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Mg and Ca isotope fractionation during $CaCO_3$ biomineralisation

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Abstract

The natural variation of Mg and Ca stable isotopes of carbonates has been determined in carbonate skeletons of perforate foraminifera and reef coral together with Mg/Ca ratios to assess the influence of biomineralisation processes. The results for coral aragonite suggest its formation, in terms of stable isotope behaviour, approximates to inorganic precipitation from a seawater reservoir. In contrast, results for foraminifera calcite suggest a marked biological control on Mg isotope ratios presumably related to its low Mg content compared with seawater. The bearing of these observations on the use of Mg and Ca isotopes as proxies in paleoceanography is considered.

Calcium carbonate is one of the most important products of biological cycling in the oceans. Marine organisms are part of this cycling: they take up Ca, Mg, and other elements from seawater, and transport them by various mechanisms into the carbonate lattices of their skeletons. The biogenic $CaCO_3$ minerals are expected to reflect both the composition and temperature of the seawater in which the organisms lived. In this regard, of those organisms producing $CaCO_3$ biominerals, foraminifera, and coral have been the most exploited [1–3]. However, observations on these carbonates often differ from those to be expected from straightforward consideration of inorganic chemical and isotope equilibria [4–7]. Such differences are often termed "vital effects," and need to be recognised when using proxy-observations on biogenic carbonate to infer environmental parameters. Extensive studies of C and O isotopes [6–9] and various elemental abundances in these $CaCO_3$ minerals [4,5,10] are a routine part of the characterisation of oceanographic variables in climate studies. Comparatively, little attention has been paid to the stable isotopes of Mg and Ca. This study presents the first combined study of these and Mg/Ca ratios. The aims are to address outstanding questions surrounding the processes of biomineralisation in foraminifera and coral, and to provide a fuller evaluation of their potential as proxies for environmental parameters.

Samples and analytical methods

A variety of samples, including three samples of surface seawater, five samples of modern coral (two genera), and 41 samples of Holocene perforate foraminifera (11 planktonic and 2 benthic species) were selected for this study. The sources of these samples, and the estimated temperatures at the site localities, are given in Table 1. For analysis 0.5–1 mg carbonate samples were thoroughly cleaned with deionised water, ethanol, and a reducing solution (hydroxylamine hydrochloride + sodium acetate, pH −6.5). After cleaning samples were examined under the microscope and discolored fragments were discarded. Cleaned samples were dissolved in 0.3 M HNO_3, and Al/Mg, Mn/Mg, and Fe/Mg ratios in sample solutions were all <0.01.

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Table 1
Sample sources

Sample	Core	Depth (m)	Location	SST[a] (°C)
Seawater (IASO[b])	—	—	North Atlantic[c]	
Seawater	—	—	Mediterranean[c]	
Seawater	—	—	Atlantic[c]	—
Coral (*Acropora*)	—	—	Barbados[c]	~27.5
Coral (*Acropora*, *Pocillopora*)	—	—	Red Sea[c]	–22
Coral (*Acropora*)	—	—	Mauritius	~25.5
Foraminifera	BOFS5K	3547	N. Atlantic (50°41.3′N, 21°51.9′W)	14
Foraminifera	RC8-39	4330	S. Pacific (42°53′S, 42°21′W)	12.5
Foraminifera	28K	4900	N. Atlantic (24°N, 22°W)	22.5
Foraminifera	RCIO-140	1679	W. Eq. Pacific (2°39′S, 156°59′E)	29
Foraminifera	MD85	3001	S. E. Atlantic (29°42′S, 12°56′E)	21
Foraminifera	87KG	1782	Arabian Sea (23°35.33′N, 64°13.02′E)	25
Foraminifera	KNRI 10-80BC	2952	N. Atlantic (4°37.86′N, 43°39.03′W)	27.5

[a] Typical average for sea surface temperature at locality from Lavitus 94.

[b] Standard seawater from Ocean Scientific International, Southampton. Salinity: 34.998. Batch: 35NI.

[c] No further information about longitude and latitude of localities.

Seawater samples were acidified with HNO_3, dried and, as with the carbonate samples, dissolved in 2 M HCl. A two-stage ion-exchange chromatographic procedure employing a H17-cleaned AG50W-X12 resin was used to separate Mg from Na and Ca [11]. A Ca fraction collected from the same column chemistry was further purified from Sr using a second column of Sr-spec resin. The column yields for Mg and Ca were both >99.9%.

The isotope compositions of Mg (^{24}Mg, ^{25}Mg, ^{26}Mg) and Ca (^{12}Ca, ^{43}Ca, ^{44}Ca) in samples were measured using a Nu Instruments multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) at Oxford [11,12]. A standard-sample bracketing technique was employed, referenced to the SRM980 and SRM915a standards for Mg and Ca isotopes, respectively. Isotope ratio measurements of samples are expressed as permil deviations from the isotope reference standards:

$$\delta^{x}\mathrm{Mg} = [(^{x}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{Sample}}/(^{X}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{SRM980}} - 1] \times 1000,$$

$$\delta^{Y}\mathrm{Ca} = [(^{y}\mathrm{Ca}/^{42}\mathrm{Ca})_{\mathrm{Sample}}/(^{Y}\mathrm{Ca}/^{42}\mathrm{Ca})_{\mathrm{SRM915a}} - 1] \times 1000,$$

where x is either mass 25 or 26 and y either 43 or 44. The measurements of ^{40}Ca by ICPMS remain unreliable and are not reported because of intense interference by ^{40}Ar, but the ^{44}Ca/^{42}Ca and ^{43}Ca/^{42}Ca ratios allow straightforward comparison with ^{44}Ca/^{40}Ca ratios observed by TIMS [13–17]. The accuracy of the technique used in this study was assessed using a synthetic solution (Na:Mg:Ca:Sr = 2:1:100:1 in weight); the repeatability (2σ) is ± 0.14 on δ^{26}Mg [11] and ± 0.13 on δ^{44}Ca without isotopic fractionation by the column chemistry.

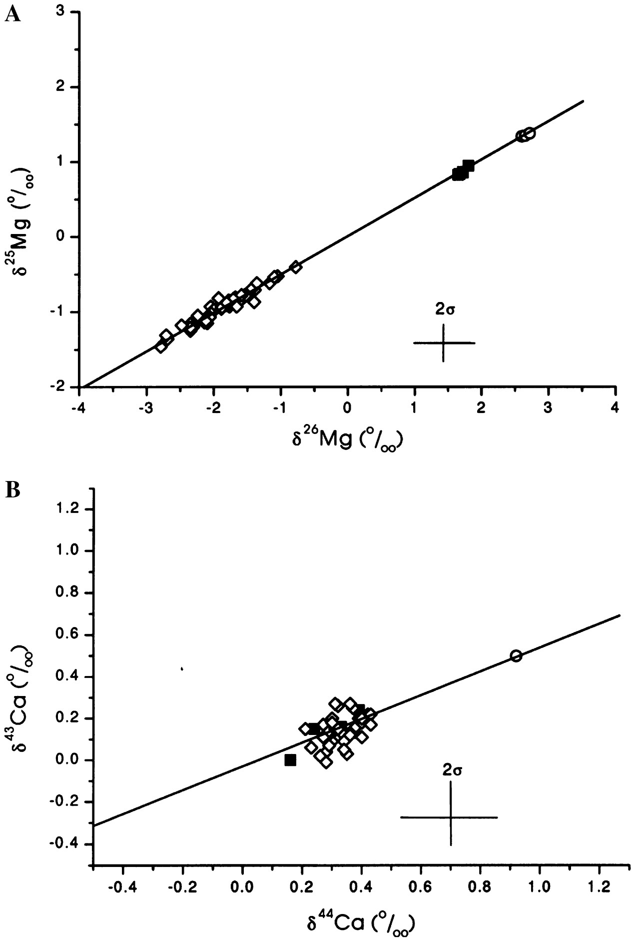

Fig. 1. Three-isotope plots for Mg (A) and Ca (B) from seawater (open circle), coral (solid square), and foraminifera (open diamond). The repeatability (2σ) is shown as crosses in the figures. Within analytical error, all samples measured in this study lie on a mass-dependent fractionation line [11,20,30] with a slope of –0.5.

Results

Mg isotopes

The Mg isotope results obtained from seawater, modern coral, and foraminifera are presented in Figs. 1–4. A three-isotope plot ($^{26/24}$Mg vs $^{25/24}$Mg) for the samples analysed is shown in Fig. 1A. All Mg isotope ratios are within experimental error on a line with a slope of ~0.5, indicating that the measurements are free of significant spectral interference [11]. The seawater samples have indistinguishable Mg-isotope compositions within analytical error. Their average is +1.35 ± 0.04% and +2.66 ± 0.12%, for δ^{25}Mg and δ^{26}Mg, respectively, which is isotopically heavier than

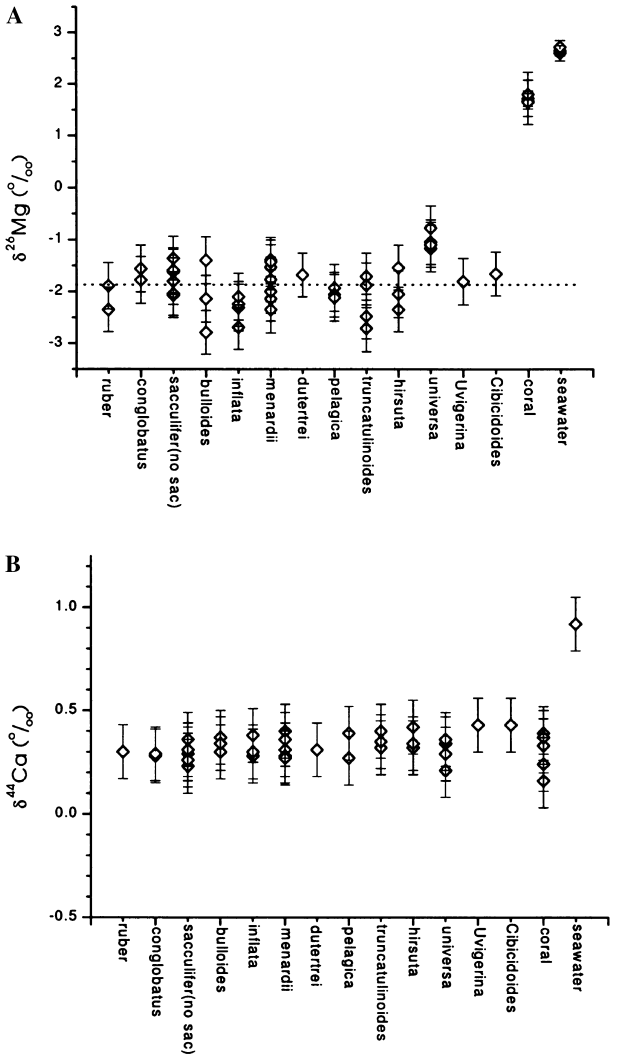

Fig. 2. δ^{26}Mg (A) and δ^{44}Ca (B) of seawater, coral, and various species of foraminifera from worldwide Holocene sediments obtained in this study. In foraminifera, except *Uvigerina* and *Cibicidoides*, all species are planktonic. The dashed line in (A) represents the average of δ^{26}Mg values of all foraminifera samples. Note that δ^{26}Mg values show a greater fractionation between seawater and foraminifera (−4.52%) than that between seawater and coral (−0.94%), but that the fractionation in δ^{44}Ca between seawater and foraminifera and seawater and coral is very close.

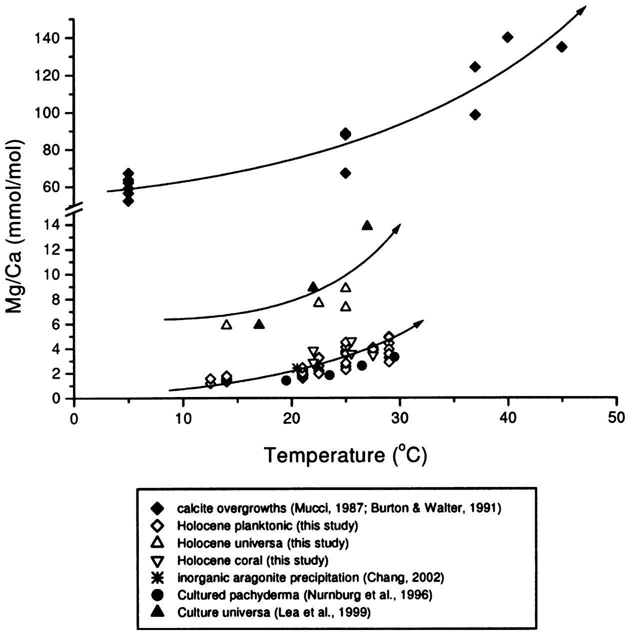

Fig. 3. Temperature dependence of Mg/Ca ratios in inorganic precipitated carbonates and biogenic carbonates, including mixed species of Holocene planktonic foraminifera (open diamond, this study), Holocene specimens of *O. universa* (open up-triangle, this study), Holocene coral (open down-triangle, this study), cultured specimens of *O. universa* (solid up-triangle) [21], cultured specimens of *Neoglobquadrina pachyderma* (solid circle) [5], inorganic precipitated aragonite (star) [20], and inorganic precipitated calcite (solid diamond) [23,24]. Note that the Mg content in coral is of the same magnitude as produced by inorganic precipitated aragonite, but that in foraminifera is much smaller.

any of the carbonate samples. This result agrees with δ^{26}Mg values of +2.54% and +2.59% reported previously [11,18]. The implied uniformity of Mg isotopes in the oceans is not unexpected, given the long, ~13 Ma, oceanic residence time of Mg [19]. All five coral samples measured, despite being of different species and from different localities, show indistinguishable Mg-isotope ratios with an average value of +1.71 ± 0.43%, for δ^{26}Mg (Fig. 1A). The foraminifera samples have the lightest Mg isotope compositions within the overall sample set (Fig. 1A). In contrast to coral, they show small but significant variations between and within species, ranging from δ^{26}Mg = −0.78% to −2.79% (Fig. 2A). In particular, δ^{26}Mg values for planktonic foraminifera *Orbulina universa*, −0.78% to −1.17%, are significantly heavier than the −1.36% to −2.79% range for other species.

Ca isotopes

The results of Ca isotope analyses are presented in Table 2(B). In a three-isotope plot of δ^{44}Ca vs δ^{43}Ca (Fig. 1B), all ratios lie within experimental error of a line with a slope of ~0.5. Seawater has δ^{44}Ca = +0.92 ± 0.13% and is the heaviest of the Ca isotope compositions measured. In agreement with previous measurements of Ca isotopes [13–17], coral, and foraminifera samples have Ca which is isotopically lighter than seawater. No significant differences outside analytical error were observed in the Ca isotope results within either the coral or the foraminifera sample set or indeed between them (Fig. 2B). These observations are consistent with Skulan and DePaolo [14] conclusion that the magnitude of Ca isotope fractionation is very similar among different organisms. The average of δ^{44}Ca for coral samples and foraminifera samples is 0.30 ± 0.19% and 0.32 ± 0.11%, respectively.

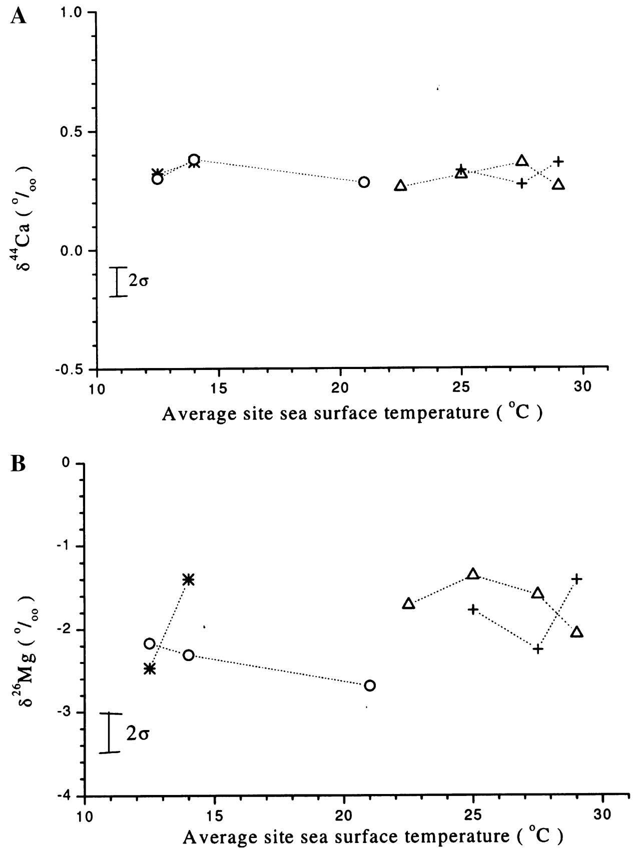

Fig. 4. Temperature dependence of δ^{44}Ca (A) and δ^{26}Mg (B) in various seawater surface dwelling species of planktonic foraminifera: *G. sacculifer* (open up-triangle), *G. bulloides* (star), *G. inflata* (open circle), and *G. menardii* (cross).

Mg/Ca ratios

Mg/Ca ratios for coral and planktonic foraminifera samples obtained in this study are given in Table 2. There are small variations between the Mg/Ca ratios of the five coral aragonite samples with a range of 2.84–4.58 mmol/mol. This is of similar magnitude to Mg/Ca ratios reported in the literature [20] for inorganic aragonite precipitation from seawater-like solutions (i.e., Mg/Ca ~ 5.14). Mg/Ca ratios for foraminifera vary between ~1 and 9 mmol/mol and show a correlation with increasing surface temperature (Fig. 3). The increase in Mg/Ca ratios of various species of planktonic foraminifera with increasing temperature corresponds to results for cultured species of planktonic foraminifera [5,21,22]. Specimens of *O. universa* show elevated Mg/Ca ratios of ~6–8.5 mmol/mol, compared with ~1–4.5 mmol/mol for other species in a similar temperature range (Fig. 3). This observation is again consistent with the results of culture experiments reported by Lea et al. [21]. Furthermore, Mg/Ca ratios are lower by a factor of 10 or more relative to inorganic seawater calcite overgrowths (Fig. 3) [23,24]. Such low-Mg calcite can only be precipitated from a solution where its Mg/Ca ratio is <0.1 [25]; the Mg/Ca ratio of seawater, in contrast, is 5.14.

Table 2
Mg/Ca ratios in perforate foraminifera

Sample	Species	Mg/Ca (mmol/mol)
Coral	*Acropora palmata* (1)	3.44
	Acropora sp.(3)	2.8 → 4.6
	Pocillopora sp.(1)	3.82
Foraminifera	*Globigerina bulloides*	—
	Cyathocrinites conglobatus	—
	Neoglobquadrina dutertrei (2)	2.4
	Globorotalia hirsuta (5)	1.85
	Globorotalia inflata (7)	1.1–2.4
	Globorotalia menardii (7)	3.2–4.4
	Globigerinoides sacculifer (no sac) (4)	2.2–4.5
	Globigerinoides sacculifer (with sac) (3)	4.1–4.9
	Hastigerina pelagica (1)	3.6
	Globigerinoides truncatulinoides (7)	1.5–3.9
	Orbulina universa (4)	5.9–8.8[a]
	Pulleniatina obliquiloculata (3)	3.6
	Sphaeroidinella dehiscens (1)	2.9
	Globigerinella siphonifera (1)	2.8
	Uvigerina sp. (2)	1.9–2.5

Numbers in parentheses indicate the number of analyses on separate samples.

Mg/Ca ratios were determined by MC-ICPMS.

[a] Note the very unusual high values, see text.

Discussion

Ca and Mg isotopes of reef coral

Although the coral samples studied include different species and are from different localities, no clear difference in either Mg or Ca isotope distribution is observed between them. This immediately implies a uniformity of Ca and Mg isotope compositions in the oceans, which is suggested by the analyses of the seawaters under Mg isotopes and Ca isotopes. Furthermore, the precipitation processes operating in different species of reef coral are likely to be very similar. The isotopic differences between the averages of seawater and reef coral are −0.62% and −0.94% for δ^{44}Ca and δ^{26}Mg, respectively. The observed difference in δ^{44}Ca of −0.62% between seawater and coral is close to the −0.7% value observed upon the inorganic precipitation of aragonite [17].

Biomineralisation in reef coral

The construction of coral skeleton has been studied in detail using optical and electron microscope methods by Constantz [26,27] and Erez et al. [28]. The controlling factor appears to be principally inorganic, physiochemical crystal growth from an aqueous solution close to seawater in composition [28]. These conclusions are consistent with the results of this study: (1) Mg/Ca ratios observed in the reef corals and inorganic aragonite precipitated from seawater are close; (2) Mg and Ca isotope compositions of different corals are indistinguishable.

Ca isotopes of foraminifera

There are no significant variations in δ^{44}Ca within and between the 11 planktonic species and 2 benthic species examined in this study (Fig. 2B). There have been several reports about Ca isotope composition of Holocene foraminifera which were measured by TIMS and the double spike techniques [15,16,29]. Despite the different species represented, the average δ^{44}Ca for 14 Holocene foraminifera samples from previous studies is 0.39 ± 0.25% [15,16,29], in agreement with the average of 0.32 ± 0.10% for this study. The overall spread from 0.2%C to 0.65% in previously reported data may be due to inter-laboratory biases or sampling.

Despite the biological differences between coral and foraminifera, the δ^{44}Ca fractionation of −0.6% is the same in coral aragonite and foraminifera calcite. Very similar Ca isotope fractionations are found for coccolith calcite [16] and inorganically precipitated aragonite [17]. This suggests that the processes of nucleation and crystallisation are similar and that Ca isotopes are not sensitive enough to distinguish various mechanisms of Ca^{2+} transport within the cells of different phyla. The basic question as to whether biomineralisation of foraminifera is a simple inorganic process or proceeds under biological control cannot be determined on the basis of Ca isotope fractionation alone.

In principle, some temperature-dependence of δ^{44}Ca in foraminifera calcite is to be expected. Such a dependence has been described in cultured *Globigerinoides sacculifer* at ~0.12% per 1 °C on δ^{44}Ca, in the range 19.5–29.5 °C [29]. A second species, *O. universa*, showed a much smaller dependence of 0.019% per 1 °C on δ^{44}Ca in the range of 10.5–29.3 °C [17].

However, analyses of natural planktonic foraminifera from different localities and different sea-surface temperatures, including *G. sacculifer* (22.5–29 °C), *Globorotalia inflata* (12.5–21 °C), *Globorotalia menardii* (25–29 °C), and *Globigerina bulloides* (12.5–14 °C) in this study, show no variation within the 2σ analytical uncertainty of ± 0.13% in δ^{44}Ca (Fig. 4A). This is consistent with the observation [17] that the most recent cultured samples of *O. universa* basically show no temperature dependence at all. In addition, these authors [17] reported that the Ca isotope fractionation observed in their cultured *G. sacculifer* samples is likely to have resulted from some other factors rather than temperature. Thus, there is a need for further controlled sampling of natural living specimens and additional culture experiments of different species.

Mg isotopes of foraminifera

In contrast to the absence of resolvable variations in Ca isotopes, δ^{26}Mg values of foraminifera range from −0.78‰ to −2.79‰. There are small but significant variations of Mg isotopes between and within different species.

The difference in δ^{26}Mg between seawater and the average value for foraminifera is −4.5% (Fig. 2A). Not only is it greater than the −0.94% difference observed in coral, it also exceeds the recorded difference of −2.7% between a speleothem and groundwater [30]. The data suggest that significant Mg isotope fractionation may occur during foraminifera chamber formation, and that in contrast to Ca isotopes, Mg isotopes have the potential to identify different mechanisms of biomineralisation between foraminifera and coral.

A plot of δ^{26}Mg vs surface seawater temperature for natural specimens is shown in Fig. 4B. Except possibly for *G. bulloides*, no clear temperature dependence is observed within analytical error. With such a small temperature difference (12.5 and 14 °C), the Mg isotope difference of ~1% between the two samples of *G. bulloides* is more likely to have resulted from variations within single species rather than from temperature.

Biomineralisation in foraminifera

The mechanism of calcification in foraminifera remains poorly understood [31,32]. Recent observations by Erez et al. [28] on a perforate foraminifera species, *Amphistegina lobifera*, show that when chamber formation commences, seawater is present in vacuoles in the cytoplasm and these vesicles may serve for shell calcite formation. Their so-called seawater pool model [10,28] would explain the similarity of Ca isotope fractionation between foraminifera and seawater (−0.6%) and in inorganic $CaCO_3$ precipitation (−0.7%). However, inorganic precipitation with a low Mg content as found in foraminifera requires a solution with Mg/Ca < 0.1 [25], compared with seawater ~5.14. Thus, if foraminifera calcite is indeed precipitated from seawater vacuole, then Mg^{2+} is effectively pumped out of this vacuole. Such a pumping process would enrich the heavy isotope of Mg in the vacuole. In addition, if inorganic precipitation of calcite produces a shift in δ^{26}Mg of −2.7% [30], then foraminifera calcite cannot be formed directly from seawater vacuole as observed by Erez et al. [28], because foraminifera calcite is as much as −4.5% lighter in isotope ratio than seawater (Fig. 2A).

The combined Mg and Ca isotope ratios and Mg/Ca ratios suggest that in foraminifera biomineralisation, Mg^{2+} and Ca^{2+} are transported from ambient seawater into the site of calcite growth by different mechanisms. Furthermore, the isotope compositions of Mg and

Mg/Ca ratio at this site differ from that of seawater. Whatever the mechanism for transportation of Mg^{2+} (e.g., diffusion and/or leaking), it results in enrichment of the lighter isotope of Mg. In contrast, Ca^{2+} transport (e.g., Ca ion channels and/or Ca pumps) does not induce significant Ca isotope fractionation.

Conclusion

(1) This work has examined the Mg and Ca isotope compositions and Mg/Ca ratios of coral aragonite and foraminifera calcite.

(2) Combination of the results in the light of possible biomineralisation processes demonstrates that foraminifera biomineralisation must be a biological dominated process. At the site of calcification the ambient Mg^{2+} content is at least fifty times lower than that in seawater. The mechanisms of Mg^{2+} and Ca^{2+} transportation from seawater into the site for calcification are not the same.

(3) The physiochemical biomineralisation of reef coral aragonite approximates well to a straightforward inorganic process. The fluid composition at the site of aragonite biomineralisation is likely to approximate seawater in Ca/Mg ratio.

(4) Significant dependence of Ca or Mg isotope compositions on temperature in foraminifera has not been observed. Although such a dependence is to be expected, as shown by culture experiments, the results of this study may be used to apply limits to the natural situation.

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