On the contrary, the culture experiments carried out by Delaney et al. (1985) failed to show this strong temperature dependence and instead, exhibited only a slight increase of 26% in the Mg/Ca ratios. Consequently, they ascribed the trends observed in sediment trap material and sediment cores to additional environmental parameters (e.g., light, nutrient content and growth rate). However, because Delaney et al. (1985) did not distinguish between gametogenic and pre-gametogenic, a clear temperature signal can, in fact, not be expected. Since GAM specimens exhibit drastically enhanced Mg concentrations and the proportion of GAM specimens and pre-GAM specimens will differ for the two temperatures they investigated (30°C is very close to the upper temperature limit (Bijma et al., 1990)), their mixed signal masks the pure temperature effect.

Katz (1973) determined the effect of temperature on the partition coefficient for Mg in calcite. Applying the relationship (1)

$$\left(\frac{\mathrm{Mg}}{\mathrm{Ca}}\right)_{\mathrm{calcite}} = D_{\mathrm{Mg}} \left(\frac{\mathrm{Mg}}{\mathrm{Ca}}\right)_{\mathrm{seawater}}, \qquad (1)$$

where $(\mathrm{Mg/Ca})_{\mathrm{calcite}}$ is the molar ratio of magnesium to calcium in the calcite crystal, $(\mathrm{Mg/Ca})_{\mathrm{seawater}}$ is the molar ratio of magnesium to calcium in seawater (=5.15 according to Broecker and Peng, 1982), and D_{Mg} is the partition coefficient of magnesium in calcite, and the resulting inclination of the regression line (2)

$$D_{\mathrm{Mg}} = 0.0009\ (T°\mathrm{C}) + 0.035, \qquad (2)$$

one can subsequently predict the ratio of Mg to calcium in inorganically precipitated calcite at various temperatures. The apparent partition coefficients for *G. sacculifer* from this study ($D_{\mathrm{Mg}} = 0.03 * 10^{-2}$ to $0.07 * 10^{-2}$), calculated from the observed Mg/Ca ratios and a constant Mg/Ca ratio of 5.15 in seawater, are two orders of magnitude lower than partition coefficients predicted from the Katz (1973) equations ($D_{\mathrm{Mg}} = 5.3 * 10^{-2}$ to $6.2 * 10^{-2}$). Similarly, partition coefficients from *N. pachyderma* sin. ($D_{\mathrm{Mg}} = 0.003 * 10^{-2}$ to $0.02 * 10^{-2}$) are definitely lower than the predicted values ($D_{\mathrm{Mg}} = 3.5 * 10^{-2}$ to $4.8 * 10^{-2}$), suggesting that planktic foraminifers partition Mg differently than do inorganic precipitates. This corresponds to the investigation of Duckworth (1977), who proposes foraminiferal partition coefficients of $0.097 * 10^{-2}$ to $0.155 * 10^{-2}$ being orders of magnitude lower than the predicted value of $4 * 10^{-2} \pm 0.7 * 10^{-2}$ from the Katz (1973) equations.

Beside the Katz (1973) studies, various efforts were undertaken to determine the partition coefficients of Mg showing a broad range of values under a variety of conditions (e.g., Winland, 1969: $D_{\mathrm{Mg}} = 1.9 * 10^{-2} \pm 0.1 * 10^{-2}$ at 20°C, Katz, 1973: $D_{\mathrm{Mg}} = 5.73 * 10^{-2} \pm 0.17 * 10^{-2}$ at 25°C, Füchtbauer and Hardie, 1976: $D_{\mathrm{Mg}} = 3.1 * 10^{-2} \pm 0.5 * 10^{-2}$ at 25°C). These results suggest that both reaction kinetics and solution chemistry influence the magnesium concentration within the solid (Berner, 1978). Nevertheless, all partition coefficients lie within one order of magnitude suggesting that the discrepancy in partition coefficients between synthetic and biogenic calcite would even remain when applying other than the Katz (1973) equations.

The discrepancy in partition coefficients between inorganically precipitated calcite and biogenic calcite is also apparent for Sr and Ba. Morse and Bender (1990) observed partition coefficients of 0.03 to 0.12 for the incorporation of Sr into inorganic calcite, which do not match partition coefficients of 0.16 ± 0.02 observed for planktic foraminifers (Bender et al., 1975; Graham et al., 1982; Delaney et al., 1985). For Ba, the partition coefficient of 0.19 observed in planktic foraminifers and appropriate parent seawater (Lea

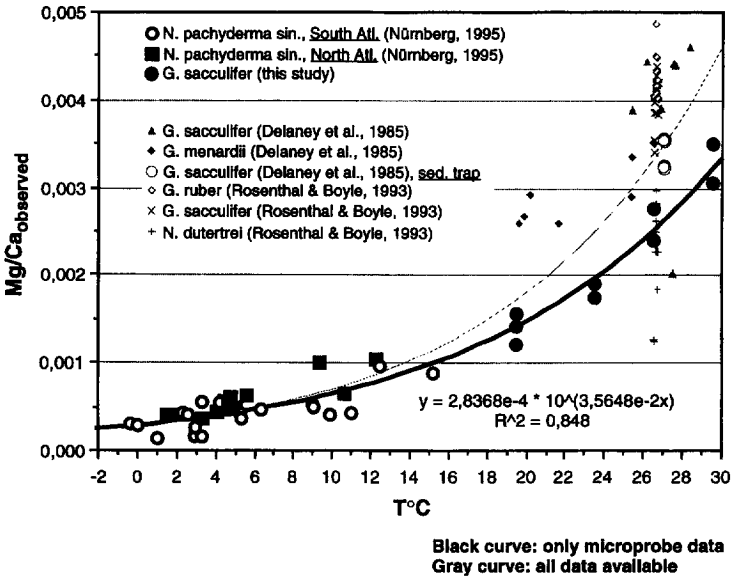

FIG. 7. Observed Mg/Ca ratios of diverse planktic foraminiferal tests from core-tops, sediment trap samples and laboratory cultures versus water temperature. Mg/Ca ratios within *G. sacculifer* (this study) and *N. pachyderma* sin. (Nürnberg, 1995) derived from microprobe investigations (large, black symbols) imply an exponential relationship between test chemistry and temperature. Literature data from Rosenthal and Boyle (1993) and Delaney et al. (1985) are presented as small, gray signals.

and Boyle, 1991) compares to and is even higher than values of 0.07–3.4 (Kitano et al., 1971) and 0.02–0.03 (Pingitore and Eastman, 1984, Pingitore, 1986, 1993), respectively, from inorganic precipitation experiments.

Recently, Erez et al. (1994) described membrane-bound granules within the endoplasm of the foraminifer *Amphistegina lobifera*, which could serve as internal pools for Ca, Mg, and sulphate. During calcification, the granules dissolve and seem to provide Ca, Mg, and sulphate for the calcification process. On the other hand, tracer experiments with the stable isotope ^{48}Ca demonstrated that if a Ca pool is present, it is very small (Lea et al., 1995). The calcification mechanism as such, however, may well explain the deviations from equilibrium of the Mg partition coefficient (Erez et al., 1994).

Figure 7 summarizes the observed Mg/Ca ratios as a function of temperature in diverse planktic foraminiferal species (Delaney et al., 1985; Rosenthal and Boyle, 1993; Nürnberg, 1995; this study) from core-top and sediment trap samples, and laboratory cultures. The observed Mg/Ca ratios are two orders of magnitude lower than the predicted values according to the Katz (1973) equation (Table 4), and are apparently undersaturated with respect to Mg for the water temperature they have experienced. Duckworth (1977) found similar conditions for *Globorotalia truncatulinoides* ($Mg/Ca_{observed}$: 0.005–0.008; $Mg/Ca_{predicted}$: 0.037–0.051). In addition, the linear relationship between temperature and Mg/Ca ratios observed for inorganically precipitated calcite (Katz, 1973) is not apparent for biogenic calcite. Considering only data derived from microprobe studies (Nürnberg, 1995; this study), an exponential relationship best fits the data (3):

$$Mg/Ca_{observed} = 0.000284 * 10^{(0.0354 * T°C)}. \quad (3)$$

Data from the literature were not included because of the apparent slight deviations in absolute concentrations between microprobe and wet-chemical analyses (see accuracy section above). Inclusion of those data, however, would also result in an exponential relationship. In this respect, the linear relationship between temperature and Mg/Ca ratios derived from culture experiments (Fig. 5) should instead be exponential.

Both, the orders of magnitude lower Mg/Ca ratios in foraminifers compared to inorganically precipitated calcite (Table 4), and the exponential relationship between Mg/Ca ratios and temperature (Fig. 7) suggests that the biologically mediated partitioning of Mg into foraminiferal calcite is substantially different from magnesium uptake during inorganic precipitation of calcite. To what extent precipitation rates bias this relationship has been the subject of much debate (e.g., MacKenzie et al., 1983; Mucci and Morse, 1983; Burton and Walter, 1987; Morse and Bender, 1990), yet there is a general lack of agreement (Carpenter and Lohman, 1992). It should be mentioned, however, that partition coefficients of Sr, Cd, Mn, Co, and Ba in inorganic calcite are definitely dependant on precipitation rates (Lorens, 1981; Pingitore and Eastman, 1984; Pingitore, 1986; Morse and Bender, 1990; Carpenter and Lohman, 1992).

Unfortunately, we have no data on the calcification rates (calcite added per unit time), but may compare growth rates at different temperatures. Only at the lowermost temperature, do growth rates of foraminifers decrease significantly (Fig. 5). Accordingly, there is no clear relationship between magnesium content and growth rate. The laboratory cultures of *G. sacculifer* showed that cold specimens survived longer than the warm ones, which was interpreted as a slow down of metabolic processes (Hemleben et al., 1987). In this respect, small salinity changes seem to have no obvious effect.

In summary, temperature or processes directly related to

TABLE 4. Partitioning coefficient for magnesium in inorganic calcite (D_{Mg}) and the corresponding Mg/Ca ratios predicted from the Katz (1973) equation for various temperatures in relation to Mg/Ca ratios observed in foraminiferal tests and corresponding foraminiferal partition coefficients ($D_{Mg\ foram}$).

Species	Region	Kind of sample	T (°C)	D Mg	Mg/Ca pred.	D Mg foram	Mg/Ca observed	Source
G. sacculifer		cult. experiment	19,5	0,05255	0,27063	0,00030	0,00155	This study
			23,5	0,05615	0,28917	0,00037	0,00191	
			26,5	0,05885	0,30308	0,00047	0,00240	
			29,5	0,06155	0,31698	0,00059	0,00306	
			19,5	0,05255	0,27063	0,00023	0,00120	
			23,5	0,05615	0,28917	0,00034	0,00174	
			26,5	0,05885	0,30308	0,00054	0,00277	
			29,5	0,06155	0,31698	0,00068	0,00350	
			19,5	0,05255	0,27063	0,00028	0,00142	
N. pachyderma sinistral	Southern South Atlantic	core-top	15,2	0,04868	0,25070	0,00017	0,00088	Nürnberg (1995)
			12,4	0,04616	0,23772	0,00019	0,00096	
			11,0	0,04490	0,23124	0,00009	0,00044	
			9,0	0,04310	0,22197	0,00010	0,00053	
			9,0	0,04310	0,22197	0,00010	0,00052	
			6,3	0,04067	0,20945	0,00009	0,00048	
			5,3	0,03977	0,20482	0,00007	0,00036	
			5,2	0,03968	0,20435	0,00008	0,00044	
			4,2	0,03878	0,19972	0,00011	0,00056	
			3,3	0,03797	0,19555	0,00003	0,00017	
			3,3	0,03797	0,19555	0,00011	0,00055	
			2,9	0,03761	0,19369	0,00003	0,00017	
			2,9	0,03761	0,19369	0,00005	0,00026	
			2,6	0,03734	0,19230	0,00008	0,00040	
			-0,4	0,03464	0,17840	0,00006	0,00031	
			9,9	0,04391	0,22614	0,00008	0,00042	
			2,3	0,03707	0,19091	0,00008	0,00043	
			1,0	0,03590	0,18489	0,00003	0,00015	
			0,0	0,03500	0,18025	0,00005	0,00028	
N. pachyderma sinistral	Norwegian Sea	core-top	1,5	0,03635	0,18720	0,00008	0,00040	Nürnberg (1995)
			4,8	0,03932	0,20250	0,00012	0,00061	
			1,9	0,03671	0,18906	0,00008	0,00042	
			9,3	0,04337	0,22336	0,00020	0,00101	
			10,6	0,04454	0,22938	0,00012	0,00064	
			12,3	0,04607	0,23726	0,00020	0,00104	
			4,5	0,03905	0,20111	0,00011	0,00058	
			5,6	0,04004	0,20621	0,00012	0,00064	
			4,5	0,03905	0,20111	0,00009	0,00049	
			3,3	0,03797	0,19555	0,00007	0,00036	
			5,0	0,03950	0,20343	0,00010	0,00049	
			4,0	0,03860	0,19879	0,00009	0,00045	
N. dutertrei	Sierra Leone Rise	core-top	26,6	0,05894	0,30354	0,00044	0,00228	Rosenthal & Boyle (1993)
			26,6	0,05894	0,30354	0,00058	0,00297	
			26,6	0,05894	0,30354	0,00049	0,00251	
			26,7	0,05903	0,30400	0,00044	0,00228	
			26,7	0,05903	0,30400	0,00036	0,00184	
			26,6	0,05894	0,30354	0,00051	0,00263	
			26,6	0,05894	0,30354	0,00055	0,00282	
			26,5	0,05885	0,30308	0,00024	0,00125	
			26,5	0,05885	0,30308	0,00025	0,00128	
G. ruber	Sierra Leone Rise	core-top	26,6	0,05894	0,30354	0,00081	0,00415	Rosenthal & Boyle (1993)
			26,6	0,05894	0,30354	0,00080	0,00410	
			26,6	0,05894	0,30354	0,00084	0,00433	
			26,6	0,05894	0,30354	0,00087	0,00448	
			26,7	0,05903	0,30400	0,00078	0,00402	
			26,7	0,05903	0,30400	0,00082	0,00422	
			26,6	0,05894	0,30354	0,00079	0,00409	
			26,6	0,05894	0,30354	0,00094	0,00485	
			26,6	0,05894	0,30354	0,00079	0,00408	
			26,5	0,05885	0,30308	0,00068	0,00350	
			26,5	0,05885	0,30308	0,00078	0,00404	
G. sacculifer	Sierra Leone Rise	core-top	26,6	0,05894	0,30354	0,00083	0,00428	Rosenthal & Boyle (1993)
			26,6	0,05894	0,30354	0,00080	0,00413	
			26,7	0,05903	0,30400	0,00082	0,00420	
			26,7	0,05903	0,30400	0,00075	0,00384	
			26,6	0,05894	0,30354	0,00085	0,00438	
			26,6	0,05894	0,30354	0,00075	0,00385	
			26,6	0,05894	0,30354	0,00081	0,00419	
			26,6	0,05894	0,30354	0,00080	0,00412	
			26,5	0,05885	0,30308	0,00077	0,00397	
			26,5	0,05885	0,30308	0,00075	0,00385	
			26,5	0,05885	0,30308	0,00069	0,00355	
			26,5	0,05885	0,30308	0,00066	0,00341	

temperature appear to serve as the most important controlling factors for Mg uptake in foraminiferal tests (Fig. 5), provided that salinity variations are negligible (<3‰). Considering the discrepancy between partition coefficients for foraminiferal and for synthetic calcite on the one hand, and the exponential correlation between observed Mg/Ca ratios in foraminifers and temperature on the other hand, it is deduced that (1) organisms are apparently capable of regulating the

Table 4. (Continued)

Species	Region	Kind of sample	T (°C)	D Mg	Mg/Ca pred.	D Mg foram	Mg/Ca observed	Source
G. sacculifer	Indian Ocean	core-top	27,5	0,05975	0,30771	0,00039	0,00201	Delaney et al. (1985)
			25,4	0,05786	0,29798	0,00075	0,00388	
			26,7	0,05903	0,30400	0,00079	0,00405	
			26,2	0,05858	0,30169	0,00086	0,00443	
			26,9	0,05921	0,30493	0,00076	0,00390	
			27,6	0,05984	0,30818	0,00085	0,00439	
			27,5	0,05975	0,30771	0,00085	0,00440	
			28,4	0,06052	0,31170	0,00089	0,00458	
G. menardii	Indian Ocean	core-top	25,4	0,05786	0,29798	0,00056	0,00289	Delaney et al. (1985)
			25,4	0,05786	0,29798	0,00065	0,00333	
			20,2	0,05318	0,27388	0,00056	0,00290	
			19,9	0,05291	0,27249	0,00052	0,00267	
			21,7	0,05453	0,28083	0,00050	0,00258	
			19,7	0,05273	0,27156	0,00050	0,00259	
G. sacculifer	Panama Basin	sediment trap	27,0	0,05930	0,30540	0,00063	0,00325	Delaney et al. (1985)
			27,0	0,05930	0,30540	0,00069	0,00356	
			27,0	0,05930	0,30540	0,00069	0,00354	
			27,0	0,05930	0,30540	0,00063	0,00323	
G. menardii	Panama Basin	sediment trap	20,0	0,05300	0,27295	0,00044	0,00227	

magnesium concentration of their carbonate shells, and (2) the physiological processes that are responsible for such regulation are mainly driven by temperature.

4.5. GAM Effect

Prior to gametogenesis, a significant amount of secondary calcite, the so-called GAM calcite, is added to the shell. This secondary calcite, which can provide a third or more of a shell's mass (Bé, 1980; Erez and Honjo, 1981), is added to the shell of the commonly shallow-dwelling *G. sacculifer* in deeper areas. According to Bijma and Hemleben (1994), reproduction of *G. sacculifer* takes place somewhere between 60 m and 100 m, whereas Duplessy et al. (1981) define the reproduction depth even deeper (300–800 m). As inferred from Figs. 3 and 4, the GAM calcite is enriched with respect to Mg in average by ca. 230%. This effect apparently surpasses the Mg increase due to temperature (ca. 130% for a 10°C change) and salinity effects (ca. 110% for a 10‰ change). If temperature is the only driving force for the Mg uptake, and GAM calcite is added in a deeper (i.e., colder) environment, it should be depleted relative to normal calcite. Since this is obviously not the case, some kind of vital effects must be active during gametogenesis, severely influencing the Mg uptake.

Apart from the significantly enhanced Mg/Ca ratio in GAM calcite, Mg also increases from inner to outer primary calcite (Fig. 4), an observation which we can only speculate on. When a new chamber is formed, a thin layer of calcite is added to the interior of the two most proximal chambers and a thicker layer of calcite is also laid over the external surface of previously formed chambers (Hemleben et al., 1986). We suppose that a decrease in the calcification rate and/or an increase in the proportion of epitactically grown, inorganic calcite during the process of chamber formation may control the increase in the Mg concentration from the inside to the outside of a chamber wall's cross-section.

As long as the differences between the two modes of calcification, normal vs. GAM, are not fully understood, the GAM-effect should be kept in mind when applying Mg for paleoceanographic reconstructions. Lohmann (1995) presented a model from which stable isotope geochemistry of different shell components (primary and secondary calcite) can be inferred. The application of this model to magnesium should allow one to differentiate between Mg incorporated by different modes of biomineralization and, thus, to decipher the environmental signal.

4.6. Diagenetic Constraints

The influence of temperature and salinity on shell magnesium demonstrated by the culturing results of *G. sacculifer* naturally raises the question of the applicability of shell Mg for reconstructing past water mass properties. Processes which might alter the Mg concentration through the geological record have been discussed by Nürnberg (1995). Despite many indications for an increasing susceptibility to selective solution with water depth (e.g., Rosenthal and Boyle, 1993), we did not find a strong relationship between Mg in core-top *Neogloboquadrina pachyderma* sinistral and water depths (Nürnberg, 1995). Further, Mg concentrations do not systematically co-vary with the fragmentation grades of foraminiferal tests downcore (Nürnberg, 1995).

Core-top investigations of Rosenthal and Boyle (1993) instead show definitely reduced magnesium concentrations below ca. 5000 m water depth implying geochemical alteration below the lysocline. Postdepositional alteration due to carbonate dissolution was also proposed by Lorens et al. (1977). Walls et al. (1977) pointed out that magnesium cations, which reside in nonlattice sites, can be easily removed during early diagenesis, whereas there is only little diffusion of Mg from the crystal interior (Berner, 1967). As inferred from the above considerations, any magnesium analysed within the inner calcite is most probably in lattice sites, thus being rather unassailable for diagenetic alteration. Further, the fact that foraminiferal calcite generally has too little Mg when compared to that expected from the Katz (1973) equations led Duckworth (1977) to speculate that if diagenetic alteration were to occur, foraminiferal tests would act as a sink for Mg rather than a source. From this consideration, any diagenetic impact should be considered to be minor.

Nevertheless, when applying Mg as a proxy for paleotemperature, specific prerequisites should be fulfilled: (1) only well-preserved foraminiferal specimens should be selected for analysis, (2) sites of investigation should be located well above the carbonate compensation depth, over the entire time period under investigation, and (3) calcite dissolution should be assessed from sedimentological and geochemical observations (e.g., foraminiferal test fragmentation) in order to identify periods of intense dissolution. The role of salinity changes perturbing the magnesium record during the geologic past is considered to be negligible in all cases where paleosalinity variations are <3‰.

5. CONCLUSIONS

Culture experiments with *G. sacculifer* at variable temperature (19.5–29.5°C) and relatively constant salinity (33–36‰) conditions show that the Mg/Ca ratio is primarily driven by temperature. A linear increase of Mg concentrations of ca. 130% is observed when increasing the culture solution by ca. 10°C. In contrast, salinity becomes the dominating regulation mechanism for magnesium uptake, when maintaining the foraminifers at drastically varying salinities (22–45‰), but constant temperature (26.5°C). A salinity increase of 10‰ is reflected by a ca. 110% increase of magnesium uptake. Specimens which underwent gametogenesis during culture experiments have significantly higher magnesium concentrations than specimens which did not reproduce, demonstrating the impact of GAM-calcification.

From the calculation of the partitioning coefficients at various temperatures, the discrepancy between predicted Mg/Ca ratios in calcite inorganically precipitated from seawater and Mg/Ca ratios observed in foraminiferal tests becomes evident. Foraminiferal tests are definitely undersaturated with respect to Mg for the water temperature they have experienced, suggesting that physiological processes drive the internal Mg concentration. Since the observed Mg/Ca ratios are closely correlated to temperature, it is speculated that these physiological processes are temperature-controlled.

This study demonstrates that temperature, and to a lesser extent salinity, have a major influence on the magnesium content of *G. sacculifer* tests. Therefore, it should be possible to use foraminiferal magnesium as a paleotemperature proxy. However, the effective use of this proxy will require consideration of the potential impact of GAM effects, postdepositional chemical alteration and large salinity variations on shell magnesium.

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