Precise magnesium isotope measurements in core top planktic and benthic foraminifera

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[1] This study presents a new methodology to obtain highly precise measurements (±0.1‰) of magnesium isotope ratios in very small samples of foraminiferal carbonate (40–50 μg). Here this technique is used to examine Mg isotopic variation among different species of core top foraminifera over a range of different ambient conditions. Despite the high degree of temperature control on the abundance of elemental Mg incorporated into foraminiferal tests, analyses of surface dwelling *Globigerinoides ruber* and *G. sacculifer* from five cores, with associated sea surface temperatures ranging from 20 to 31°C, show no significant temperature-dependent variations in their Mg isotope ratios. Analyses of different size fractions of *G. sacculifer* show an increase in Mg/Ca with test size but no variation of Mg isotope ratio. In all, nine planktic and benthic species were analyzed; all show identical Mg isotope ratios with a mean of δ^{26}Mg = −4.72‰, apart from small differences in three species, namely *O. universa*, *G. sacculifer* (which are both ∼0.4‰ lighter than the average), and *P. obliquiloculata* (which is ∼0.4‰ heavier). These results highlight the constancy of foraminiferal Mg isotope ratios, despite changing environmental conditions which dominate Mg/Ca variation and arguably affect Ca isotope fractionation. This is an important observation which needs to be included in any model of foraminiferal calcification. The insusceptibility of δ^{26}Mg values to external parameters makes Mg isotopes ideally suited to constraining past variations in the Mg isotope budget of the oceans and the information this carries about the history of oceanic dolomitization, continental weathering, and hydrothermal behavior.

1. Introduction

[2] Analyses of foraminiferal calcium carbonate have become one of the most important methods of determining the radiogenic and stable isotopic composition of seawater in the geological past [e.g., *Urey et al.*, 1951; *Emiliani*, 1955; *Shackleton*, 1967; *Burke et al.*, 1982; *Hodell et al.*, 1991]. Attention has recently focused on stable light isotopes as tracers for low-temperature processes because of the large relative mass differences between different isotopes of the same element [*Johnson et al.*, 2004]. Recent developments in
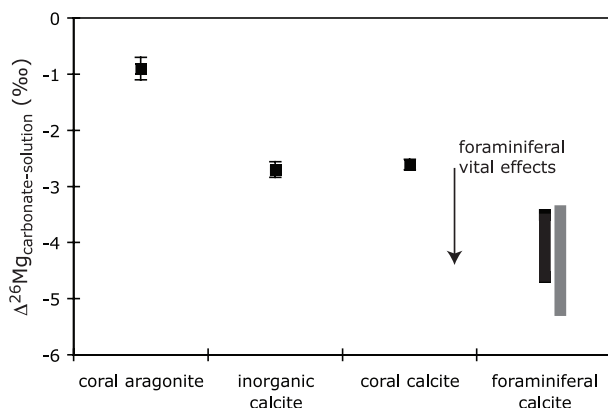
Figure 1. Relative δ^{26}Mg fractionation from growth solution for aragonite coral [*Chang et al.*, 2004; *Wombacher et al.*, 2006], inorganic calcite [*Galy et al.*, 2002], calcite coral (this study), and foraminifera (black band is the range from this study; gray band is the range from *Chang et al.* [2004]).

plasma-source multicollector mass spectrometers have allowed relatively easy, rapid, and precise measurements of several of these systems and has opened up new avenues of investigation, including the analysis of Mg isotopes in biological carbonate [*Chang et al.*, 2003, 2004; *Young and Galy*, 2004].

[3] Magnesium isotopes promise to be an exciting new tracer for surface processes, such as continental weathering. The dominant magnesium source to the oceans consists of continental weathering via riverine runoff. Oceanic sinks are hydrothermal exchange, dolomite precipitation, and ion-exchange reactions with clays. The latter is thought to be a negligible Mg sink, and hydrothermal exchange is thought to be quantitative, hence resulting in no isotope fractionation [*Elderfield and Schultz*, 1996; *Holland*, 2003; *Tipper et al.*, 2006b]. Recent studies have shown that Mg isotopes are fractionated during weathering processes on the continents and during dolomite formation in the oceans [*de Villiers et al.*, 2005; *Tipper et al.*, 2006a, 2006b; *Pogge von Strandmann et al.*, 2008a]. Therefore it seems likely that the Mg isotopic mass balance of the oceans will be perturbed by variations in these sources and sinks. These perturbations may then be preserved by marine carbonates, e.g., foraminifers (Figure 1). The long oceanic residence time of magnesium ($\sim$10 Ma) [*Berner and Berner*, 1996] is ideally suited to constrain long-term global variations in continental and dolomitic fluxes. However, in order to determine past changes in these environmental parameters, it is necessary to measure Mg isotopes to a high degree of accuracy and precision. To date, the only published study of Mg isotopes in

foraminifers [*Chang et al.*, 2004] made a vital start in the development of this technique, and achieved an analytical uncertainty of $\leq$0.5‰ on δ^{26}Mg in 0.5–1 mg of foraminiferal calcite, i.e., $\sim$100 specimens. Such a large amount of sample limits the possible applications (for monospecific benthic species work in particular) to those concerning only the most abundant species and hinders tests for ontogenetic effects and investigations of species-specific incorporation of Mg isotopes.

[4] This study seeks to improve upon these measurements, by analyses of Mg isotopes to a precision of better than $\pm$0.1‰ in 40–50 μg of foraminiferal carbonate (4–5 tests in the 355–425 μm fraction). The relevance of high-precision analyses can be demonstrated by a simple box model [e.g., *Tipper et al.*, 2006b]: a 0.2‰ δ^{26}Mg change in the modern oceans (which could be resolved by this study) could be caused by a $\sim$0.2‰ shift in the isotope ratio of continental rivers (which is well within the range shown even by modern rivers) [*Tipper et al.*, 2006a] or a $\sim$15% increase in the relative dolomite to hydrothermal sink, which is thought to have occurred within the last 10 Ma [*Zimmermann*, 2000; *Holland*, 2003; *Tipper et al.*, 2006b]. In comparison, the previous study on Mg isotopes in foraminifera [*Chang et al.*, 2004], would only be able to resolve a >0.8‰ variation in the δ^{26}Mg of the riverine input or a $\sim$45% increase in the relative dolomite to hydrothermal sink.

[5] Previous studies have shown that the incorporation of Mg into foraminiferal tests is strongly temperature dependent [*Mucci and Morse*, 1983; *Mucci*, 1987; *Busenberg and Plummer*, 1989; *Nürnberg et al.*, 1996; *Elderfield and Ganssen*, 2000] and much lower than predicted by inorganic equilibrium [*Lea et al.*, 1999]. Given such a large biogenic influence on Mg incorporation, it is possible that environmental conditions, most notably temperature, could influence the magnitude of Mg isotope fractionation during incorporation into the foraminifera. For example, temperature related fractionation of up to 0.2‰/°C has been reported for calcium isotopes in several studies (although the magnitude of this fractionation is disputed and discussed later) [*Nägler et al.*, 2000; *Sime et al.*, 2005; *Hippler et al.*, 2006].

[6] Multiple planktic and benthic foraminiferal species have been analyzed in this study, to examine the effect of temperature, carbonate saturation, growth rate, and species differences in Mg isotope composition of foraminiferal tests. This high accu-

Table 1. Mg Isotope Values of the Standards Measured During This Study[a]

	n	δ^{25}Mg	2sd	δ^{26}Mg	2sd
Purified Standards					
CAM-1	24	−1.38	0.06	−2.64	0.08
OU-Mg	13	−1.39	0.07	−2.66	0.09
Standards Passed Through Chemistry					
DSM-3	3	0.00	0.04	0.01	0.05
CAM-1	4	−1.39	0.05	−2.68	0.07
Seawater	11	−0.44	0.08	−0.83	0.09
Coral	7	−1.77	0.04	−3.43	0.09
Coral 50 ng	2	−1.77	0.06	−3.44	0.06
Coral 250 ng[b]	1	−1.76	0.02	−3.42	0.02
Coral 500 ng	3	−1.79	0.05	−3.49	0.08
Coral-DSM mix (50:50)	2	−0.87	0.01	−1.73	0.07

[a] See text for description of coral-DSM-3 mix.
[b] Where n = 1, 2se is reported instead of 2sd.

racy and precision in small sample sizes allows the ready determination of interspecies Mg isotope variations and ultimately suggests that accurate and precise measurements of past Mg isotope ratios in foraminifera will record variations in the Mg isotope composition of seawater with a high fidelity.

2. Samples and Analytical Methods

2.1. Samples and Sample Preparation

[7] Samples were picked from the Holocene aged core tops from several Ocean Drilling Program Sites, including Site 664C (Ocean Drilling Program (ODP) Leg 108, central equatorial Atlantic), Site 806B (ODP Leg 130, Ontong Java Plateau), Site 925B (OPD Leg 154, Ceara Rise), Site 999A (ODP Leg 165, Caribbean), and GeoB 1207 (Walvis Ridge–Cape Basin) [*Bickert et al.*, 1997; *Raymo et al.*, 1997; *Lea et al.*, 2000; *Schmidt et al.*, 2004b; *Foster*, 2008]. Samples were also analyzed from the slightly older late Pleistocene core top of Site 1241A (OPD Leg 202, Panama Basin) [*Mix et al.*, 2003]. These sites provide a wide range in available foraminiferal species, as well as variations in temperature and calcite saturation state of the overlying water column.

[8] Although the isotopic method requires only four to five planktic tests, 10 planktic, and four to five benthic tests were picked per sample (0.5– 1 orders of magnitude less than *Chang et al.* [2004]), to allow for trace element abundance, as well as isotopic, analysis and to avoid biases relating to small sample size. The picked foraminifera were

crushed and cleaned as described for trace element analysis [*Barker et al.*, 2003]. Briefly, this included repeated ultrasonications with methanol and 18.2 MΩ H_2O to remove clays, followed by heating with ammonia buffered 1% hydrogen peroxide to remove foraminiferal organics [*Wei et al.*, 2007]. A fraction of the cleaned, dissolved samples were analyzed by an Element 2 inductively coupled mass spectrometer (ICP-MS) to determine relative trace element abundances, in particular Mg/Ca and Al/Ca, the latter in order to determine whether the cleaning process had efficiently removed clay material. Removal of clay material is vital for accurate measurement of Mg isotope ratios, as many silicate clays are Mg-rich, and have a much heavier δ^{26}Mg than foraminifera ($\sim$0‰ [*Tipper et al.*, 2006a; *Pogge von Strandmann et al.*, 2008a]). All analyzed samples had an Al/Ca ratio <90 μmol/ mol. Mass balance calculations show that Al/Ca ratios would have to be >350 μmol/mol for silicate-based Mg to affect the Mg isotope ratio of the carbonate beyond analytical uncertainty.

2.2. Chemistry and Analysis

[9] Samples were purified for Mg by passing them through high-aspect ratio (14.2) cation exchange columns containing AG-50W X12 (2.4 ml dry volume), using ultrapure 2.0N HNO_3 as an elution agent [*Lee and Papanastassiou*, 1974; *Lee et al.*, 1976; *Black et al.*, 2006; *Teng et al.*, 2007]. Exactly 4.2 column volumes were eluted before collection of 4.6 column volumes. This is, to date, the first published study to use HNO_3 as an eluant, rather than HCl, to purify carbonates. This method allows complete separation from Ca^{2+}, with the added benefit of a very low chemistry total procedural blank (0.17 ng). This, combined with a cleaning blank of <0.1 ng (also using ultrapure reagents [*Wei et al.*, 2007]), gives a total blank of $\sim$0.27 ng.

[10] As cation exchange resin fractionates Mg isotopes during purification, it is vital to collect 100% of the sample. In order to validate this, a separate fraction of the eluent was collected before and after the Mg elution and then analyzed for Mg content. The Mg yield from this method is better than 99.9%. Mg standards (DSM-3 and CAM-1) passed through chemistry yield identical results to unprocessed standards (Table 1), also showing that Mg separation does not induce any significant isotopic fractionation. Ca/Mg ratios of samples thus purified are reduced by $\sim$5 orders of magnitude relative to unpurified samples (postchemistry molar Ca/Mg <0.002; molar Sr/Mg ratios are

$\sim 10^{-5}$), showing separation of Mg from the dominant matrix components.

[11] Purified samples were analyzed for Mg isotope ratios using a Thermofinnigan Neptune multicollector ICP-MS at Bristol, using a combination Scott double pass cyclonic quartz spray chamber with a 50 μl/min ESI PFA-50 nebulizer tip. This suppresses CN^+ formation on ^{26}Mg, which is introduced by desolvating nebulizers [*Wiechert and Halliday*, 2007]. Although CN^+ can be resolved on the Neptune, the necessity of running it at medium resolution leads to a greater than fivefold reduction in sensitivity, which is comparable to the difference between dry and wet plasma. Therefore, given that wet plasma has the advantage that the analyte beam is more stable than with a desolvating nebulizer, with a similar signal-to-noise ratio compared to dry plasma, all analyses were performed under wet plasma conditions.

[12] Using faraday cups with amplifiers with 10^{11} Ω resistors, 50 ng of Mg typically gives a beam size of $\sim$3 V on ^{24}Mg, compared to a background of $\sim$0.008 V. The isotope ratio and intensity of the background (2% HNO_3) is measured after each analysis, and used to correct the isotope ratio of the sample. This correction is less than 0.01‰. A sample-standard bracketing procedure was adopted, relative to the Mg standard DSM-3 [*Galy et al.*, 2003], which was diluted to within ±10% of the concentration of the samples. Internal precision on both δ^{25}Mg and δ^{26}Mg at these concentrations is generally 0.01–0.02‰ (2σ). Each sample was analyzed three times during an analytical procedure, with each analysis separated by several hours. Each individual analysis consisted of 20 ratios (80 s), giving a total analysis time of 240 s/sample. The averages and 2 standard errors of these measurements are reported in Table 2.

[13] External precision, as determined by repeated analyses of seawater and a sample of deep-sea coral, is better than 0.09‰ (2σ_{SD}; Table 1). Because previous Mg isotope studies have reported high background and blank (and have therefore analyzed more concentrated solutions), this study assessed any possible effect of blank by processing 50, 250, and 500 ng of the same coral sample (it should be noted that the coral samples were not cleaned in a manner similar to the foraminifera). The different amounts of coral were passed through the columns and then diluted to 50 ng/g Mg and analyzed. All analyses give identical Mg isotope ratios within external uncertainty (Table 1). In order to ascertain whether carbonate samples were returning an accurate isotope ratio, a sample of

coral was spiked $\sim$50:50 (the precise ratio of coral:DSM-3 Mg as measured by weight and ICP-MS is 49.1:50.9) with DSM-3 prior to column separation [*Tipper et al.*, 2008]. The results yield the expected values within uncertainty (Table 1).

[14] All standards and samples measured for Mg isotopes lie on a single trend in three-isotope space, where delta values have been converted to describe a linear regression (δ^{25}Mg′ versus δ^{26}Mg′) [*Young and Galy*, 2004] (Figure 2). The slope of this line (when factoring in external uncertainty) is 0.513 ± 0.005, which is identical to the terrestrial fractionation line shown in other studies of Mg isotopes in terrestrial material [*Chang et al.*, 2004; *Young and Galy*, 2004; *Young et al.*, 2005], and demonstrates that the measurements are free of significant spectral interference. The measured δ^{26}Mg value of CAM-1 is −2.64 ± 0.08‰, which compares well to other studies (−2.60 ± 0.14‰ [*Tipper et al.*, 2006a]; −2.58 ± 0.14‰ [*Pearson et al.*, 2006]; −2.78 ± 0.15‰ [*Pogge von Strandmann et al.*, 2008b]; −2.59 ± 0.08‰ [*Tipper et al.*, 2008]). Seawater measured in this study (−0.83 ± 0.09‰) also is identical within uncertainty to other studies (−0.83 ± 0.12‰ [*Chang et al.*, 2004]; −0.84 ± 0.06‰ [*Young and Galy*, 2004]; −0.84 ± 0.14‰ [*Tipper et al.*, 2006a]; −0.89 ± 0.18‰ [*Pogge von Strandmann et al.*, 2008b]; −0.80 ± 0.06‰ [*Tipper et al.*, 2008]).

3. Results

[15] Temperatures determined from the Mg/Ca ratios measured by this study (using calibrations from *Lear et al.* [2002] and *Anand et al.* [2003]) correspond well to directly measured water temperatures (World Ocean Atlas Database) (Table 2), in keeping with the surface habitat of *G. ruber*. *G. sacculifer* derived temperatures, on the other hand, are slightly lower than directly measured SST, as would be expected from this species' migratory lifestyle [*Hemleben et al.*, 1989]. Increasing size fractions of *G. sacculifer* show an increasing trend of Mg/Ca, as reported by several other studies [*Elderfield et al.*, 2002; *Ni et al.*, 2007], although in this study the relative differences are small.

[16] To test for environment and preservation-dependent fractionation, *G. ruber* and *G. sacculifer* were analyzed from all sampled cores, which have a relative temperature difference of $\sim$10°C. *G. ruber* has an average of −4.77 ± 0.14‰ (2sd) and *G. sacculifer* an average of −5.18 ± 0.24‰ (2sd). Both species show no isotope variation with the

Table 2. Mg Isotope Ratios and Mg/Ca for Foraminifera Analyzed During This Study[a]

	δ^{25}Mg (‰)	2se	δ^{26}Mg (‰)	2se	Mg/Ca (mmol/mol)	SST[b] (°C)
	Core 999 (355−425 μm)					
G. truncatulinoides	−2.36	0.05	−4.64	0.06	2.5	
	−2.37	0.02	−4.59	0.01		
G. sacculifer[c]	−2.61	0.03	−5.11	0.05	4.4	
	−2.59	0.04	−5.06	0.05		
N. dutertrei	−2.45	0.02	−4.73	0.02	3.4	
	−2.39	0.02	−4.71	0.03		
G. ruber[d]	−2.42	0.03	−4.73	0.05	5.0	
O. universa	−2.61	0.03	−5.05	0.03	4.9	
G. tumida	−2.51	0.03	−4.75	0.05	2.6	
P. obliquiloculata	−2.23	0.02	−4.34	0.05	2.5	
C. mundulus	−2.41	0.01	−4.61	0.01		
C. wuellerstorfi	−2.38	0.01	−4.63	0.01	1.4	
	G. ruber (355−425 μm) Cores					
806	−2.45	0.05	−4.71	0.06	5.4	30.4
664	−2.44	0.02	−4.83	0.05	5.2	28.8
	−2.42	0.03	−4.73	0.04		
1241	−2.41	0.03	−4.70	0.04	5.3	30.1
	−2.40	0.04	−4.63	0.05		
925	−2.51	0.01	−4.85	0.01	3.9	26.8
	−2.48	0.01	−4.80	0.02		
	−2.48	0.01	−4.86	0.01		
	−2.44	0.02	−4.83	0.02		
999[d]	−2.42	0.03	−4.73	0.05	5.0	28.6
GeoB1207	−2.44	0.03	−4.78	0.06	2.3	19.7
	G. sacculifer (355−425 μm) Cores					
806	−2.63	0.02	−5.08	0.03	5.0	30.4
664	−2.68	0.02	−5.25	0.03	4.4	28.8
1241	−2.71	0.01	−5.31	0.02	4.9	30.1
925	−2.73	0.02	−5.27	0.02	3.9	26.8
999[c]	−2.59	0.04	−5.06	0.05	4.4	28.6
GeolB1207	−2.68	0.03	−5.25	0.06	2.7	19.7
	G. sacculifer					
250−300 μm	−2.64	0.05	−5.21	0.05	4.0	
355−425 μm[c]	−2.59	0.04	−5.06	0.05	4.2	
425−500 μm	−2.70	0.06	−5.23	0.07	4.4	
500−600 μm	−2.64	0.04	−5.17	0.06	4.5	

[a] SST is sea surface temperature. The 2 standard error is gained from triplicate repeats of each sample.
[b] SST measured directly (World Ocean Atlas Database).
[c] *G. sacculifer* analysis repeated in different table sections.
[d] *G. ruber* analysis repeated in different table sections.

temperature variation nor with the range of ∼0.5 Ω CaCO₃ calcite saturation state variation exhibited in the deep water columns immediately above these core sites [*Foster*, 2008] (Ω is the ratio of the product of Ca^{2+} and CO_3^{2-} concentrations measured in seawater to those in seawater at saturation [*Zeebe and Wolf-Gladrow*, 2001]).

[17] Four different *G. sacculifer* test size fractions (from 250 to 600 μm) were also analyzed from core 999A to test for fractionation due to growth rate/calcification rate and/or ontogeny. Again, all samples show identical δ^{26}Mg within analytical uncertainty.

[18] Finally, to test for species-specific differences in Mg isotope fractionation, several different planktic and benthic foraminiferal species from a single core (999A) were analyzed: the symbiont-bearing shallow-dwelling species *G. ruber*, *G. sacculifer*, and *O. universa*; the intermediate-dweller *Pulleniatina obliquiloculata*; the thermo-cline-dwellers *Neogloboquadrina dutertrei* and *Globorotalia tumida*, and the deep dweller *G.*
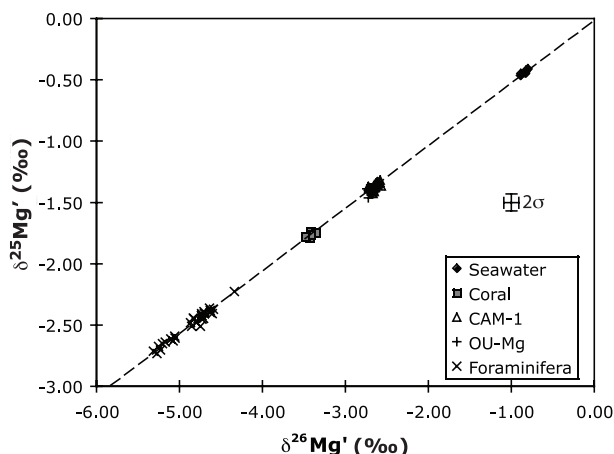
Figure 2. Three-isotope plot for Mg for all standards and samples analyzed. The error bars represent the external uncertainty of the analyses.

truncatulinoides, as well as the benthic species *Cibicidoides mundulus* and *C. wuellerstorfi*. The average δ^{26}Mg value of the seven planktic species is $-4.71 \pm 0.55‰$ (2sd), ranging from -5.31 to $-4.34‰$. This range is clearly resolvable with an external uncertainty of $\pm0.09‰$. Despite the very different environment and conditions of growth, the benthic species do not have obviously different Mg isotope ratios (average $-4.62 \pm 0.03‰$ (2sd)).

[19] *G. sacculifer* and *G. ruber* are, given the number of repeat measurements conducted on both, clearly distinguishable on the basis of Mg isotope ratios. The average of planktic species excluding *G. sacculifer* is $-4.69‰$, compared to

the δ^{26}Mg average of *G. sacculifer*, which is $-5.17‰$ (Figure 3). *O. universa* and *P. obliquiloculata* also have δ^{26}Mg values significantly offset from the planktic average (*O. universa* is $\sim0.5‰$ lighter, whereas *P. obliquiloculata* is $\sim0.4‰$ heavier), although both these samples are based on single analyses. Excluding these species, the planktic mean is $-4.74‰$ (±0.16, 2sd), which is identical to that of the benthic species at $-4.62‰$ (Figure 3).

4. Discussion

4.1. Calcite Saturation Dependence

[20] Several studies have suggested that foraminiferal gametogenic and ontogenetic calcite have different elemental concentrations and isotope ratios [e.g., *Bé*, 1977, 1980; *Benway et al.*, 2003; *Eggins et al.*, 2003; *Ni et al.*, 2007], partly because the calcification mechanism may be different [*Erez*, 2003] and partly because the environment of deposition has different properties [*Ni et al.*, 2007]. For example, some studies have reported a Mg/Ca correlation with test size in *G. sacculifer* (as also observed in this study) but not in *G. ruber* [*Elderfield et al.*, 2002; *Ni et al.*, 2007]. *Ni et al.* [2007] suggest that the presence/absence of gametogenic calcite and its subsequent preservation plays a role, rather than growth rate. Varying preservation of gametogenic calcite can therefore lead to variations in concentration and isotope ratio. The sampled cores show a high variation in the calcite saturation state of the overlying water column: from below
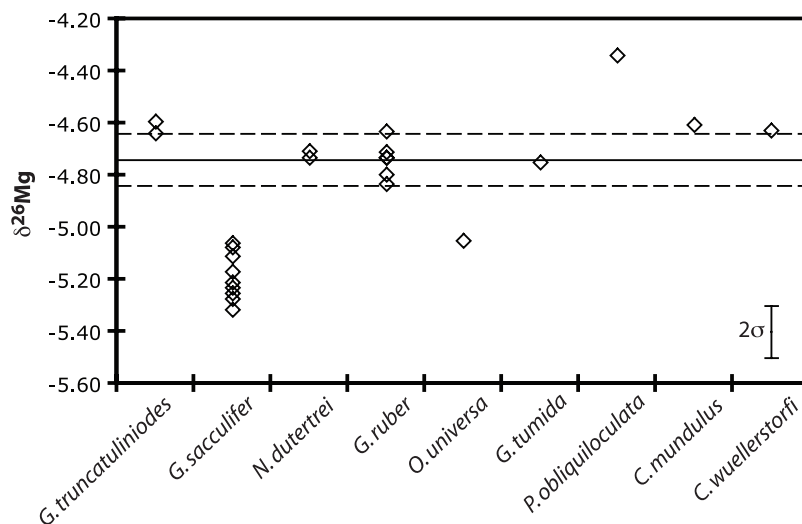
Figure 3. The δ^{26}Mg of various species of planktic and benthic foraminifera from Ocean Drilling Program core 999. The solid line represents the average value of all species except *G. sacculifer*, *O. universa*, and *P. obliquiloculata*. The dashed lines show the external uncertainty of the average value.

saturation (664C; Ω CaCO$_3$ is 0.98), through saturation (806B; Ω CaCO$_3$ is 1.03), to two Sites (999A and 925B), which are >50% above saturation [*Foster*, 2008]. The analyses of *G. ruber* and *G. sacculifer* show no variation with measured Ω CaCO$_3$. The constant δ^{26}Mg values within uncertainty of *G. ruber* (although this species has no or little gametogenic calcite, and therefore isotopic perturbation during partial dissolution is not expected) and *G. sacculifer* (which consists of up to 30% gametogenic carbonate) therefore shows that partial test dissolution does not significantly affect Mg isotope behavior. Variation in surface water calcite saturation state also does not appear to significantly affect the Mg isotope ratio (surface water Ω CaCO$_3$ is 6.06–7.03). The lack of isotope variation is an especially interesting result, as the seawater calcite saturation state has been observed to affect Mg incorporation into tests via biomineralization stress [*Russell et al.*, 2004; *Elderfield et al.*, 2006]. Mg/Ca ratios from this study show a general decrease with increasing Ω CaCO$_3$, suggesting a similar process.

[21] *G. ruber* and *G. sacculifer* were also analyzed from the late Pleistocene core top of 1241A (Table 2), where foraminiferal preservation is poor and planktonic tests appear strongly dissolved [*Mix et al.*, 2003]. The calcite saturation state of the overlying water column (Ω CaCO$_3$) is ~1.02. For both species, Mg isotope ratios are within uncertainty of their species' Holocene average, suggesting that partial test dissolution even over longer time periods does not significantly affect whole-test Mg isotope ratios.

4.2. Temperature Dependence

[22] Numerous studies have shown that Mg/Ca ratios in foraminifera are very strongly affected by environmental controls, predominantly temperature [e.g., *Nürnberg et al.*, 1996; *Elderfield and Ganssen*, 2000; *Lear et al.*, 2000; *Barker et al.*, 2003]. The uptake of Mg^{2+} by foraminifera is significantly more temperature dependent than inorganic processes [*Oomori et al.*, 1987; *Lea et al.*, 1999]. On the basis of published data and those presented here, during foraminiferal calcification the Mg^{2+} concentration of the carbonate is reduced almost 1000 times from that of ambient seawater, and the δ^{26}Mg value decreases by ~4‰ from seawater. An initial Mg isotope study of surface waters and carbonates concerned the fractionation during the formation of speleothems [*Galy et al.*, 2002]. This is significantly smaller than foraminif-

eral fractionation, the δ^{26}Mg variation between speleothems and their respective drip waters is ~2.7‰ [*Galy et al.*, 2002] (Figure 1). This study also reported a very small temperature dependence during speleothem formation of <0.02‰/AMU/°C. This means that even with high-precision measurements, only relatively large temperature differences could be resolved. Given that the temperature-controlled foraminiferal Mg incorporation is greater than inorganic processes, it is reasonable to expect that there may be a larger temperature control on organic Mg isotope fractionation. However, the data of *Chang et al.* [2004] show that there is no obvious temperature dependence of the Mg isotope fractionation in foraminifers over ~10°C, although analytical uncertainty in this study is relatively high (±0.5‰) [*Chang et al.*, 2004].

[23] The work presented here reports *Globigerinoides ruber* and *G. sacculifer* from five cores with a directly measured surface temperature difference of ~10°C (Figure 4a) (World Ocean Atlas Database). However, even at the higher precision of this study, there is no resolvable temperature-dependent fractionation of Mg isotopes. A similar picture emerges when comparing Mg/Ca from these samples to Mg isotope ratios: as expected, Mg/Ca increases with temperature, but δ^{26}Mg remains constant within uncertainty (Figure 4b). Thus the Mg concentration increase in the tests is not accompanied by a resolvable Mg isotope fractionation. This suggests that Mg isotopes in modern foraminiferal carbonates are not primarily controlled by sea surface temperatures and therefore that the Mg isotope ratios of *G. ruber* or *G. sacculifer* cannot be used as a proxies for past seawater temperature variations.

4.2.1. Modeling the Temperature-Dependent Isotope Fractionation

[24] Using generalized partition coefficients for foraminiferal and inorganic calcite precipitated from seawater (D$_{Mg}$ ~ 0.001 and 0.01, respectively; measured organic partition coefficients range from 0.001 to 0.002 and inorganic from 0.01 to 0.017 in the temperature range 20–30°C [*Mucci*, 1987; *Busenberg and Plummer*, 1989; *Lea et al.*, 1999]), a simple Rayleigh fractionation model has been constructed to determine the expected temperature-dependent Mg isotope fractionation. This model assumes that the mode of calcification is precipitation in situ, occurs in an extracellular vacuole and utilizes seawater as a parent solution [*Elderfield et al.*, 1996; *Bentov and Erez*, 2006].
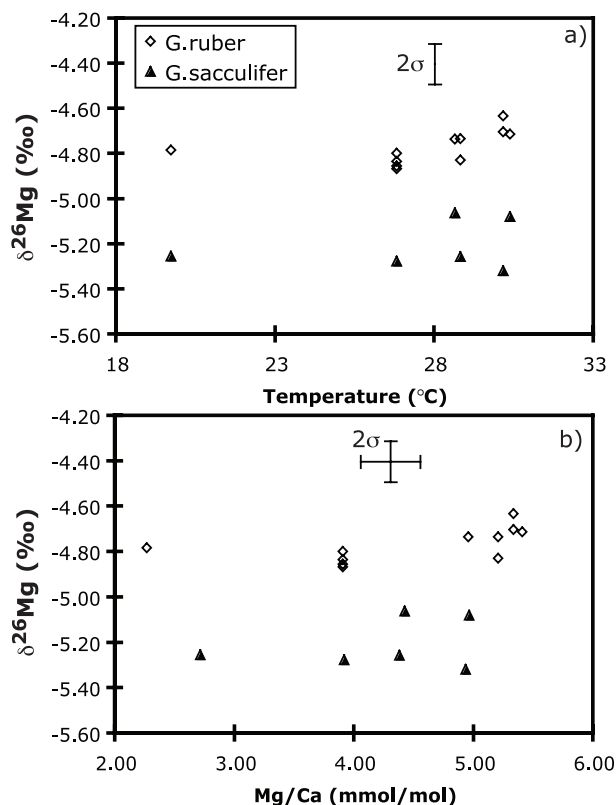
Figure 4. (a) Temperature (directly measured sea surface temperature) dependence of δ^{26}Mg in *G. ruber* and *G. sacculifer*. (b) Relationship between δ^{26}Mg and Mg/Ca in the same species. The error bars represent the external uncertainty of the analyses.

The seawater in the vacuoles undergoes chemical modification, including the removal of Mg. The model also assumes that the subsequent calcification from the modified solution is essentially an inorganic process. Considering that the Mg/Ca temperature-dependent fractionations of these species of foraminifera are well known [*Nürnberg et al.*, 1996; *Lear et al.*, 2002; *Anand et al.*, 2003] and that the ultimate foraminiferal δ^{26}Mg has been determined in this study, this allows Rayleigh modeling of the Mg isotope composition of the modified vacuole solution, which must be ~2.7‰ heavier than the composition of the foraminiferal calcite (Figure 1) [*Galy et al.*, 2002]. Note that this model does not provide an explanation for the differing Mg isotope ratios of *G. ruber* and *G. sacculifer* and only attempts to calculate the temperature-dependent Mg isotope fractionation. Assuming initially that the inorganic fractionation is not temperature dependent, this gives an isotope fractionation of ~0.005‰/AMU/°C for both *G. ruber* and *G. sacculifer* for the temperature range 20–30°C, meaning that this study cannot resolve

temperature-dependent Mg isotope fractionation. The use of minimum partition coefficient data give a maximum estimate of fractionation (e.g., if inorganic $D_{Mg} = 0.017$ (rather than 0.01), the isotope fractionation decreases to 0.003‰/AMU/°C). This degree of fractionation agrees well with the Mg isotope compositions of the measured foraminifera (Figure 5). *Galy et al.* [2002] predicted <0.02‰/AMU/°C Mg isotope fractionation for speleothems in the 4–18°C temperature range, resulting in ~0.0075‰/AMU/°C in the 20–30°C range (A. Galy, personal communication, 2008). Thus in this temperature range, temperature-dependent fractionation during inorganic calcification would also be difficult to resolve. However, to quantify this fully, more data are required on Mg isotope fractionation during both organic and inorganic calcification.

4.3. Size Fraction Dependence

[25] It is been argued that different foraminiferal test sizes reflect differences in growth rate [*Schmidt et al.*, 2004a], which in turn may be related to the CO_3^{2-} concentration of the seawater [*Russell et al.*, 2004]. Growth rate might induce kinetic fractionations of both trace element ratios and potentially isotopes, leading to changes in isotope fractionation from seawater [*Elderfield et al.*, 2002; *Anand et al.*, 2003; *Hönisch and Hemming*, 2004; *Ni et al.*, 2007]. At higher inferred growth rates, the Mg concentration in the foraminiferal carbonate has been shown to increase for a given temperature and
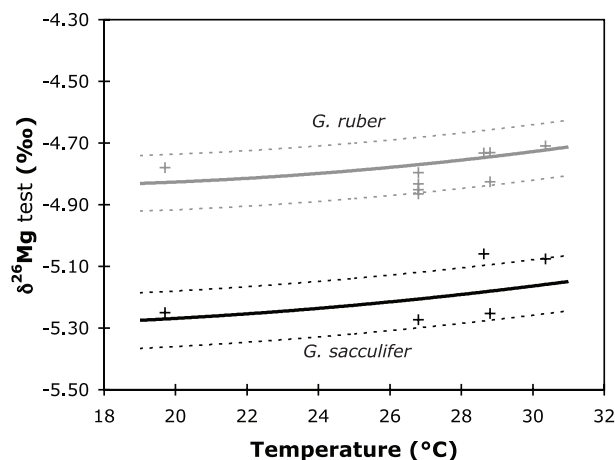
Figure 5. Results of a Rayleigh fractionation model predicting the response of test Mg isotope ratio to changes in ocean temperature for *G. ruber* and *G. sacculifer* (see text for details). Dotted lines represent the range of this study's external uncertainty. Crosses show data measured by this study.
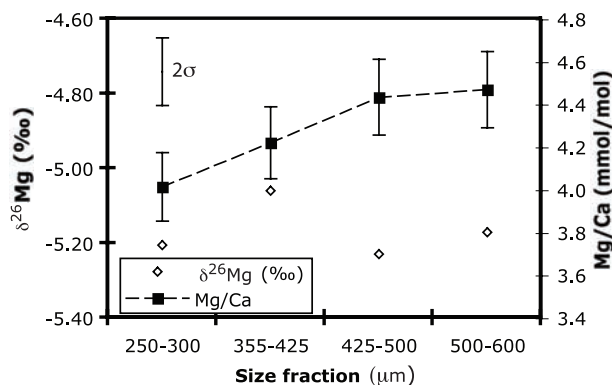
Figure 6. Variation of Mg/Ca and δ^{26}Mg due to test size, and thus growth rate, of *G. sacculifer* at Site 999A. The error bars represent the external uncertainty of the analyses.

carbonate ion concentration [*Elderfield et al.*, 2002; *Schmidt et al.*, 2008]. In order to rule out growth rate as a controlling factor of Mg isotope fractionation in foraminiferal calcium carbonate, four different size fractions of *G. sacculifer* were examined from Site 999A. Mg/Ca ratios increase with test size by ~0.5 mmol/mol; however, Mg isotope ratios remain constant, with values ranging between −5.06 and −5.23‰ (Figure 6). Early ontogenetic stages of these samples were not examined; however, it is unlikely that *G. sacculifer* tests exist fully grown at 250 μm. There is no trend with size, and all results are within analytical uncertainty, suggesting that foraminiferal growth rate and ontogeny are also not a determining factor in controlling the Mg isotope ratio of this species.

4.4. Species Variability

[26] As described above, most planktic and benthic species measured in this study are within uncertainty of a common average δ^{26}Mg value (−4.7‰). Three species exhibit a resolvable difference: *G. sacculifer* and *O. universa* are ~0.5‰ lighter and *P. obliquiloculata* is ~0.4‰ heavier than this average value (Figure 3). The range in Mg isotope ratio measured in this study is significantly smaller than that reported by *Chang et al.* [2004] (−6.19 to −4.19‰ (relative to DSM-3)). However, the average value here (−4.74‰) and that of Chang et al. (−5.3‰) is within analytical uncertainty of the latter study. *Chang et al.* [2004] similarly report that nearly all of the 13 species (including two benthic species) they analyzed lie within uncertainty of this average value. Similarly, the benthic species analyzed in this study are within uncertainty of the average.

[27] *Chang et al.* [2004] reported that uniquely, *O. universa* was ~1‰ heavier than this average value, which is in contrast to the results obtained in this study. As yet there is no explanation as to why the offset of the Mg isotope ratio of *O. universa* is opposite in this study compared to Chang et al. nor why *G. sacculifer*, *O. universa* and *P. obliquiloculata* are significantly offset from the average value. *G. sacculifer* and *O. universa* have among the highest Mg/Ca of the species measured from the core, but there is no statistically significant interspecies trend between Mg/Ca and δ^{26}Mg for the species analyzed here.

[28] Mg isotope ratios of foraminifera are significantly different from corals measured in this and other studies. Aragonitic corals have isotope ratios ~1‰ lighter than seawater (δ^{26}Mg = −1.71‰ [*Chang et al.*, 2004]; −1.7‰ [*Wombacher et al.*, 2006]). Calcite corals, on the other hand, have much lighter isotope ratios: δ^{26}Mg = −3.43‰ (this study), −3.3‰ [*Wombacher et al.*, 2006]. The degree of fractionation of these corals from seawater is similar to that shown by inorganic calcite (~2.7‰) [*Galy et al.*, 2002]. The isotopic fractionation from seawater shown by foraminifers (~4‰) is however significantly greater than inorganic calcite precipitation. This suggests that the processes during foraminiferal biomineralization, as Mg is transported from seawater to the site of calcification, and the ambient Mg concentration is reduced ~1000 times, more strongly favor light Mg isotopes than inorganic precipitation or coral formation do. Therefore there must be some level of control by the organism on isotope incorporation during calcification.

[29] *O. universa* is the closest relative to *G. sacculifer* [*Pearson et al.*, 1997; *Darling et al.*, 1999], and consequently the similar Mg isotope fractionation may result from a similar process which is unique to these species. *P. obliquiloculata* has an anomalously thick outer calcite layer [*Hemleben et al.*, 1989; *Kunioka et al.*, 2006]. The heavier δ^{26}Mg may suggest faster precipitation resulting in fractionation more similar to inorganic precipitation [*Galy et al.*, 2002]; however, this is inconsistent with the low measured Mg/Ca of this species.

[30] An explanation which has been proposed for calcium isotope fractionation during uptake by foraminifera has been kinetic Ca isotope fractionation during diffusion in solution [*Gussone et al.*, 2003]. Recent experiments have shown that Mg isotopes do not noticeably fractionate during dif-

fusion in water [*Richter et al.*, 2006], suggesting that kinetic isotope fractionation of Mg isotopes is unlikely to be responsible for the observed fractionation in foraminifera. A possible corollary of these experiments suggests that transport of ions across membranes can cause isotopic fractionations much larger than those which can take place during diffusion in water itself [*Fritz*, 1992; *Richter et al.*, 2006].

4.5. Comparison to Ca Isotope Fractionation and Implications for Mg Incorporation

[31] The use of Mg/Ca as a paleotemperature proxy has also given rise to the potential (disputed) similar use of calcium isotopes [e.g., *Zhu and MacDougall*, 1998; *De La Rocha and DePaolo*, 2000; *Nägler et al.*, 2000; *Gussone et al.*, 2003; *Chang et al.*, 2004; *DePaolo*, 2004; *Marriott et al.*, 2004; *Heuser et al.*, 2005; *Sime et al.*, 2005, 2007; *Griffith et al.*, 2008; *Kasemann et al.*, 2008]. Some studies [e.g., *Nägler et al.*, 2000; *Gussone et al.*, 2003; *Kasemann et al.*, 2008] show an order of magnitude greater temperature-dependent fractionation in *G. sacculifer* compared to *O. universa*. However, others have reported identical values within uncertainty for many planktic species, including *G. sacculifer* and *O. universa*, as well as *G. ruber* and *P. obliquiloculata* [*Sime et al.*, 2005] and have suggested that culture-based experiments may have been masked by so far unrecognized and unquantified metabolic and/or physiological processes occurring in natural habitats [*Chang et al.*, 2004; *Sime et al.*, 2005]. Proposed mechanisms for temperature-dependent Ca isotope fractionation in foraminifera include fractionation during diffusion across cell membranes or though aqueous media [*Gussone et al.*, 2003] or alternatively equilibrium fractionation occurring during the change from bonding to water molecules to bonding to the carbonate structure. The latter theory suggests that the similarity of Ca isotope fractionation in inorganic calcite and *O. universa* is because it is an inorganic process, whereas the greater fractionation in *G. sacculifer* is thought to be because the latter species actively pumps Ca into a biologically mediated internal Ca pool [*Anderson and Faber*, 1984; *Lea et al.*, 1995; *Wolf-Gladrow et al.*, 1999; *Marriott et al.*, 2004; *Griffith et al.*, 2008].

[32] In any of these cases, the behavior of Mg isotopes is different from that of Ca isotopes in these species analyzed here. As discussed in section 4.4, Mg isotopes have been shown not to fractionate

during diffusion in aqueous media. The similarity of Mg isotope composition of *O. universa* and *G. sacculifer* shows that if the two species have different Ca uptake mechanisms, the same processes do not appear to cause separate Mg isotope fractionation behavior. For example, the Ca isotope temperature-dependent fractionation of *O. universa* is similar to inorganic fractionation, whereas the Mg isotope ratio of *O. universa* is not a dominantly inorganic process. If it were, the Mg isotope ratio of *O. universa* would be expected to be heavier, rather than lighter, than the average [*Galy et al.*, 2002]. In addition, if *G. sacculifer* does utilize a large internal Ca pool [*Marriott et al.*, 2004; *Griffith et al.*, 2008; *Kasemann et al.*, 2008], which is associated with Ca isotope fractionation, this does not necessarily imply that Mg is affected. However, it is obvious that the Mg isotope ratio as well as the Mg content is being modified by the organism. For the low-Mg calcite of the foraminifers analyzed here, it has been proposed that the organism modifies the Mg concentration of the parent solution, thus keeping a low intracellular Mg^{2+} activity [*Bentov and Erez*, 2006]. Mechanisms for this process include Mg transport systems, such as channels which selectively allow Mg transport against the concentration gradient across the cell membrane [*Bentov and Erez*, 2006]. Assuming that there is Mg isotope fractionation, associated with this transport (i.e., heavy Mg isotopes are transported out, leaving the residue from which the organism precipitates its test isotopically light), it is possible that the selectivity of these channels might be different for different species. In this case, the Mg transport is unaffected by the environment of calcification (e.g., temperature).

5. Conclusions

[33] During calcification, both the Mg concentration and isotope ratio of tests are significantly reduced relative to seawater by a process or processes which are greater than that experienced during inorganic calcification. While the Mg concentration shows significant control by environmental factors, the Mg isotope ratio remarkably appears unaffected by temperature, Mg kinetic fractionation during aqueous transport, seawater calcite saturation state, test size (i.e., inferred test growth rate), or the size or existence of an internally controlled calcium pool. Of the nine benthic and planktic species analyzed, only three show deviation from an average Mg isotope ratio. It seems likely that the dominant fractionating pro-

cess is isotope fractionation occurring during cross-membrane Mg transport, as the organism modifies the parent solution from which it crystallizes. This process appears to be species dependent but not temperature dependent.

[34] Hence, species calibrations must be undertaken before reconstructing paleorecords (e.g., of past rates of dolomitization and/or continental weathering). Nevertheless, the insensitivity to environmental parameters suggests that foraminifera are a viable carrier phase of past seawater Mg isotope ratios, provided a precise determination of the biological fractionation factor exists.

Acknowledgments

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